Steven A. Treese
Peter R. Pujadó
David S. J. Jones
Editors

Handbook of Petroleum Processing

Second Edition

Springer Reference

Handbook of Petroleum Processing

Steven A. Treese • Peter R. Pujadó
David S. J. Jones
Editors

Handbook of Petroleum Processing

Second Edition

With 571 Figures and 395 Tables

Springer Reference

Editors
Steven A. Treese
Puget Sound Investments LLC
Katy, TX, USA

Peter R. Pujadó
UOP LLC (A Honeywell Company)
Kildeer, IL, USA

David S. J. Jones
Calgary, AB, Canada

ISBN 978-3-319-14528-0 ISBN 978-3-319-14529-7 (eBook)
ISBN 978-3-319-14530-3 (print and electronic bundle)
DOI 10.1007/978-3-319-14529-7

Library of Congress Control Number: 2015937620

Springer Cham Heidelberg New York Dordrecht London
1st edition: © Springer Science + Business Media B.V. 2006
2nd edition: © Springer International Publishing Switzerland 2015
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Printed on acid-free paper

Springer International Publishing AG Switzerland is part of Springer Science+BusinessMedia (www.springer.com)

Preface to the Second Edition

This Second Edition of the *Handbook of Petroleum Processing* follows in the footsteps and traditions of the First Edition. We have greatly updated and expanded the information and scope in this edition. We have included many new processes and unconventional feedstocks that are encountered in today's facilities. The book has been reorganized to better facilitate its use as a reference.

This Handbook provides a basic knowledge of petroleum refining and processing as a foundation. This general knowledge may be sufficient for many users, but we have continued to provide detailed, practical approaches to designing units and solving the most common challenges facing today's processing and design professionals. Where possible, we have included additional information for those who must operate the process units. Not all the information is at the same level of detail, but we have provided more detail in this edition about operation-related issues.

Most of the calculation techniques described here are manual. We authors and editors grew up using many of these methods; however, we recognize that computer process simulation and applications play the major roles in designing and operating plants today. Many of the methods provided here are behind the simulation software or can be converted easily to computer applications. These methods can quickly provide rough checks on computer results, or they can be used if you do not have a computer or simulation package readily available.

In different chapters, you will find the use of different units of measure. The units reflect those familiar to the chapter authors. Some chapters provide both English and metric units and some only English or only metric. The petroleum industry is accustomed to mixing units and converting between units. In fact, many product specifications use mixed systems. Several common conversion factors are provided in Appendix D.

This edition of the Handbook was structured with both electronic and print publication in mind. It is primarily conceived as a comprehensive book, and the organization of the chapters reflects that premise. For electronic publication, however, we have made the individual chapters as self contained as possible. This means that the information in a chapter generally includes the needed reference materials. The self-contained approach only takes us so far. Lest we have to repeat large portions of other chapters or resources, individual chapters will still contain references to other chapters or appendices in this Handbook and to other resources.

The book is organized into six parts:

Part I: General Refinery Processes and Operations

This part describes crude oil and the processes used to convert it to finished products along with the design and operation of these processes.

Included here are

- A general understanding of crude and crude properties
- An understanding of products and their important properties
- How a refinery is configured to match the desired crudes and markets
- Detailed discussions of the processes, design, and operation of crude and vacuum distillation units, light ends processing, catalytic reforming, fluid catalytic cracking, hydroprocessing, alkylation, olefin condensation, isomerization, gas treating, residual oil upgrading, and hydrogen production
- How product qualities are specified, measured, and controlled
- Techniques for planning refinery operations and economic analyses
- How a petroleum processing project is executed

Part II: Variations

Today's petroleum processing facility typically runs or handles more than just traditional crude oil and may make more than just fuel products.

This part of the Handbook explores facilities that make

- Lube oils
- Petrochemicals
- Other chemicals

It also provides insights into nonconventional feedstocks which find their way into the processing scheme or are processed somewhat like petroleum, e.g., coal and gas liquids, shale oil, shale crude, bitumens, and renewable stocks.

One chapter discusses biorefineries, which are increasingly providing fuels and fuel blend stocks.

Part III: Support Systems

All process facilities need certain common support systems. These are discussed in some detail in Part III, along with many design and operating techniques.

Included here are discussions of

- Instrumentation and control systems
- Utilities (steam, condensate, fuel, water, air, power, nitrogen, others)
- Off-site facilities (storage, blending, loading, waste hydrocarbons, wastewater)
- Environmental controls and practices (air emissions, aqueous effluents, solid wastes, noise)

Part IV: Safety Systems

Today, it is an absolute requirement that process facilities operate safely. Facilities must not endanger employees or the community. Facilities that cannot do this are usually not allowed to operate at all. While a large part of safety derives from the way a facility is operated, many features can be designed into the plant to enable safer operations.

This part of the Handbook focuses on the systems and practices that allow for excellent safety. Included here, you will find discussions of

- Process safety management (PSM) basics
- Safety systems for pressure and temperature
- Oxygen deficiency protection practices
- Confined space entry practices
- Facility siting considerations
- Hazardous materials
- Fire prevention and protection

Part V: Reference

The Reference part of the book provides detailed discussion of several general equipment types and how to design them:

- Vessels
- Fractionation towers
- Pumps
- Compressors
- Heat exchangers
- Fired heaters
- Piping and pressure drop

This part also has a comprehensive (and in some cases fairly detailed) dictionary of abbreviations, acronyms, expressions, and terms you will hear around refineries and petroleum processing facilities. We have added many terms and eliminated most of the repetition in the first edition. Many of these terms we use in the industry without even realizing they have specific connotations in our business. Having them all in one place helps. Where appropriate, the definitions provide references back to specific chapters in the book for additional information.

Part VI: Appendices

The appendices include reference materials that either did not fit elsewhere or were needed in multiple chapters. The appendices are divided into four sections:

Appendix “Examples of Working Flow Sheets in Petroleum Refining” provides examples of various flow sheets and documents used in petroleum processing.

Appendix “General Data for Petroleum Processing” contains general data on petroleum properties and some equipment properties. Included here, you will find relationships for viscosity, specific gravity, °API gravity, boiling points, freezing points, and tray geometry.

Appendix “Selection of Crude Oil Assays for Petroleum Processing” has several examples of crude and other oil properties in the form of simple assays. This appendix has been expanded to include many of the newer stocks, such as shale crudes, bitumens, and synthetic crudes. Some of these assays are dated, so for design or planning work, it is best to always get an updated assay from your supplier.

Appendix "Conversion Factors Used in Petroleum Processing" contains conversion factors. No Handbook worth its salt can get away without some common conversion factors. While we have not included all the factors you will need here, we have included those we found most useful or hardest to find in the literature. The tables include general factors plus pressure and viscosity interconversions.

We have tried to make this work as comprehensive as possible, but it is not feasible to conceive of or include everything you might want to know. There are numerous outside references provided, which can lead you to more references. Online searches often provide good information but can sometimes be misleading or wrong as well. Always apply your own judgment when looking online, or even when using information in this book for that matter. Things should make sense – processing of petroleum is not a great mystery.

This book has been edited by Steven A. Treese (retired from Phillips 66 Company) and Peter R. Pujadó (retired from UOP LLC, a Honeywell Company). Our fellow editor emeritus was David S.J. Jones (retired from Fluor Corporation), who passed away a few years ago. His contributions are found throughout this book, especially in the detailed techniques for calculation. He is missed.

We appreciate the help of Karin Bartsch with Springer Reference, who provided good guidance in making this an "electronic-friendly" work, as well as a useful reference book.

We would like to also acknowledge our many contributing authors for lending their excellent and invaluable expertise: Mark P. Lapinski, Stephen M. Metro, Mark Moser, Warren Letzch, Maureen Bricker, Vasant Thakkar, John Petri, Peter Kokayeff, Steven Zink, Pamela Roxas, Douglas A. Nafis, Kurt A. Detrick, Robert L. Mehlberg, Dennis J. Ward, Dana K. Sullivan, Bipin Vora, Greg Funk, Andrea Bozzano, Stanley J. Frey, and Geoffrey W. Fichtl. Hopefully, we have not missed anyone.

As a final disclaimer, we have made every effort to provide accurate information in this work, but we offer no warrantees in any specific application. The user assumes all responsibility when applying the information contained herein.

We hope you find this Handbook useful. It has been an interesting adventure for us (and a good review) in compiling it. Use it in safety and good health!

Peter R. Pujadó and Steven A. Treese
Editors and Authors

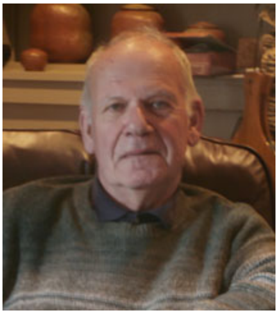
Contents

Volume 1

Volume 2

About the Editors

Steven A. Treese retired from Phillips 66 in 2013 as the Hydroprocessing Team Lead after 40 years but continues to take on the occasional consulting assignment in process engineering and refining as a consultant with Puget Sound Investments, L.L.C. He started his professional career with Union Oil Company of California in 1973 as a Research Engineer after obtaining a B.S. in Chemical Engineering from Washington State University. He followed company heritages through Unocal, Tosco, Phillips, ConocoPhillips, and Phillips 66. Steve's range of experience includes catalyst development, hydroprocessing, hydrogen production, utilities, sulfur recovery, geothermal, shale oil, nitrogen fertilizers, process design, procurement, and licensing. He is a licensed Professional Engineer. Steve has several publications, a few patents, and was on the 1994 NPRA Question and Answer Panel. He is a member of the American Institute of Chemical Engineers. Steve's hobbies include woodworking, boating, fermentation, and photography. He is a mentor for FIRST Robotics Team 624, CRyptonite, in Katy, Texas.



Peter Pujadó retired from UOP LLC (a Honeywell subsidiary) in 2005 as Senior Manager/R&D Fellow responsible for the development and commercialization of technologies for the production of light olefins (ethylene and propylene) by the catalytic conversion of methanol. He started his career as a lecturer at the University of Manchester Institute of Science and Technology (UMIST) in Manchester, England; he then worked as a process engineer for SA Cros in Barcelona, Spain, in areas as diverse as chlorine, caustic, chlorinated hydrocarbons, ammonia, urea, nitric acid, and NPK fertilizers; he joined UOP LLC as an R&D process coordinator responsible for the production of cumene, phenol/acetone, aromatics isomerization, aromatics disproportionation and transalkylation, terephthalic acid, acrylonitrile, acetic acid, etc. After retirement from UOP LLC, he again worked as a lecturer at Northwestern University, Evanston, Illinois, and has done some consulting in the petrochemicals area. Peter had graduated with an M.S. in Chemical and Petroleum Refining Engineering from the Colorado School of Mines, a Ph.D. in Chemical Engineering from the University of Minnesota, and an MBA from the University of Chicago. He is a licensed Professional Engineer and a Fellow Member of the American Institute of Chemical Engineers. He is the author of over 95 papers and publications and of 44 patents. Peter's hobbies include travel, mountain hiking, and reading.

David S. J. Jones was from a small coal mining village (Ynystawe) in South Wales, UK. He left school at the age of 16 and joined the army, where he ended up in India as a Regimental Sergeant Major. After that, he returned to Wales and worked for BP in a quality control lab.

He had ambition, a remarkable ability, and dogged determination to study Chemical Engineering in order to improve on his lot in this world. He studied Chemical Engineering at night school and obtained a Bachelor of Science degree. He had a striking career and made it to the top of the tree, spending many years with Fluor as well as consulting.

When he retired, he occupied himself with the writing of several publications on chemical engineering, such as the *Elements of Petroleum Processing* (Wiley and Sons 1995) and the *Handbook of Petroleum Processing* (Springer 2006), mainly aimed at students and young graduate engineers with an emphasis on problem-solving.

Stan passed away in 2005.

Contributors

Andrea Bozzano UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Maureen Bricker UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Kurt A. Detrick UOP, A Honeywell Company, Des Plaines, IL, USA

Geoffrey W. Fichtl UOP, A Honeywell Company, Des Plaines, IL, USA

Stanley J. Frey UOP, A Honeywell Company, Des Plaines, IL, USA

Gregory Funk UOP LLC, A Honeywell Company, Des Plaines, IL, USA

David S. J. Jones Deceased. Formerly at: Calgary, AB, Canada

Peter Kokayeff UOP, A Honeywell Company, Des Plaines, IL, USA

Mark P. Lapinski UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Warren Letzsch Technip-Stone & Webster, Houston, TX, USA

Consulting PC, Ellicott City, MD, USA

Robert L. Mehlberg UOP, A Honeywell Company, Des Plaines, IL, USA

Stephen Metro UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Mark Moser UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Douglas A. Nafis UOP, A Honeywell Company, Des Plaines, IL, USA

John Petri UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Peter R. Pujadó UOP LLC, A Honeywell Company, Kildeer, IL, USA

Pamela Roxas UOP, A Honeywell Company, Des Plaines, IL, USA

Dana Sullivan UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Vasant Thakkar UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Steven A. Treese Puget Sound Investments LLC, Katy, TX, USA

Bipin Vora R&D, UOP LLC, A Honeywell Company, Des Plaines, IL, USA

Dennis J. Ward Deceased. Formerly at: Ft. Myers, FL, USA

Steven Zink UOP, A Honeywell Company, Des Plaines, IL, USA

Part I

General Refinery Processes and Operations

Introduction to Crude Oil and Petroleum Processing

David S. J. Jones

Contents

David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_24

Abstract

This introduction to crude oil and petroleum processing provides a working knowledge of crude oil properties and refining to make the large array of petroleum-based products we enjoy today. Topics include the composition of crude oil, the crude assay, product properties, and the basic processes used to convert crude to useful products. This chapter sets the stage for the detailed discussions, descriptions, and calculation methods contained in the balance of this handbook.

Keywords
Refinery • Refining • Petroleum • Crude oil

Introduction

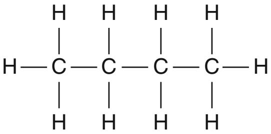
The wheel, without doubt, was man's greatest invention. However, until the late eighteenth century and early nineteenth century, the motivation and use of the wheel was limited either by muscle power, man or animal, or by energy naturally occurring from water flow and wind. The invention of the steam engine provided, for the first time, a motive power independent of muscle or the natural elements. This ignited the industrial revolution of the nineteenth century, with its feverish hunt for fossil fuels to generate the steam. It also initiated the development of the mass production of steel and other commodities.

Late in the nineteenth century came the invention of the internal combustion engine with its requirement for energy derived from crude oil. This, one can say, sparked the second industrial revolution, with the establishment of the industrial scene of today and its continuing development. The petroleum products from the crude oil used initially for the energy required by the internal combustion engine have mushroomed to become the basis and source of some of our chemical and pharmaceutical products.

The development of the crude oil refining industry and the internal combustion engine had influenced each other during the twentieth century. Other factors have also contributed to accelerate the development of both. The major factors are the increasing awareness of environmental contamination and the increasing demand for faster travel which led to the development of the aircraft industry with its need for higher-quality petroleum fuels. The purpose of this introductory chapter is to describe and define some of the basic measures and parameters used in the petroleum refining industry. These set the stage for the detailed examination of the industry as a whole which is provided in other chapters of this handbook.

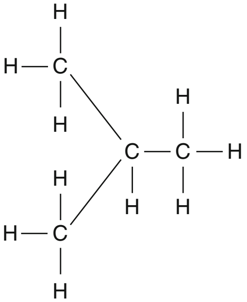
The Composition and Characteristics of Crude Oil

Crude oil is a mixture of literally hundreds of hydrocarbon compounds ranging in size from the smallest, methane, with only one carbon atom, to large compounds containing 300 and more carbon atoms. A major portion of these compounds are paraffins or isomers of paraffins. A typical example is butane shown below:



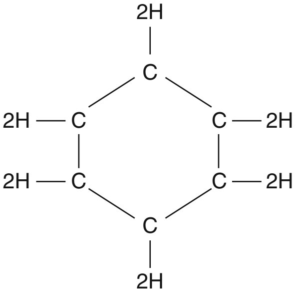
$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & \mid & & \mid & & \mid & & \mid & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & \mid & & \mid & & \mid & & \mid & & \\ & & H & & H & & H & & H & & \end{array}$$

Normal butane(denoted as nC4)

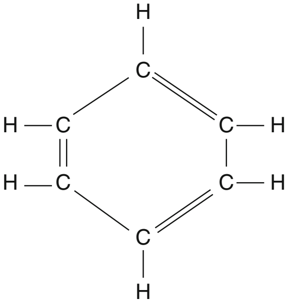


Isobutane (denoted as iC4)

Most of the remaining hydrocarbon compounds are either cyclic paraffins called naphthenes or deeply dehydrogenated cyclic compounds as in the aromatic family of hydrocarbons. Examples of these are shown below:



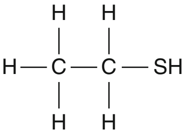
Cyclohexane (Naphthene)



Benzene (Aromatic)

Only the simplest of these homologues can be isolated to some degree of purity on a commercial scale. Generally, in refining processes, isolation of relatively pure products is restricted to those compounds lighter than C7s. The majority of hydrocarbon compounds present in crude oil have been isolated, however, but under delicate laboratory conditions. In refining processes the products are identified by groups of these hydrocarbons boiling between selected temperature ranges. Thus, for example a naphtha product would be labeled as a 90–140 °C cut.

Not all compounds contained in crude oil are hydrocarbons. There are present also as impurities small quantities of sulfur, nitrogen, and metals. By far the most important and the most common of these impurities is sulfur. This is present in the form of hydrogen sulfide and organic compounds of sulfur. These organic compounds are present through the whole boiling range of the hydrocarbons in the crude. They are similar in structure to the hydrocarbon families themselves, but with the addition of one or more sulfur atoms. The simplest of these is ethyl mercaptan which has a molecular structure as follows:



$$H-CH_2-CH_2-SH$$

Ethyl Mercaptan

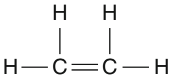
The higher carbon number ranges of these sulfur compounds are thiophenes which are found mostly in the heavy residuum range and disulfides found in the middle distillate range of the crude. The sulfur from these heavier sulfur products can only be removed by converting the sulfur to H_2S in a hydrotreating process operating under severe conditions of temperature and pressure and over a suitable catalyst. The lighter sulfur compounds can be removed as mercaptans by extraction with caustic soda or other suitable proprietary solvents or by other processes, like hydrotreating.

Organic chloride compounds are also present in crude oil. These are not removed as such but metallic protection is applied against corrosion by HCl in the primary distillation processes. This protection is in the form of Monel lining in the sections of the process most vulnerable to chloride attack. Injection of ammonia or amines is also applied to neutralize the HCl in these sections of the equipment.

The most common metal impurities found in crude oils are nickel, vanadium, and sodium. These are not very volatile and are found in the residuum or fuel oil products of the crude oil. These are not removed as metals from the crude and normally they are only a nuisance if they affect further processing of the oil or if they are a deterrent to the saleability of the fuel product. For example, the metals cause severe deterioration in the catalyst life of most catalytic processes. Also, high concentrations of nickel and vanadium are unacceptable in fuel oils used in the production of certain steels. The metals can be removed with the glutinous portion of the fuel oil product called asphaltenes. The most common process used to accomplish this is the extraction of the asphaltenes from the residue oils using propane as solvent. Coking is also common for removal of these heavy components.

Nitrogen, the remaining impurity, is usually found as dissolved gas in the crude or as amines or other nitrogen compounds in the heavier fractions. It is a problem with certain processes, such as catalytic reforming and hydrocracking. Nitrogen is removed along with the sulfur compounds by hydrotreating the feedstocks to these processes.

Although the major families or homologues of hydrocarbons found in all crude oils as described earlier are the paraffins, cyclic paraffins, and aromatics, there is a fourth group. These are the unsaturated or olefinic hydrocarbons. They are not naturally present in any great quantity in most crude oils, but are often produced in significant quantities during the processing of the crude oil to refined products. This occurs in those processes which subject the oil to high temperature for a relatively long period of time. Under these conditions the saturated hydrocarbon molecules break down, permanently losing one or more of the four atoms attached to the quadrivalent carbon. The resulting hydrocarbon molecule is unstable and readily combines with itself (forming double-bond links) or with similar molecules to form polymers. An example of such an unsaturated compound is as follows:



$$\mathrm{H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H}$$

Ethylene

Note the double bond in this compound linking the two carbon atoms.

Although all crude oils contain the compounds described above, rarely are there two crude oils with the same characteristics. This is so because every crude oil from whatever geographical source contains different quantities of the various compounds that make up its composition. Crude oils produced in Nigeria, for example, would be high in cyclic paraffin content and have a relatively low specific gravity. Crude drilled in some of the fields in Venezuela on the other hand would have a very high specific gravity and a low content of material boiling below 350 °C. Table 1 summarizes some of the crude oils from various locations.

Worthy of note in the table is the difference in the character of the various crudes that enables refiners to improve their operation by selecting the best crude or crudes that meet their product marketing requirements. For example, where a refining product slate demands a high quantity of "no-lead" gasoline and a modest outlet for fuel oils, then a crude oil feed such as Hassi Messaoud would be a prime choice. Its selection provides a high naphtha yield with a high naphthene content as catalytic reforming feedstock. Fuel oil in this case also is less than 50 % of the barrel. The Iranian light crude would also be a contender but for the undesirably high metal content of the fuel oil (residuum).

In the case of a good middle of the road crude, Kuwait or the Arabian crude oils offer a reasonably balanced product slate with good middle distillate quality and yields.

For bitumen manufacture and lube oil manufacture, the South American crude oils are formidable competitors. Both major crudes from this area, Bachequero, the heavier crude, and Tia Juana, the lighter, are highly acidic (naphthenic acids) which enhances bitumen and lube oil qualities. There is a problem with these crude oils however as naphthenic acids are very corrosive in atmospheric distillation columns, particularly in the middle distillate sections. Normal distillation units may require relining of sections of the tower with 410 stainless steel and/or injection of caustic if extended processing of these crude oils is envisaged.

Refiners often mix selected crude oils to optimize a product slate that has been programmed for the refinery. This exercise requires careful examination of the various crude assays (data compilation) and modeling the refinery operation to set the crude oil mix and its operating parameters.

The Crude Oil Assay

The crude oil assay is a compilation of laboratory and pilot plant data that define the properties of the specific crude oil. At a minimum, the assay should contain a distillation curve for the crude and a specific gravity curve. Most assays however contain data on pour point (flowing criteria), sulfur content, viscosity, and many other properties. The assay is usually prepared by the company selling the crude oil; it is used extensively by refiners in their plant operation, development of product schedules, and examination of future processing ventures. Engineering companies

Table 1 Characteristics of some crude oils from various worldwide locations

	Arabian light	Arabian heavy	Iranian light	Iranian heavy (Gach Saran)	Iraq (Kirkuk)	Kuwait	Algerian (Hassi Messaoud)	Libyan (Brega)	Nigerian (Bonny medium)	North Sea (Ekofisk)	South American (Bachequero)
% vol. boiling below 350 °C	54.0	46.5	55.0	53.0	61.1	49.0	75.2	64.0	54.5	61.2	30.0
Gravity, API	33.4	28.2	33.5	30.8	35.9	31.2	44.7	40.4	26.0	36.3	16.8
Sulfur, wt%	1.8	2.84	1.4	1.6	1.95	2.5	0.13	0.21	0.23	0.21	2.4
PONA of heavy naphtha, vol%											
Cut, °C	100–150	100–150	149–204	149–204	100–150	100–150	95–175	100–150	100–150	100–200	93–177
Paraffins	69.5	70.3	54.0	50	69.0	67.9	56.5	53.0	27.5	56.5	27.6
Olefins	–	–	–	–	265 ppm	–	–	20 ppm	1.5	–	–
Naphthenes	18.2	21.4	30.0	35	21.0	22.1	32.9	39.3	57.0	29.5	58.5
Aromatics	12.3	8.3	16.0	15	9.8	10.0	10.6	7.7	14.0	14.0	13.9
Metals in residuum											
Residuum temp. °C	>565	>565	>538	>538	>370	>370	>350	>570	>535	>350	>350
Vanadium, wt ppm	94	171	188	404	58	59	<5	24	7	1.95	437
Nickel, wt ppm	22	53	70	138	<3	18	<5	32	52	5.04	75

The Bachequero pour point is 16 °C

use the assay data in preparing the process design of petroleum plants they are bidding on or, having been awarded the project, they are now building.

In order to utilize the crude oil assay, it is necessary to understand the data it provides and the significance of some of the laboratory tests that are used in its compilation. Some of these are summarized below and are further described and discussed in other chapters of the handbook.

The True Boiling Point Curve

This is a plot of the boiling points of almost pure components, contained in the crude oil or fractions of the crude oil. In earlier times this curve was produced in the laboratory using complex batch distillation apparatus of a hundred or more equilibrium stages and a very high reflux ratio. Nowadays, this curve is produced by mass spectrometry techniques much quicker and more accurately than by batch distillation. A typical true boiling point curve (TBP) is shown in Fig. 10.

The ASTM Distillation Curve

While the TBP curve is not produced, on a routine basis the ASTM distillation curves are. Rarely, however, is an ASTM curve conducted on the whole crude. This type of distillation curve is used on a routine basis for plant and product quality control. This test is carried out on crude oil fractions using a simple apparatus designed to boil the test liquid and to condense the vapors as they are produced. Vapor temperatures are noted as the distillation proceeds and are plotted against the distillate recovered. Because only one equilibrium stage is used and no reflux is returned, the separation of components is poor. Thus, the initial boiling point (IBP) for ASTM is higher than the corresponding TBP point and the final boiling point (FBP) of the ASTM is lower than that for the TBP curve. There is a correlation between the ASTM and the TBP curve, and this is dealt with later in this chapter.

API Gravity

This is an expression of the density of an oil. Unless stated otherwise the API gravity refers to density at 60 °F (15.6 °C). Its relationship with specific gravity is given by the following expression:

$$\text{API}^\circ = \frac{141.5}{\text{sp.gr.}} - 131.5 \tag{1}$$

Flash Points

The flash point of an oil is the temperature at which the vapor above the oil will momentarily flash or explode. This temperature is determined by laboratory testing using an apparatus consisting of a closed cup containing the oil, heating and stirring equipment, and a special adjustable flame. The type of apparatus used for middle distillate and fuel oils is called the Pensky-Martens (PM), while the apparatus used in the case of kerosene and lighter distillates is called the Abel. References to these tests are given later in this handbook, and full details of the test methods and procedures are given in ASTM Standards Part 7, Petroleum Products and Lubricants. There are many empirical methods for determining flash points from the ASTM distillation curve. One such correlation is given by the following expression:

$$\text{Flash point } ^\circ\text{F} = 0.77(\text{ASTM } 5\ \%\ ^\circ\text{F} - 150\,^\circ\text{F}) \tag{2}$$

Octane Numbers

Octane numbers are a measure of a gasoline resistance to knock or premature detonation in a cylinder of a gasoline engine. The higher this resistance, the higher will be the efficiency of the fuel to produce work. A relationship exists between the antiknock characteristic of the gasoline (octane number) and the compression ratio of the engine in which it is to be used. The higher the octane rating of the fuel, the higher the compression ratio of the engine in which it can be used.

By definition, an octane number is that percentage of isooctane in a blend of isooctane (2,2,4-trimethylpentane) and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90 octane gasoline matches the knock characteristic of a blend containing 90 % isooctane and 10 % *n*-heptane. The knock characteristics are determined in the laboratory using a standard single cylinder test engine equipped with a super sensitive knock meter. The reference fuel (isooctane blend) is run and compared with a second run using the gasoline sample. Details of this method are given in the ASTM Standards Part 7, Petroleum Products and Lubricants.

Two octane numbers are usually determined. The first is the research octane number (ON res or RON) and the second is the motor octane number (ON mm or MON). The same basic equipment is used to determine both octane numbers, but the engine speed for the motor method is much higher than that used to determine the research number. The actual octane number obtained in a commercial vehicle would be somewhere between these two. The significance of these two octane numbers is to evaluate the sensitivity of the gasoline to the severity of operating conditions in the engine. The research octane number is usually higher than the motor number; the difference between them is termed the “sensitivity of the gasoline.”

Viscosity

The viscosity of an oil is a measure of its resistance to internal flow and is an indication of its lubricating qualities. In the oil industry it is usual to quote viscosities either in centistokes (which is the unit for kinematic viscosity), Saybolt universal seconds, Saybolt Furol seconds, or Redwood seconds. These units have been correlated and such correlations can be found in most data books. In the laboratory, test data on viscosities is usually determined at temperatures of 100 °F, 130 °F, or 210 °F. In the case of fuel oils, temperatures of 122 °F and 210 °F are used.

Cloud and Pour Points

Cloud and pour points are tests that indicate the relative coagulation of wax in the oil. They do not measure the actual wax content of the oil. In these tests, the oil is reduced in temperature under strict control using an ice bath initially and then a frozen brine bath and finally a bath of dry ice (solid CO_2). The temperature at which the oil becomes hazy or cloudy is taken as its cloud point. The temperature at which the oil ceases to flow altogether is its pour point.

Sulfur Content

This is self-explanatory and is usually quoted as %wt or wt ppm (wppm) for the total sulfur in the oil.

Assays change in the data they provide as the oils from the various fields change with age. Some of these changes may be quite significant and users usually request updated data for definitive work, such as process design or evaluation. The larger producers of crude oils provide laboratory test services on an “ongoing” basis for these users.

The next few sections of this chapter illustrate how the assay data and basic petroleum refining processes are used to develop a process configuration for an oil refining complex.

Other Basic Definitions and Correlations

As described earlier, the compositions of crude oil and its fractions are not expressed in terms of pure components, but as “cuts” expressed between a range of boiling points. These “cuts” are further defined by splitting them into smaller sections and treating those sections as though they were pure components. As such, each of these components will have precise properties such as specific gravity, viscosity, mole weight, pour point, etc. These components are referred to as pseudo components and are defined in terms of their mid-boiling point.

Before describing in detail the determination of pseudo components and their application in the prediction of the properties of crude oil fractions, it is necessary to define some of the terms used in the crude oil analysis. These are as follows:

Bubble Point

Bubble point is the temperature and pressure at which a hydrocarbon begins to boil. An example of bubble point calculation for a stream is provided here as an example. The bubble point can also be calculated using process simulation software (HYSYS, Pro/II, or other programs) with selection of appropriate thermodynamic/equilibrium systems. Understanding the manual calculation approach is useful in interpreting and evaluating the computer calculation results.

Consider an overhead stream from a fractionator that has the following composition:

Mole fraction composition:

C_2	0.008
C_3	0.054
iC_4	0.021
nC_4	0.084
C_5s	0.143
C_6	0.155
C_7	0.175
Comp 1	0.124
Comp 2	0.124
Comp 3	0.075
Comp 4	0.037
Total	1.00

The components 1–4 are pseudo components that have properties similar to real components with the same boiling point. These pseudo components are discussed more below. The mid-boiling points of the components are taken as:

	°F
Comp 1	260
Comp 2	300
Comp 3	340
Comp 4	382

The reflux drum temperature will be fixed at 100 °F. You want to determine the pressure for the reflux drum at ***the bubble point*** of this material at 100 °F.

Now, at the bubble point, the sum of all y's = sum of all Kx's.

x is the mole fraction of a component in the liquid phase and y is the mole fraction of the component in the vapor phase at equilibrium. At bubble point $\Sigma y = \Sigma Kx$.

K is the equilibrium constant and can be read from the curves found in textbooks such as Maxwell's *Data Book on Hydrocarbons* or can be considered (rough and not be used for definitive design) as

$$K = \text{Vapor Pressure(at temperature)/Total Pressure} \tag{3}$$

This relationship will be used for this calculation. The calculation is iterative (trial and error) as follows (at 100 °F):

		1st Trial at 5 psig		2nd Trial at 12 psig	
	Mol fract. X	K	$Y = KX$	K	$Y = KX$
C_2	0.008	40.6	0.325	32.4	0.259
C_3	0.054	9.3	0.502	7.42	0.401
iC_4	0.021	3.55	0.075	2.38	0.05
nC_4	0.084	2.54	0.213	2.03	0.171
C_5	0.143	0.89	0.127	0.71	0.102
C_6	0.155	0.254	0.039	0.20	0.031
C_7	0.175	0.084	0.015	0.067	0.011
Comp 1	0.124	0.023	0.003	0.020	0.002
Comp 2	0.124	NEG	NEG		
Comp 3	0.075	NEG	NEG		
Comp 4	0.037	NEG	NEG		
	1.000		1.299		1.027

For second trial (estimate)

Take the K value of the highest fraction of y (in this case C3) where $K = 9.3$.

Take this $K = 7.42$ (new K).

Make the second trial with K_{C3} at 7.42 which gives a systems pressure P as follows: VP $C_3 = 7.1$ where VP C3 at 100 °F is 190 psia.

Then P = 190/7.1 = 26.5 psia.

Second trial pressure = 26.5 psia = 11.8 psig. Let's set it at 12 psig.

The second trial gives sum of Y's = 1.027 and this is considered close enough to 1.000. Then the drum will be operated at 100 °F and at 12 psig.

Cut Point

A cut point is defined as that temperature on the whole crude TBP curve that represents the limits (upper and lower) of a fraction to be produced. Consider the curve shown in Fig. 1 of a typical crude oil TBP curve.

A fraction with an upper cut point of 100 °F produces a yield of 20 % volume of the whole crude as that fraction. The next adjacent fraction has a lower cut point of 100 °F and an upper one of 200 °F; this represents a yield of 30–20 % = 10 % volume on crude.

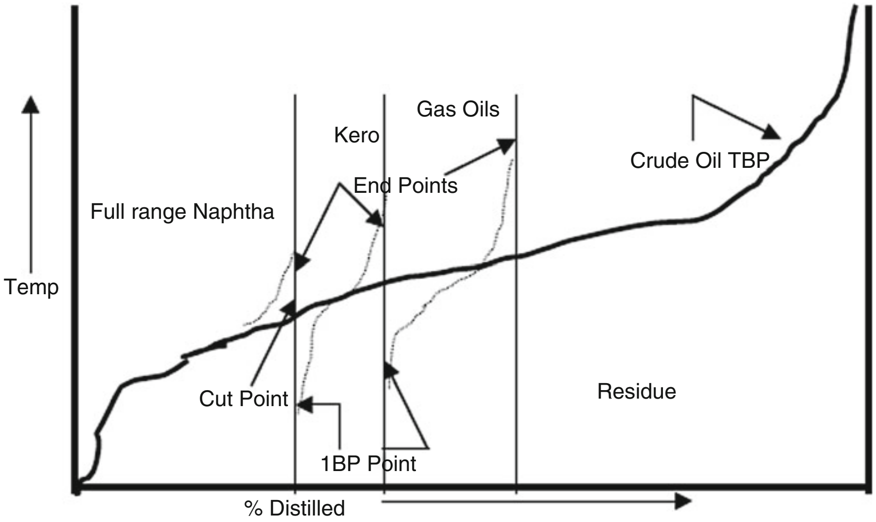


Fig. 1 Cut points and end points

End Points

While the cut point is an ideal temperature used to define the yield of a fraction, the end points are the actual terminal temperatures of a fraction produced commercially. No process has the capability to separate perfectly the components of one fraction from adjacent ones. When two fractions are separated in a commercial process, some of the lighter components remain in the adjacent lighter fraction. Likewise some of the heavier components in the fraction find their way into the adjacent heavier fraction. Thus, the actual IBP of the fraction will be lower than the initial cut point, and its FBP will be higher than the corresponding final cut point. This is also shown in Fig. 1.

Mid-boiling Point Components

In compiling the assay narrow boiling fractions are distilled from the crude and are analyzed to determine their properties. These are then plotted against the mid-boiling point of these fractions to produce a smooth correlation curve. To apply these curves for a particular calculation, it is necessary to divide the TBP curve of the crude, or fractions of the crude, into mid-boiling point components. To do this, consider Fig. 2. For the first component take an arbitrary temperature point A. Draw a horizontal line through this from the 0 % volume. Extend the line until the area between the line and the curve on both sides of the temperature point A are equal. The length of the horizontal line measures the yield of component

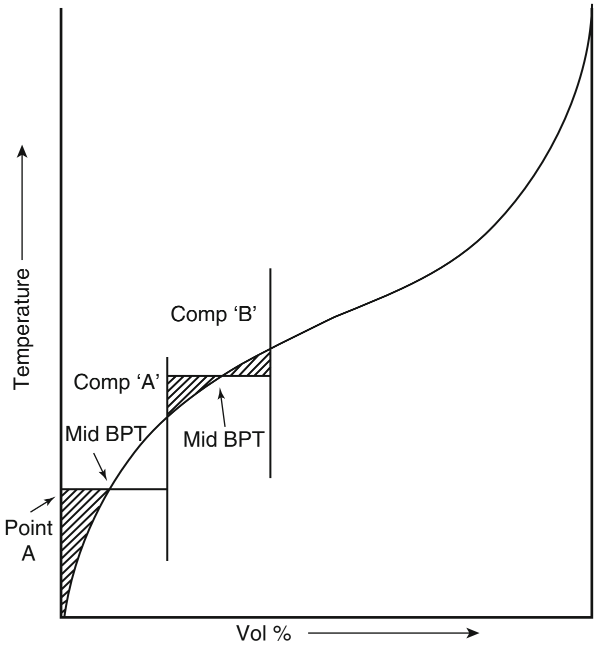


Fig. 2 Example of mid-boiling points

A having a mid-boiling point A °F. Repeat for the next adjacent component and continue until the whole curve is divided into these mid-boiling point components.

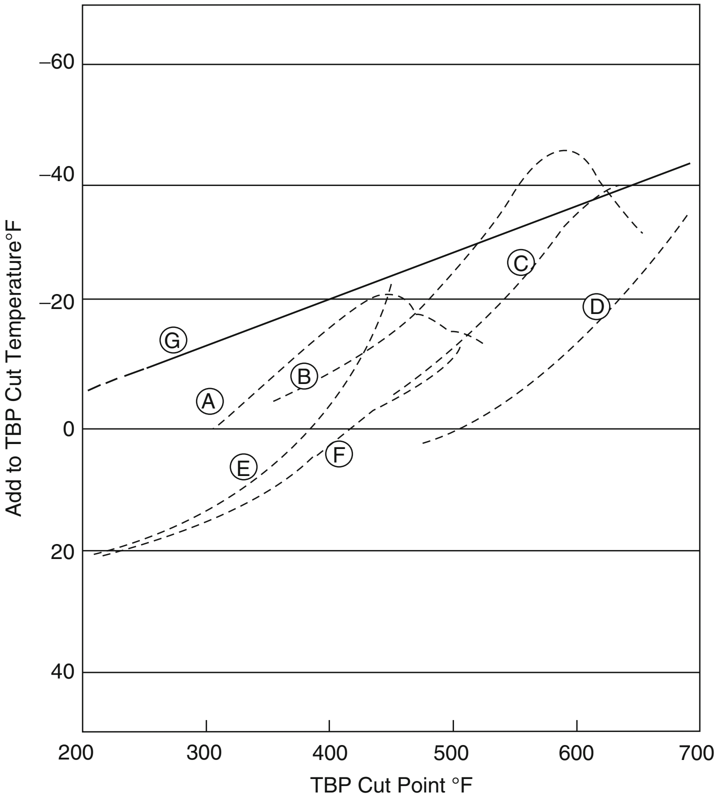
Mid-volume Percentage Point Components

Sometimes the assay has been so constructed as to correlate the crude oil properties against components on a mid-volume percentage basis. In using such data as this, the TBP curve is divided into mid-volume point components. This is easier than the mid -boiling point concept and requires only that the curve be divided into a number of volumetric sections. The mid-volume figure for each of these sections is merely the arithmetic mean of the volume range of each component.

Using these definitions the determination of the product properties can proceed using the distillation curves for the products, the pseudo component concept, and the assay data. This is given in the following discussion.

Predicting TBP and ASTM Curves from Assay Data

The properties of products can be predicted by constructing mid-boiling point components from a TBP curve and assigning the properties to each of these components.



A End Points Vs TBP Cut Point for fractions statrting at 200°F TBP or Lower
B End Points Vs TBP Cut Point for fractions statrting at 300
C End Points Vs TBP Cut Point for fractions statrting at 400
D End Points Vs TBP Cut Point for fractions statrting at 500
E & F ASTM End Points Vs TBP Cut Point 300 ml STD col & 5 ft Packed Towers.
G 90% vol temp Vs 90% vol TBP cut (All Fractions).

Fig. 3 Correlation between TBP and ASTM end points

These assigned properties are obtained either from the assay data, known components of similar boiling points, or established relationships such as gravity, molecular weights, and boiling points. However, before these mid-boiling points (pseudo) components can be developed, it is necessary to know the shape of the product TBP curve. The following is a method by which this can be achieved. Good et al. (1944) accumulated data to relate the ASTM end point to a TBP cut point over the light and middle distillate range of crude. Their correlation curves are given in Fig. 3 and are self-explanatory. Thrift (1961) derived a probable shape of ASTM data. The probability graph that he developed is given in Fig. 4. The product ASTM curve from a well-designed unit would be a straight line from 0 % vol to 100 % vol

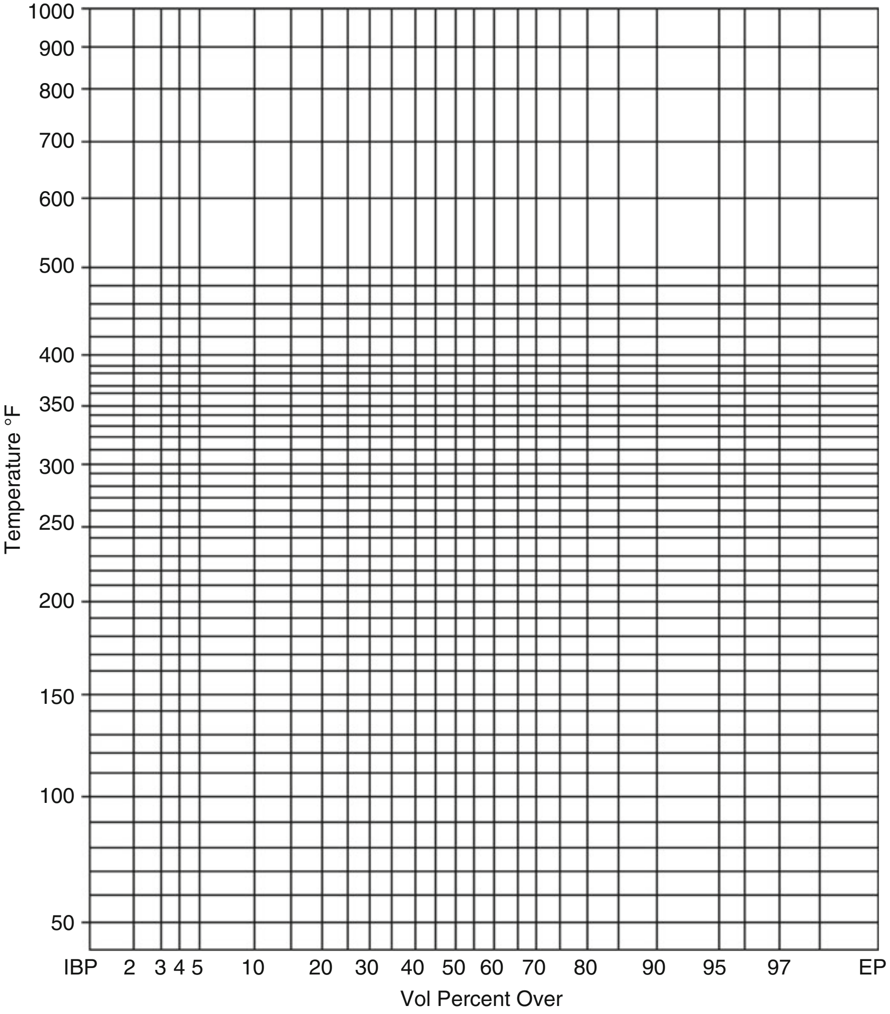


Fig. 4 ASTM distillation probability curves

on this graph. Using these two graphs it is possible now to predict the ASTM distillation curve of a product knowing only its TBP cut range.

An example of this calculation is given below:

It is required to predict the ASTM distillation curve for kerosene, cut between 387 and 432 °F cut points on Kuwait crude.

Solution Yield on crude = 3.9 % vol

Cut range = 27.3–31.2 % vol on crude.

Ninety percent vol of cut = 30.81 which is = 430 °F

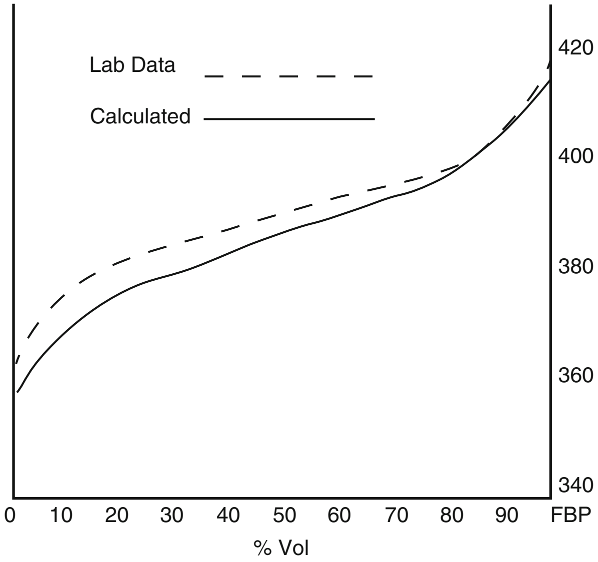


Fig. 5 Comparison between calculated ASTM curve and lab data

From Fig. 3, curve B ASTM end point = 432–13 °F = 419 °F

From Fig. 3, curve G ASTM 90 % point = 430–24 °F = 406 °F

These two points are plotted in Fig. 4 and a straight line drawn through them to define the probable ASTM distillation of the cut. This is plotted linearly in Fig. 5 and can be seen to compare well with laboratory results of the actual product from a crude distillation unit.

Developing the TBP Curve and the Equilibrium Flash Vaporization (EFV) Curve from the ASTM Distillation Curve

Using a product ASTM distillation curve developed as shown above, the TBP curve is developed as follows:

Converting the Product ASTM Distillation to TBP

Most crude distillation units take a full-range naphtha cut as the overhead product. This cut contains all the light ends, ethane through pentanes, in the crude and of course the heavier naphtha cut. All the light ends are in solution; therefore, it is not possible to prepare a meaningful ASTM distillation on this material directly. Two routes can be adopted in this case: the first is to take naphtha samples of the heavy naphtha and debutanized light naphtha from downstream units. Alternatively the sample can be subject to light end analysis in the lab such as using POD apparatus (Podbielniak), a gas chromatograph, or and carrying out an ASTM distillation on the stabilized sample. It is the third route that is chosen for this case.

There are two well-proven methods for this conversion. The first is by Edmister and given in his book *Applied Hydrocarbon Thermodynamics* and the second by

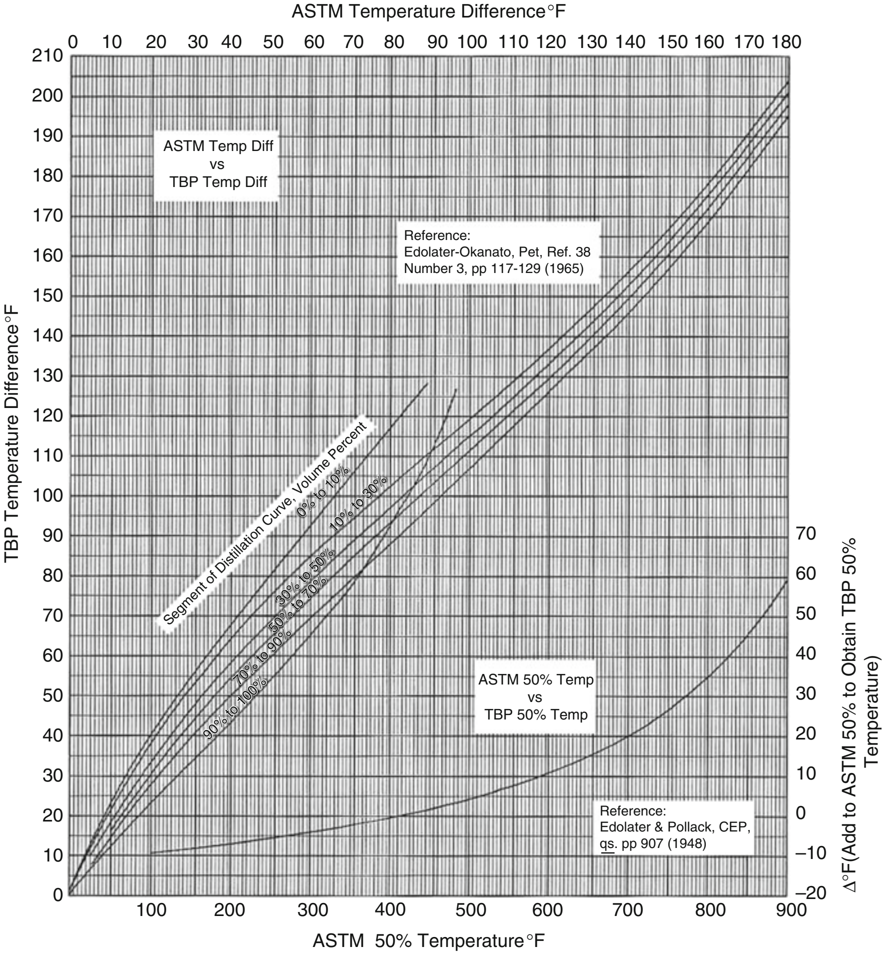
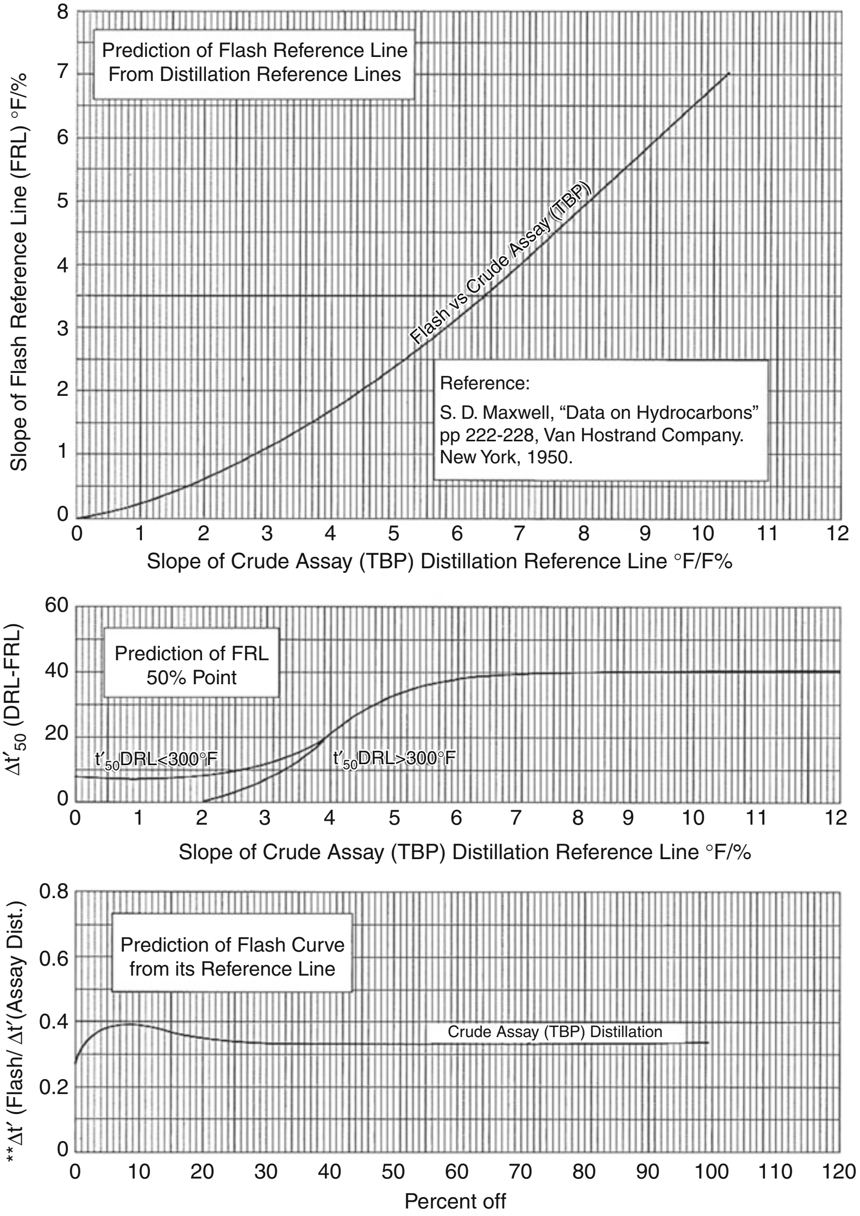


Fig. 6 ASTM–TBP correlation – Edmister method

Maxwell (1968) in his book *Data Book on Hydrocarbons*. The correlation curves from both these sources are given as Figs. 6 and 7. In this exercise Edmister's method and correlation will be used.

The ASTM distillation is tabulated as the temperature for IBP, 10 %, 20 %, through to the FBP. IBP is the initial boiling point (equivalent to 0 % over) and the FBP is the final boiling point (equivalent to 100 % vol over). The multiples of 10 % reflect the volume distilled and the temperature at which each increment is distilled. Using Fig. 6, the 50 % vol TBP point (in degrees Fahrenheit) is calculated from the 50 % vol point of the ASTM distillation.

Figure 6 is then used to determine the TBP temperature difference from the ASTM temperature difference for the 0–10 % vol, 10–30 % vol, 30–50 % vol, 50–70 % vol, 70–90 % vol, and 90–100 % vol. Moving from the established 50 % vol TBP figure


Prediction of Flash Reference Line From Distillation Reference Lines

Reference:
S. D. Maxwell, "Data on Hydrocarbons" pp 222-228, Van Hostrand Company. New York, 1950.

Prediction of FRL 50% Point

Prediction of Flash Curve from its Reference Line

NOTE: * Flash and distillation reference lines (FRL and DRL) are straight lines through the 10% and 70% points. The temperature of the 50% points refer to these reference lines.

** $\Delta t'$ is the departure of the actual flash and distillation curves from their respective reference lines. While the individual ($\Delta t'$)'s may be either plus or minus, the ratio is always positive.

Fig. 7 EFV–TBP correlation – Maxwell method

Table 2 Converting ASTM to TBP distillation

	ASTM (lab data)		TBP (from Fig. 6)	
	°F	Δ°F	Δ°F	°F
IBP	424	29	61	361
10 %vol	453	31	52	423
30 %vol	484	18	52	475
50 %vol	502			507
70 %vol	504	2	31	538
90 %vol	536	32	41	579
FBP	570	34	40	619

and using the temperature differences given by Fig. 6, the TBP temperatures at 0 %, 10 %, 30 %, 50 %, 70 %, 90 %, and 100 % vol are obtained (Table 2).

Developing the Equilibrium Flash Vaporization Curve (EFV)

The Maxwell curves given as Fig. 7 are used to develop the equilibrium flash vaporization curve (EFV) from the TBP. The EFV curve gives the temperature at which a required volume of distillate will be vaporized. This distillate vapor is always in equilibrium with its liquid residue. The development of the EFV curve is always at atmospheric pressure. Other temperature- and pressure-related conditions may be determined by using the vapor pressure curves or by constructing a phase diagram.

The TBP reference line (DRL) is first drawn by a straight line through the 10 % vol point and the 70 % vol point on the TBP curve. The slope of this line is determined as temperature difference per volume percent. These data are then used to determine the 50 % volume temperature of a flash reference line (FRL). The curve in Fig. 7 relating Δt_{50} (DRL–FRL) to DRL slope is used for this. Finally, the curve on Fig. 7 relating the ratio of temperature differences between the FRL and flash curve (EFV) from that for the TBP to DRL is applied to each percent volume. From this the atmospheric EFV curve is drawn.

A sample calculation for the compilation of the EFV curve follows. Note that the TBP curve is used to define product yields, while the EFV curve is used to define temperature/pressure conditions in distillation. This example uses the TBP curve developed above as a starting point (Table 3).

Calculating Vapor and Liquid Compositions from Equilibrium Flash

When a mixture of compounds vaporizes or condenses, there is a unique relationship between the composition of the mixture in the liquid phase and that in the corresponding phase at any condition of temperature and pressure. This relationship is termed the equilibrium flash vaporization for the mixture. An equilibrium flash can be calculated using the procedure detailed in Appendix 1 of the current chapter.

Today these calculations are normally performed using process simulation software; however, the principles are the same as the manual calculation method.

Table 3 Converting TBP to EFV distillation

% Volume	Δt (TBP – DRL), °F	ΔT (Flash FRL)/ ΔT (TBP–DRL)	Δt (Flash–FRL), °F	Flash, °F
0	−46	0.2	−9.2	453
10	0	0.4	0	469
20	9	0.38	3.4	482
30	14	0.37	5.2	491
40	13	0.37	4.8	498
50	7	0.37	2.6	507
60	4	0.37	1.5	511
70	0	0.37	0	514
80	−2	0.37	−0.8	523
90	0	0.37	0	531
100	22	0.37	8.1	547

The resulting TBP curves and EFV curves are shown in Fig. 8

Flash calculations are among the most common calculations required to design and analyze petroleum processing operations.

Predicting Product Qualities

The following paragraphs describe the prediction of product properties using pseudo components (mid-boiling point) and assay data. A diesel cut with TBP cut points 432–595 °F on Kuwait crude (Fig. 9) will be used to illustrate these calculations. The actual TBP of this cut is predicted using the method already described. The curve is then divided into about six pseudo mid-boiling point components as described earlier and is shown in Fig. 10.

Predicting the Gravity of the Product

Using the mid-boiling point versus specific gravity curve from the assay given in Appendix C of this handbook, the SG for each component is obtained. The weight factor for each component is then obtained by multiplying the volume percent of that component *by the specific gravity. The sum of the weight factors divided by the 100 % volume* total is the specific gravity of the gas oil cut. This is shown in Table 4.

The Prediction of Product Sulfur Content

The prediction of sulfur content is similar to the method used for gravity. First the TBP curve for the product is determined and split into pseudo boiling

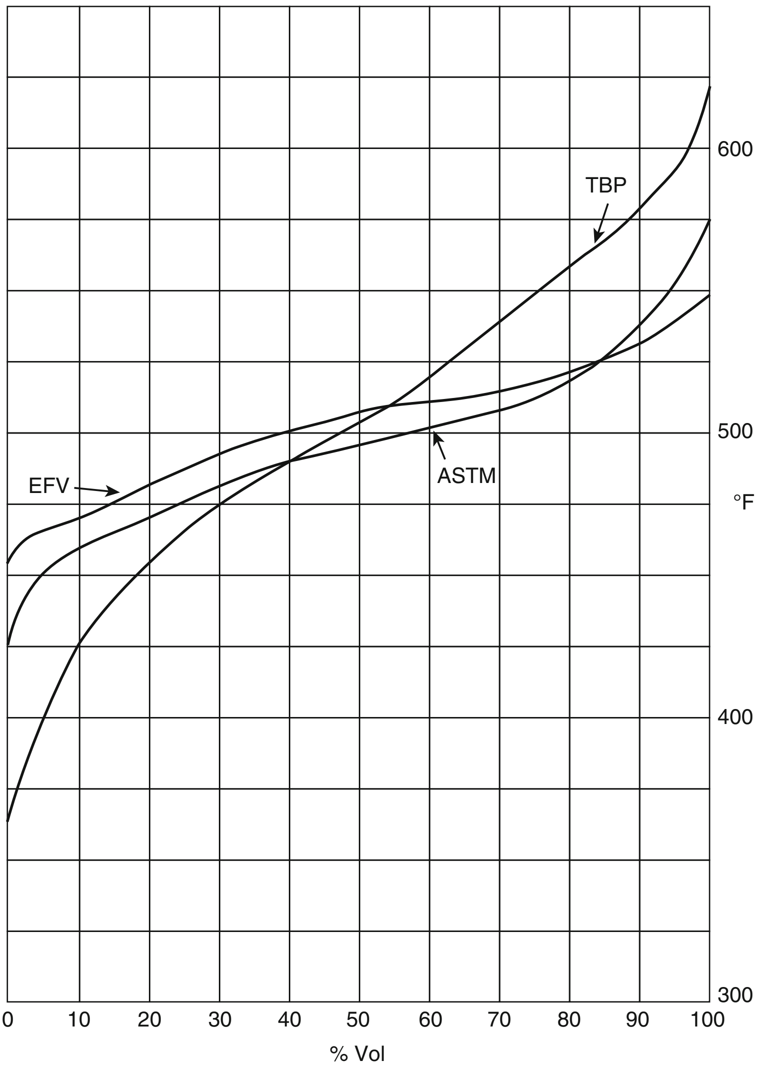


Fig. 8 Types of distillation curves

point components. The weight factor is then determined for each component as before. Note that sulfur content is always quoted as a percent weight. Using the relationship of percent sulfur to mid-boiling point given in the assay, the sulfur content of each component is read off. This is multiplied by the weight factor for each component to give a sulfur factor. The sum of the total sulfur factors divided by the total weight factor gives the weight percent sulfur content of the fraction. For example, using the same gas oil cut as before, its sulfur content is determined as shown in Table 5.

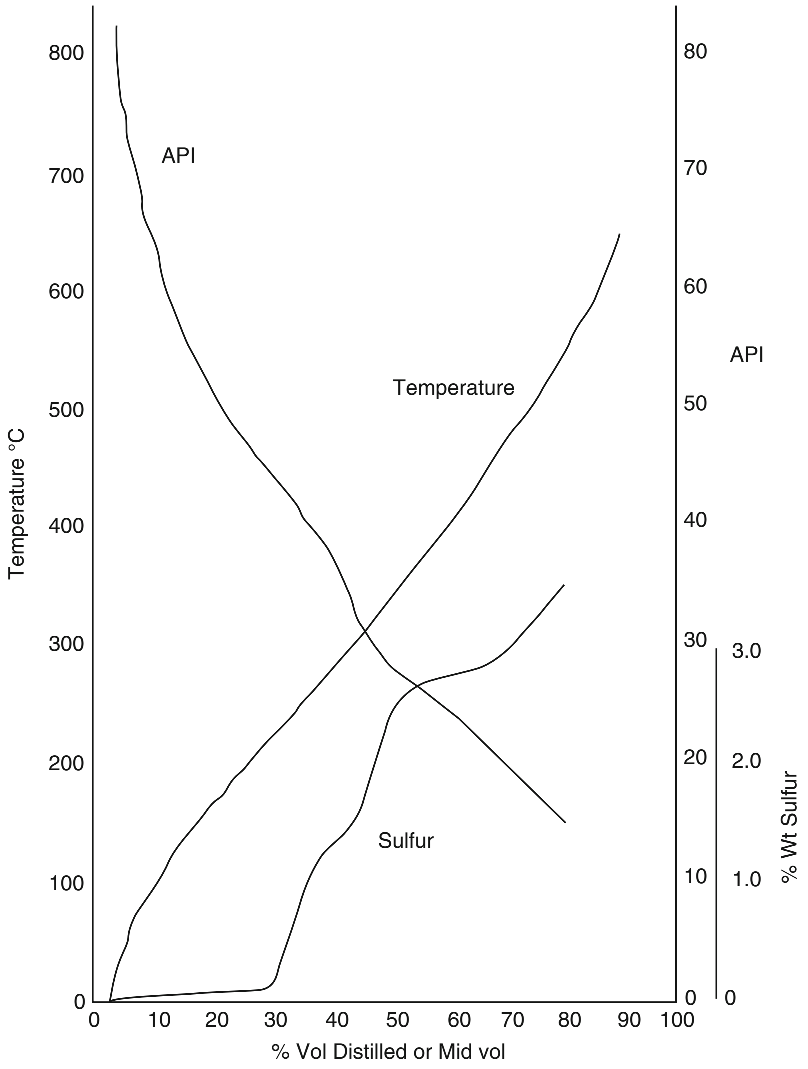


Fig. 9 Typical crude assay curves (based on Kuwait crude)

Viscosity Prediction from the Crude Assay

Unlike sulfur content and gravity, viscosity cannot be arithmetically related directly to components. To determine the viscosity of a blend of two or more components, a blending index must be used. A graph of these indices is given in Maxwell's *Data Book on Hydrocarbons*, and part of this graph is reproduced in Fig. 11. Using the blending indices and having divided the TBP curve into components as before, the viscosity of the fraction can be predicted as shown in Table 6.

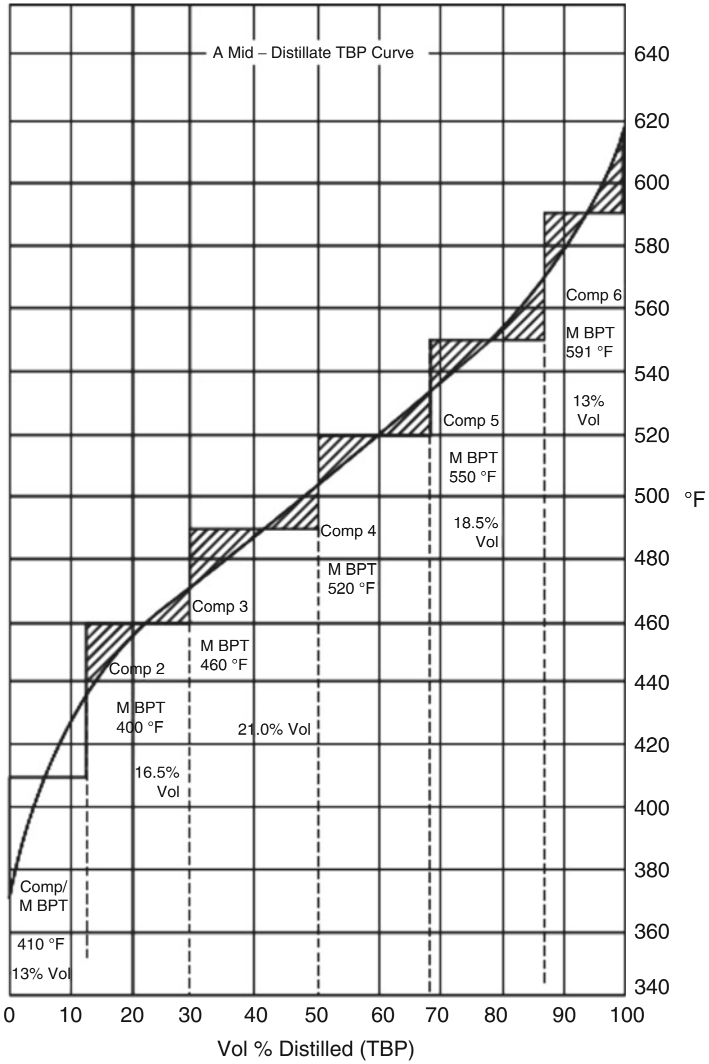


Fig. 10 Typical pseudo component breakdown

Cloud and Pour Points

In predicting these properties, it is not necessary to break down the product TBP as we have done for specific gravity, sulfur, etc. The accuracy of the tests and of blending indices does not warrant this. These properties are therefore read off directly from the mid-boiling point of the whole product. Considering the gas oil used in the previous example, its mid-boiling point is about 510 °F, from the crude assay its pour point is −5 °F, and cloud point is +4 °F. Determining pour point for a blend of two or more products is rather more difficult. In this case blending indices

Table 4 Calculating the SG of a cut

Component	Volume %	Mid-BPt, °F	SG at 60 °F	Weight factor
1	13.0	410	0.793	10.3
2	16.5	460	0.801	13.2
3	21.0	489	0.836	17.6
4	18.0	520	0.844	15.2
5	18.5	550	0.846	15.7
6	13.0	592	0.850	11.1
Total	100.0			83.1

$\text{SG of cut} = \frac{83.1}{100} = 0.831$

Table 5 Calculating the sulfur content of a cut

Component	Weight factor	Mid-BPt, °F	Sulfur, % wt	Sulfur factor
1	10.3	410	0.2	2.06
2	13.2	460	0.41	5.41
3	17.6	489	0.84	14.78
4	15.2	520	1.16	17.63
5	15.7	550	1.35	21.2
6	11.1	592	1.5	16.65
Total	83.1			77.73

$\text{Sulfur \% weight} = \frac{77.7}{83.1} \times 100 = 0.935\,\%\text{wt. (actual plant data gave } 0.931\,\%\text{wt.)}$

are used for this purpose. A graph of these indices is given in Fig. 12. It is self-explanatory and its application is explained in Table 7.

Flash Points

The flash point of a product is related to its ASTM distillation by the expression:

$$\text{Flash point} = 0.77(\text{ASTM } 5\,\% \text{ in } {}^\circ\text{F} - 150\,{}^\circ\text{F}) \tag{4}$$

Thus, for the gas oil product in the above example, the flash point will be as follows:

$$\text{Flash point} = 0.77(420 - 150) = 208\,{}^\circ\text{F}.$$

Blending Products of Different Flash Points

As with pour points and viscosity, the flash point of a blend of two or more components is determined by using a flash blending index. Figure 13 gives these indices. Again the indices are blended linearly as in the case of viscosity. Consider the following example:

2,000 BPSD of kerosene with a flash point of 120 °F is to be blended with 8,000 BPSD of fuel oil with a flash point of 250 °F. Calculate the flash point of the blend (Table 8).

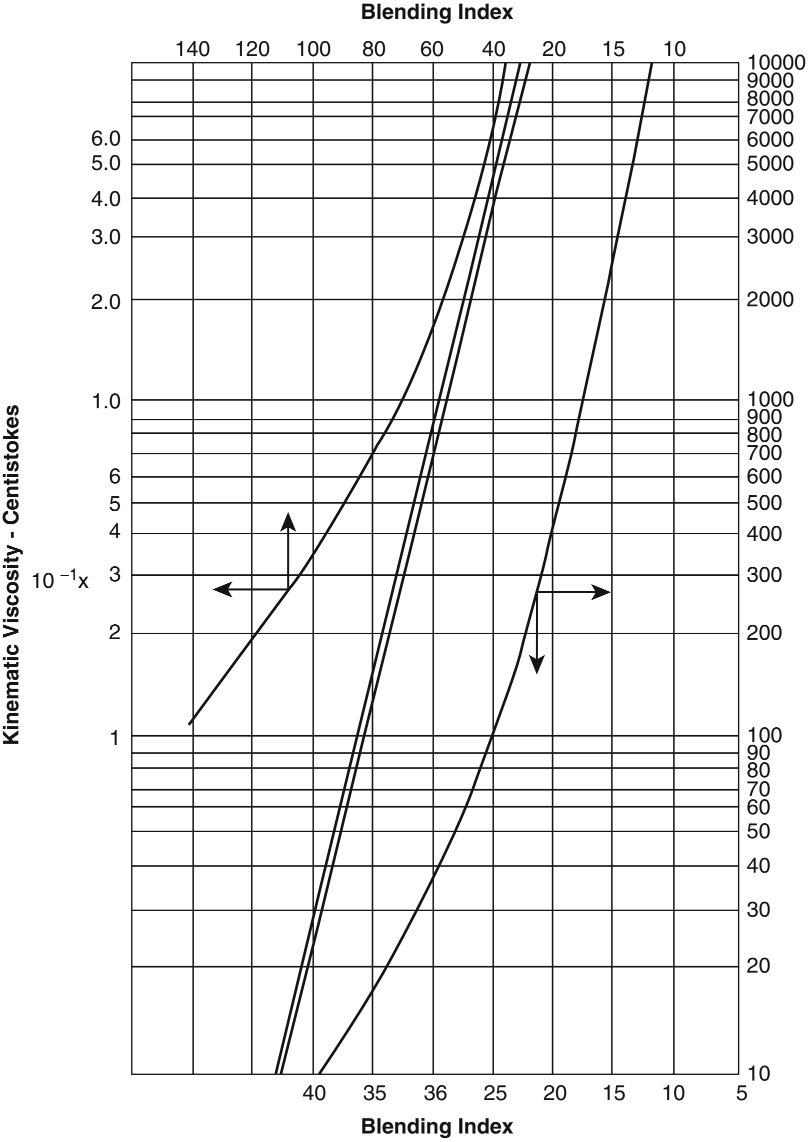


Fig. 11 Viscosity blending index

Predicting the Mole Weights of Products

The prediction of molecular weights of product streams is often required for the design of the processes that are going to produce those products. There are other more rigorous calculations that can and are used for definitive design and in

Table 6 Calculating the viscosity of a cut

Component	Volume % (A)	Mid-BPt °F	Viscosity cS 100 °F	Blending index (B)	Viscosity factor (A × B)
1	13.0	410	1.49	63.5	825.5
2	16.5	460	2.0	58.0	957
3	21.0	489	2.4	55.0	1,155
4	18.0	520	2.9	52.5	945
5	18.5	550	3.7	49.0	906.5
6	13.0	592	4.8	46.0	598
Total	100.0				5,387.0

Overall viscosity index $= \frac{5,387}{100} = 53.87$

From Fig. 11 an index of 53.87 = 2.65 cSt (actual plant test data was 2.7 cSt)

building up computer simulation packages. The method presented here is a simple method by which the mole weight of a product stream can be determined from a laboratory ASTM distillation test. The result is sufficiently accurate for use in refinery configuration studies and the like.

A relationship exists between the mean average boiling point of a product (commonly designated as MEABP), the API gravity, and the molecular weight of petroleum fractions. This is shown in Fig. 14.

Using a gas oil fraction as an example, the MEABP of the product is calculated from its ASTM distillation in degrees Fahrenheit as given below:

% Vol	°F
0	406
10	447
30	469
50	487
70	507
90	538
100	578

$$\text{The slope of the curve is calculated by } \frac{T^\circ\text{F@}\,90\% - T^\circ\text{F@}\,10\,\%}{80} = \frac{538-447}{80} = 1.14\ ^\circ\text{F\%} \tag{5}$$

$$\text{Volume average boiling point} = \frac{T^\circ\text{F@ }10\,\% + (2\times T^\circ\text{F@}\,50\,\%) + T\ ^\circ\text{F@}\,90\%}{4} = \frac{447+974+538}{4} = 490^\circ\text{F} \tag{6}$$

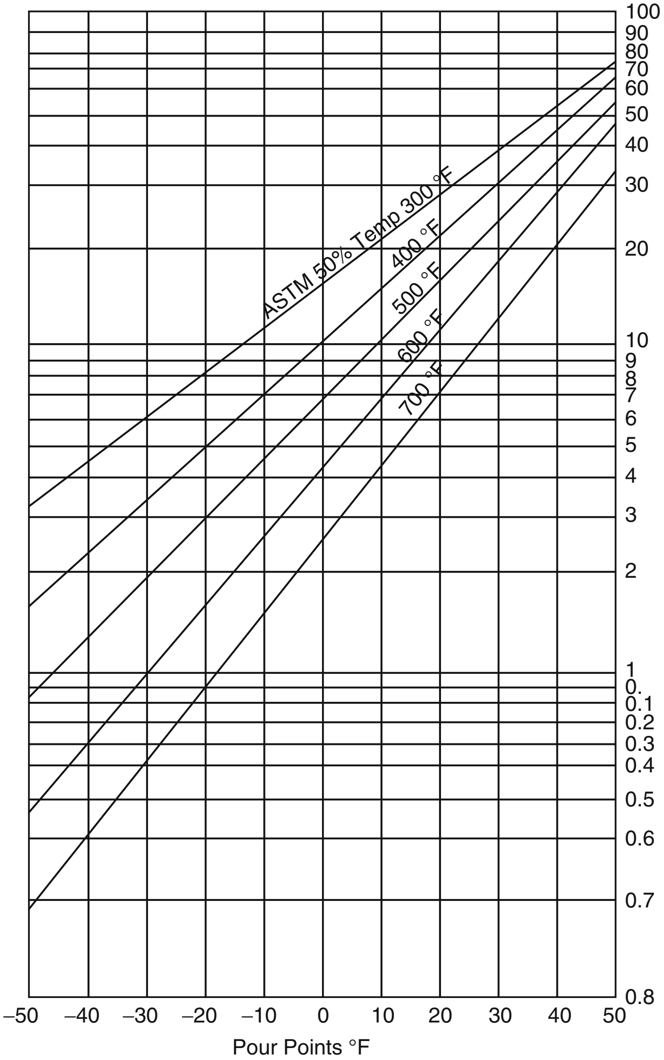


Fig. 12 Pour point blending index

Table 7 Calculating pour points of a cut

	Composition		ASTM dist		Pour point		
Components	BPSD	Fraction	50 % °F	Factor	Pour point °F	Index	Factor
Gas oil	2,000	0.33	500	85.8	−5	5.8	1.9
Waxy dist	4,000	0.67	700	249	30	12.7	8.5
Total	6,000	1.00	634	334	22		10.4

The pour point of the blend is read from Fig. 12 where the ASTM 50 % point is 634 °F and the index is 10.4. In this case the pour point is 22 °F

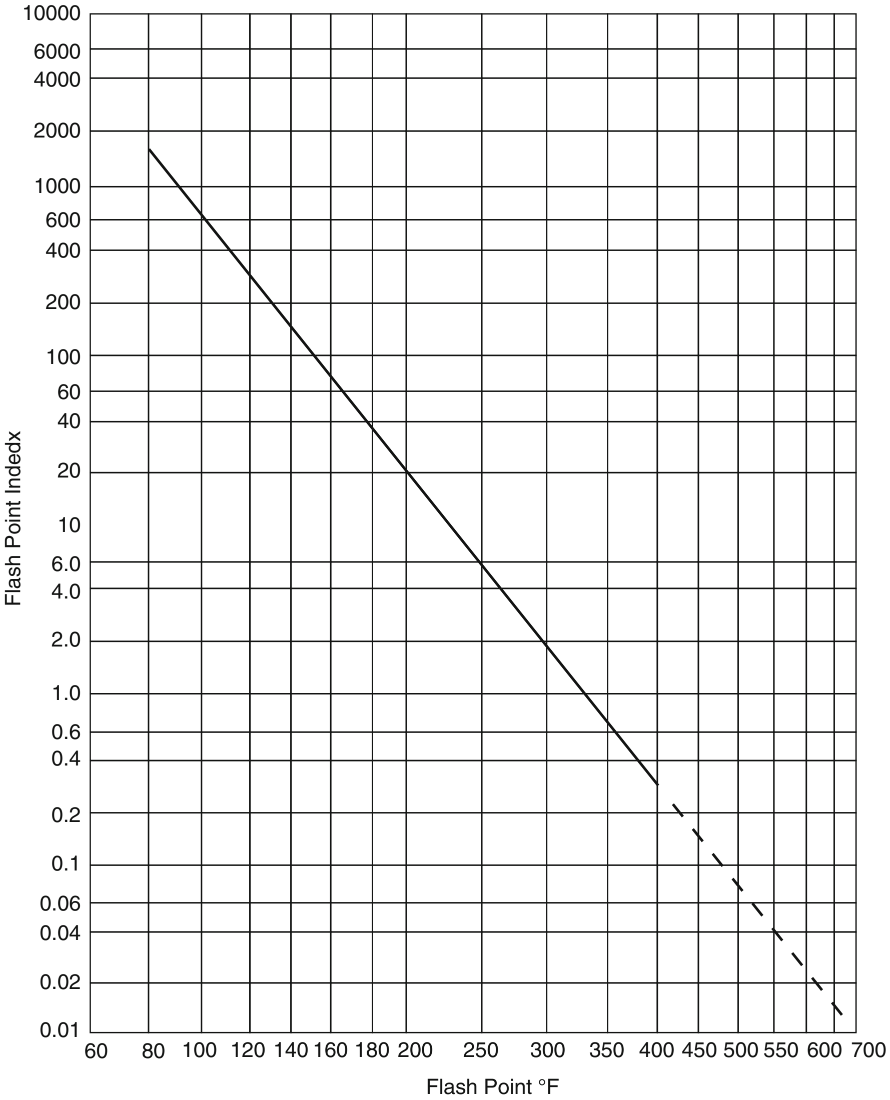


Fig. 13 Flash point blending index

Table 8 Blending streams for flash points

	Volume	Fraction		Flash index	Factor
Components	BPSD	(A)	Flash point, °F	(B)	(A × B)
Kerosene	2,000	0.2	120	310	62.0
Fuel oil	8,000	0.8	250	5.5	4.4
Total	10,000	1.0			66.4

The flash point corresponding to an index of 66.4 (from Fig. 13) is 166 °F

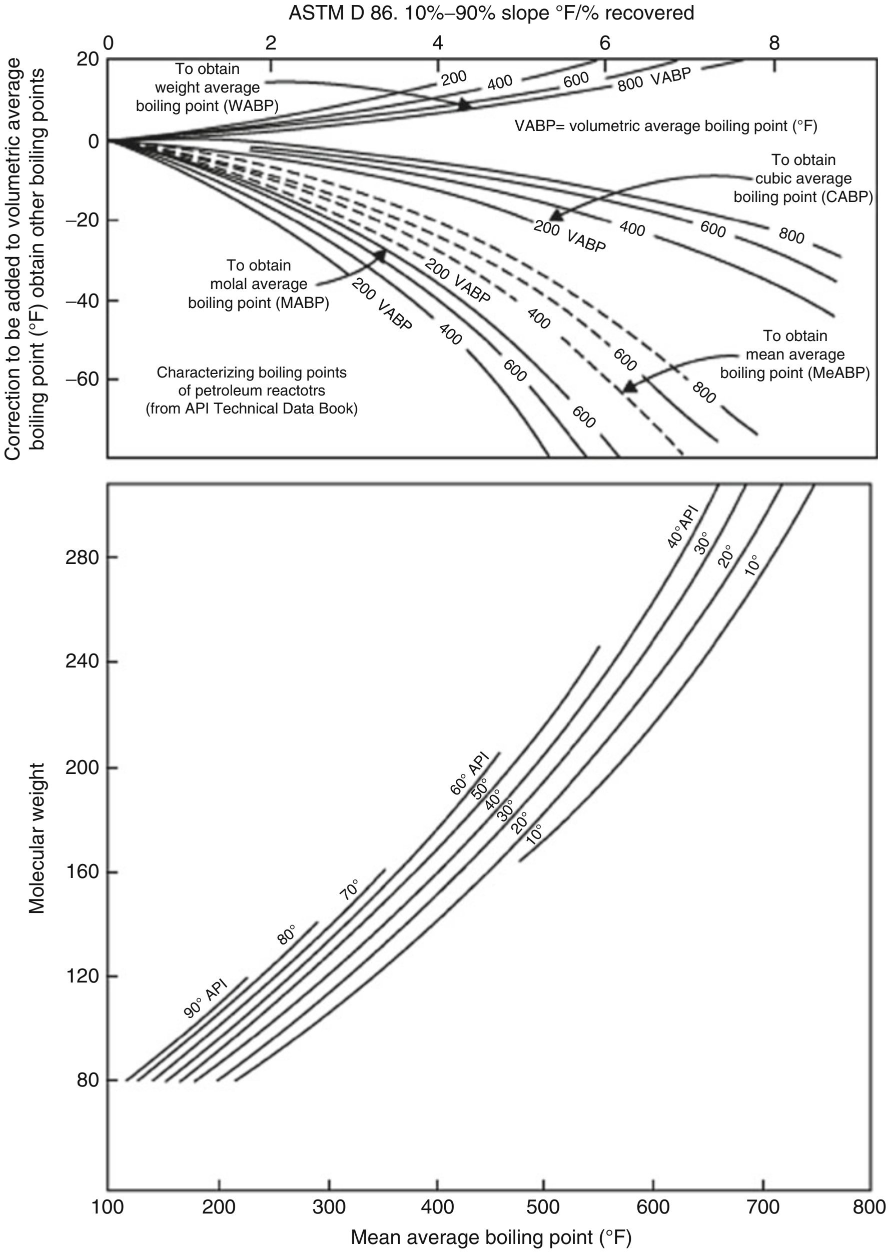


Fig. 14 Correlation between boiling point, molecular weight, and gravity

From the upper series of curves given in Fig. 14, the correction to the volumetric average boiling point (VABP) to obtain the mean average (MEABP) is −5 °F. Thus, the MEABP is

$$490 + (-5) = 485\ ^\circ\mathrm{F}$$

The °API of the stream from the calculation for gravity is 38.8. Using this figure and the MEABP in the lower series of curves in Fig. 14, a molecular weight of 201 is read off.

Basic Petroleum Refining Processes

This chapter provides an introduction to some of the most common processes included in fuel-oriented and nonenergy-oriented refineries. These processes are only discussed here in summary form. They are treated in more detail later in individual topics and chapters.

The Atmospheric Crude Distillation Unit

In refining the crude oil, it is first broken up into those raw stocks that are the basis of the finished products. This breakup of the crude is achieved by separating the oil into a series of boiling point fractions which meet the distillation requirements and some of the properties of the finished products. This is accomplished in the crude distillation units. Normally there are two units that accomplish this splitting up function: an atmospheric unit and a vacuum unit.

The crude oil is first desalted (dissolved brine is removed by washing) and heated to a predetermined temperature prior to its introduction into the atmospheric unit. This is accomplished by heat exchange with hot products and finally by a direct fired heater. The hot and partially vaporized crude is "flashed" in a trayed distillation tower. Here, the vaporized portion of the crude oil feed moves up the tower and is selectively condensed by cooled reflux streams moving down the tower. These condensates are taken off at various parts of the tower according to their condensing temperature as distillate side streams. The light oils not condensed in the tower are taken off at the top of the tower to be condensed externally as the overhead product. The unvaporized portion of the crude oil feed leaves the bottom of the tower as the atmospheric residue.

The unit operates at a small positive pressure around 5–10 psig in the overhead drum, thus its title of "atmospheric" crude unit. Typical product streams leaving the distillation tower are as follows:

Overhead distillate	Full-range naphtha	Gas to 380 °F cut point
1st side stream	Kerosene	380–480 °F cut range
2nd side stream	Light gas oil	480–610 °F cut range
3rd side stream	Heavy gas oil	610–690 °F cut range
Residue	Fuel oil	+690 °F cut point

Full details of this unit are given in the chapter entitled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries."

The Crude Vacuum Distillation Unit

Further breakup of the crude is often required to meet the refinery's product slate. This is usually required to produce low-cost feed to cracking units or to produce the basic stocks for lubricating oil production. To achieve this, the residue from the atmospheric unit is distilled under subatmospheric conditions in the crude vacuum distillation unit. This unit is similar to the atmospheric unit in so much as the feed is heated by heat exchange with hot products and then in a fired heater before entering the distillation tower. In this case, however, the tower operates under reduced pressure (vacuum) conditions. These units operate at overhead pressures as low as 10 mmHg. Under these conditions the hot residue feed is partially vaporized on entering the tower. The hot vapors rise up the tower to be successively condensed by a cooled internal reflux stream moving down the tower as was the case in the atmospheric distillation unit. The condensed distillate streams are taken off as side stream distillates. There is normally no overhead distillate stream in this case.

The high vacuum required in these units is produced by a series of steam ejectors attached to the unit's overhead system. Typical product streams from this unit are as follows:

Top side stream	Light vacuum gas oil	690–750 °F
2nd side stream	Heavy vacuum gas oil	750–985 °F
Residue	Bitumen	+985 °F

This unit is further described and discussed in the chapter entitled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries."

The Light Ends Units

The full-range naphtha distillate as the overhead product from the atmospheric crude unit is further split into the basic components of the refinery's volatile and light oil products. This is accomplished in the light ends plant, which usually contains four separate distillation units. These are:

- The de-butanizer (or debutanizer)
- The de-propanizer (or depropanizer)
- The de-ethanizer (or deethanizer)
- The naphtha splitter

The most common routing of the full-range naphtha from the atmospheric crude overhead is first to the debutanizer unit. This feed stream is heated by heat exchange with hot products before entering the feed tray of the debutanizer column. This is a distillation column containing between 30 and 40 trays. Separation of butanes and lighter gas from the naphtha occurs in this tower by fractionation. The butanes and lighter are taken off as an overhead distillate, while the naphtha is removed as the column's bottom product. The overhead distillate is then heated again by heat exchange with hot streams and fed into a depropanizer column. This column also has about 30–40 distillation trays and separates a butane stream from the propane and lighter material stream by fractionation. The butanes leave as the column's bottom product to become the butane LPG product after further "sweetening" treatment (sulfur removal). The column's overhead distillate is fed to a deethanizer column after preheating. Here the propane is separated from the lighter materials and leaves the column as the bottom product. This stream becomes part of the refinery's propane LPG product after some further "sweetening" treatment. There will be no overhead distillate product from this unit. The material lighter than propane leaves the overhead drum as a vapor containing mostly ethane and is normally routed to the refinery's fuel gas system.

The debutanized naphtha leaving the bottom of the debutanizer is subsequently fractionated in the naphtha splitter to give a light naphtha stream as the overhead distillate and a heavy naphtha as the column's bottom product. The light naphtha is essentially C5s and nC6s; this stream is normally sent to the refinery's gasoline pool as blending stock. The heavy naphtha stream contains the cycloparaffin components and the higher paraffin isomers necessary to make good catalytic reformer feed. This stream therefore is sent to the catalytic reformer after it has been hydrotreated for sulfur and nitrogen removal.

The light end units are further described and discussed in the chapter entitled "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing."

The Catalytic Reformer Unit

The purpose of the catalytic reformer plant is to upgrade low-octane naphtha to the high-octane material suitable for blending into motor gasoline fuel. It achieves this by reforming some of the hydrocarbons in the feed to hydrocarbons of high-octane value. Notably among those reactions is the conversion of cycloparaffin content of the feed to aromatics. This reaction also gives up hydrogen molecules which are subsequently used in the refinery's hydrotreating processes.

The feed from the bottom of the naphtha splitter is hydrotreated in the naphtha hydrotreater for the removal of sulfur and nitrogen. It leaves this unit to be preheated to the reforming reaction temperature by heat exchange with products and by a fired heater. The feed is mixed with a recycle hydrogen stream before entering the first of (usually) three or four reactors. The reforming reactions take place in these reactors and the reactor temperatures are sustained and controlled by intermediate fired heaters. The effluent leaves the last reactor to be cooled and partially condensed by heat exchange with cold feed and a condenser. This cooled effluent is routed to a flash drum from which a hydrogen-rich stream is removed as a gas while reformate is removed as a liquid stream and sent to a stabilizer column. The bottom from this column is debutanized reformate and is routed to the gasoline pool for blending to meet motor gasoline specifications. Part of the gas leaving the flash drum is recycled to the reactors as the unit's recycle stream. The remaining gas is normally sent to the naphtha hydrotreater for use in that process. There is also a continuous version of this process available.

Details of the catalytic reforming process are described and discussed further in the chapter entitled "▶ Catalytic Reforming in Petroleum Processing."

The Hydrotreating Units (de-sulfurization)

Most streams from the crude distillation units contain sulfur and other impurities such as nitrogen and metals in some form or other. By far the most common of these impurities is sulfur, and this is also the least tolerable of these impurities. Its presence certainly lowers the quality of the finished products and, in the processing of the crude oil, its presence invariably affects the performance of the refining processes. Hydrotreating the raw distillate streams removes a significant amount of the sulfur impurity by reacting the sulfur molecules with hydrogen to form hydrogen sulfide (H_2S); this is then removed as a gas.

Several types of hydrotreaters are described in this book. The two most common types found are:

- Naphtha hydrotreating – once through or recycle hydrogen
- Diesel hydrotreating – recycle hydrogen

In naphtha hydrotreating the naphtha from the naphtha splitter is mixed with the hydrogen-rich gas from the catalytic reformer unit and preheated to about 700 °F by heat exchange and a fired heater. On leaving the fired heater, the stream enters a reactor containing a desulfurizing catalyst (often Co Mo – cobalt molybdenum – on an alumina base). The sulfur components of the feed combine with the hydrogen to form H_2S. The effluent from the reactors is cooled and partially condensed before being flashed in a separator drum. The gas phase from this drum is still high in hydrogen content and is usually routed to other downstream hydrogen-using processes. This stream contains most of the H_2S produced in the reactors; the remainder leaves the flash drum with the desulfurized naphtha liquid to be removed in the hydrotreater's stabilizer column as an H_2S-rich gas.

Diesel hydrotreating has very much the same process configuration as the naphtha unit. The main difference is that this unit will almost invariably have a rich hydrogen stream recycle. The recycle is provided by the flashed gas stream from the flash drum. This is returned to mix with the feed and a fresh hydrogen make up stream before entering the preheater system. The recycle gas stream in these units is often treated for the removal of H_2S before returning to the reactors.

A detailed discussion and description of these processes are given in the chapter entitled "▶ Hydrotreating in Petroleum Processing."

The Fluid Catalytic Cracking Unit (FCCU)

This cracking process is among the oldest in the oil industry. Although developed in the mid-1920s, it first came into prominence during the Second World War as a source of high-octane fuel for aircraft. In the early 1950s its prominence as the major source of octane was somewhat overshadowed by the development of the catalytic reforming process with its production of hydrogen as well as high-octane material. The prominence of the fluid catalytic cracking unit (FCCU) was reestablished in the 1960s by two developments in the process. These were:

- The use of highly active and selective catalysts (Zeolites)
- The establishment of riser cracking techniques

These two developments enabled the process to produce higher yields of better-quality distillates from lower-quality feedstocks. At the same time catalyst inventory and consumption costs were significantly reduced.

The process consists of a reactor vessel and a regenerator vessel interconnected by transfer lines to enable the flow of finely divided catalyst powder between them. The oil feed (typically high-vacuum gas oil, HVGO, from the crude vacuum unit) is introduced to the very hot regenerated catalyst stream leaving the regenerator en route to the reactor. Cracking occurs in the riser inlet to the reactor due to the contact of the oil with the hot catalyst. The catalyst and oil are very dispersed in the riser so that contact between them is very high exposing a large portion of the oil to the hot catalyst. The cracking is completed in the catalyst fluid bed in the reactor vessel. The catalyst fluidity is maintained by steam injection at the bottom of the vessel. The cracked effluent leaves the top of the reactor vessel as a vapor to enter the recovery section of the plant. Here the distillate products of cracking are separated by fractionation and forwarded to storage or further treating. An oil slurry stream from this recovery plant is returned to the reactor as recycle.

The catalyst from the reactor is transferred to the regenerator on a continuous basis. In the regenerator the catalyst is contacted with an air stream which maintains the catalyst in a fluidized state. The hot carbon on the catalyst is burned off by contact with the air and converted into CO and CO_2. The reactions are highly exothermic rising the temperature of the catalyst stream to well over 1,000 °F and thus providing the heat source for the oil cracking mechanism.

Products from this process are:

- Unsaturated and saturated LPG
- Light cracked naphtha
- Heavy cracked naphtha
- Cycle oil (mid distillate)
- Slurry

Details of this process together with typical yield data are given in the chapters on "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining" and "▶ Upgrading the Bottom of the Barrel."

The Hydrocracking Process

This process is fairly new to the industry becoming prominent in its use during the late 1960s. As the title suggests the process cracks the oil feed in the presence of hydrogen. It is a high-pressure process operating normally around 2,000 psig. This makes the unit rather costly and, for many years, slowed its expansion in the industry compared with the FCCU and thermal cracking. However, the process is very flexible and is capable of making modern, high- quality distillate fuels and lubes. It can handle a wide spectrum of feeds including straight run gas oils, vacuum gas oils, thermal cracker gas oils, FCCU cycle oils, and the like. The products it produces need very little downstream treating to meet finished product specifications. The naphtha stream it produces is particularly high in naphthenes making it a good catalytic reformer stock for gasoline or aromatic production.

The process consists of one or two reactors, a preheat system, recycle gas section, and a recovery section. The oil feed (typically a vacuum gas oil) is preheated by heat exchange with reactor effluent streams and by a fired heater. Make-up and recycled hydrogen streams are introduced into the oil stream before entering the reactor(s). (Note: in some configurations the gas streams are also preheated prior to joining the oil.) The first section of the reactor is often packed with a hydrotreating catalyst to protect the more sensitive cracking catalyst further down in the reactor from injurious sulfur, nitrogen, and metal poisoning. Cracking occurs in the reactor(s) and the effluent leaves the reactor to be cooled and partially condensed by heat exchange. The stream enters the first of two flash drums. Here, the drum pressure is almost that of the reactor. A gas stream rich in hydrogen is flashed off and is recycled back to the reactors as recycle gas. The liquid phase from the flash drum is routed to a second separator which is maintained at a much lower pressure (around 150–100 psig). Because of this reduction in pressure, a second gas stream is flashed off. This will have a much lower hydrogen content but will contain C_3s and C_4s. For this reason the stream is often routed to an absorber column for maximizing LPG recovery. The liquid phase leaves the bottom of the low-pressure absorber to enter the recovery side where products are separated by fractionation and sent to storage.

Further details of this process are given in the chapters entitled "▶ Hydrocracking in Petroleum Processing", "▶ Upgrading the Bottom of the Barrel, and "▶ Non-energy Refineries in Petroleum Processing".

Thermal Cracking Units

Thermal cracking processes are the heavy work horses of the oil refining industry. The processes are relatively cheap when compared with the fluid cracker and the hydrocracker but go a long way to achieving the heavy oil cracking objective of converting low-quality material into more valuable oil products. The process family of thermal crackers has three members, which are:

- Thermal crackers
- Visbreakers
- Cokers

The term thermal cracking is given to those processes that convert heavy oil (usually fuel oil or residues) into lighter product stock such as LPG, naphtha, and middle distillates by applying only heat to the feed over a prescribed element of time. The term thermal cracker when applied to a specific process usually refers to the processing of atmospheric residues (long residues) to give the lighter products. The term visbreaking refers to the processing of vacuum residues (short residues) to reduce the viscosity of the oil only and thus to meet the requirements of a more valuable fuel oil stock. Coking refers to the most severe process in the thermal cracking family. Either long or short residues can be fed to this process whose objective is to produce the lighter products and petroleum coke. The coker process is extinctive – that is, it converts all the feed. In the other two processes, there is usually some unconverted feed although the thermal cracker can be designed to be “extinctive” by recycling the unconverted oil. The three thermal cracking processes have the same basic process configuration. This consists of a cracking furnace, a “soaking” vessel or coil, and a product recovery fractionator(s). The feed is first preheated by heat exchange with hot product streams before entering the cracking furnace or heater. The cracking furnace raises the temperature of the oil to its predetermined cracking temperature. This is always in excess of 920 °F and, by careful design of the heater coils, the oil is retained in the furnace at a prescribed cracking temperature for a predetermined period of time (the residence time). In some cases an additional coil section is added to the heater to allow the oil to “soak” at the fixed temperature for a longer period of time. In other cases the oil leaves the furnace to enter a drum which retains the oil at its cracking temperature for a little time. In the coker process, the oil leaves the furnace to enter one of a series of coker drums in which the oil is retained for a longer period of time at its coking temperature for the production of coke.

The cracked oil is quenched by a cold heavy oil product stream on leaving the soaking section to a temperature below its cracking temperature. It then enters a fractionator where the distillate products are separated and taken off in a manner similar to the crude distillation unit. In the case of the cokers, the coke is removed from the drums by high-velocity water jets on a regular batch basis. The coking process summarized here refers to the more simple “delayed coking” process. There are other coking processes which are more complicated such as the fluid coker and the proprietary Flexicoker.

Further details on thermal cracking are provided in the chapter “▶ Upgrading the Bottom of the Barrel.” This chapter includes also the treating of residues by hydrocracking and fluid catalytic cracking.

Gas Treating Processes

The processes summarized above are the more common ones to be included in a fuel or energy refinery's configuration. In addition to these, there will also be the gas treating processes and often sulfur recovery processes. These are described and discussed in the chapters "▶ Refinery Gas Treating Processes" and "▶ Environmental Control and Engineering in Petroleum Processing."

Gas treating is always required to remove the H_2S impurity generated by hydrotreating or cracking from the refinery fuel gas or hydrogen recycle streams. The removal of H_2S for these purposes is accomplished by absorbing the hydrogen sulfide into an amine or similar solution that readily absorbs H_2S. Stripping the rich absorbent solution removes the H_2S from the system to be further reacted with air to produce elemental sulfur. This latter reaction takes place in a specially designed sulfur plant.

The rich H_2S-laden gases from all the refinery sources enter below the bottom tray (or packed bed) of the absorber tower. The lean, low-H_2S absorbent solution enters the tower above the top tray (or packed bed) to move down the tower countercurrent to the gas moving upward. Mixing on the trays (or packed beds) allows the H_2S from the gas phase to be absorbed into the liquid solution phase. The H_2S-free gas ($< \sim 100$ vppm H_2S) leaves the tower top to be routed to refinery fuel or other prescribed destination.

The rich absorbent solution leaves the bottom of the absorber to be heat exchanged with hot stripped absorbent solution before entering the feed tray of the stripping column. The solution moving down the tower is stripped of most H_2S by a stripper vapor phase moving up the tower. This stripper phase is generated by conventional reboiling of the bottom tray solution. The hot stripped solution leaves the bottom of the tower to be cooled by heat exchange with the feed and then by an air or water cooler before entering the absorber tower. Conditions in the stripper column are maintained by partially condensing the rich H_2S overhead vapors and then returning the distillate as reflux to the top tray of the rectifying section of the tower (which is the section of trays above the feed tray).

The vapor not condensed leaves the reflux drum to be routed to a sulfur plant. These vapors contain a high concentration of H_2S (usually in excess of 90 % mol) and enter the specially designed fuel "gun" of the sulfur plant heater. Here, about one third is mixed with an appropriate concentration of air and "burned" in the plant's fire box to generate SO_2. The gases generated are combined with the remaining H_2S and passed over a catalyst bed where almost complete conversion to elemental sulfur occurs. This product, in molten form, enters a heated storage pit or tank. The unconverted sulfurous vapors are further incinerated before venting to atmosphere from an acceptably elevated location. Sulfur recovery is detailed in the chapter on "▶ Environmental Control and Engineering in Petroleum Processing."

Processes Not So Common to Energy Refineries

Octane Enhancement Processes

The octane enhancement processes detailed in this book are the alkylation process and the isomerization process. These processes are usually proprietary and are provided to refiners under license.

The alkylation process treated here is the HF process which uses hydrogen fluoride as the catalyst which is used to convert unsaturated C_4s and iC_4 to high-octane alkylate. The unit's recovery side is the aspect dealt with in some detail together with a descriptive item on the safe handling of hydrogen fluoride. An alternative alkylation process uses sulfuric acid, H_2SO_4, instead of HF.

The isomerization process has a similar configuration to the catalytic reformer plant. This process uses hydrogen in its conversion of low-octane hydrocarbons to higher-octane isomers.

Both these processes are described and discussed in detail in the chapters on "▶ Alkylation in Petroleum Processing" and "▶ Isomerization in Petroleum Processing."

Oxygenated Gasolines

The concentration of vehicles on the roads in most of the cities in the modern world has increased dramatically over the last two decades. The emission of pollutants from these vehicles is causing a significant addition to the already critical problem of atmospheric pollution. The problem is now so acute that governments of most developed countries are seeking legislation to curb and minimize this pollution and most countries will see further implementation of "Clean Air" acts.

Petroleum refining companies have been working diligently for many years to satisfy the requirements of "Clean Air" legislation already in place. This began in the 1970s with the elimination of tetraethyl lead from most gasoline applications. Processes such as isomerization and polymerization of refinery streams were developed together with a surge in the use of the alkylation process. However, the further decrease of pollutants now requires a move away from the traditional gasoline octane enhancers such as the aromatics and the olefins.

Catalytic reforming produces gasoline streams to meet octane requirements mainly by converting cycloparaffin to light aromatics. Fluid catalytic cracking also produces gasoline blending stocks by cracking paraffins to light olefins and the products from these two processes still make up the bulk of a refinery's gasoline pool. Unfortunately the aromatics are "dirty compounds" because they produce a sooty exhaust emission – unacceptable in meeting the "Clean Air" requirements and the aromatics are considered "toxics". Considerable work has been done with alcohol to take the place of aromatics and as octane enhancers and meeting other gasoline specs such as RVP. Essentially all companies in North America use ethanol in the gasoline blend by Federal mandate.

Much success in reducing aromatics in gasoline to date however has been in the production and blending of oxygenated compounds into the gasoline pool, but mostly outside the USA. A press release by a number of companies in 1990 is quoted as follows:

- Adding oxygenates reduces the amount of exhaust emissions (hydrocarbons and carbon monoxide) and the benefits have been quantified.
- Changing the level of olefins in gasoline does not have much of an impact on vehicle exhaust emission.
- Reducing aromatics and/or boiling range of gasoline can either reduce or increase exhaust emissions depending upon vehicle type.

Oxygenates are ether compounds derived from their respective alcohol. There are three candidates of these ethers to meet the gasoline requirements. These are:

- Methyl tertiary butyl ether (MTBE)
- Ethyl tertiary butyl ether (ETBE)
- Tertiary amyl methyl ether (TAME)

Of these three candidates MTBE is the one that has been used more extensively to meet all the gasoline pool objectives. This compound has the blending quality of 109 octane, an RVP blending of 8–10 psi, and a boiling point of 131 °F.

ETBE octane blending properties seem to be slightly better than those of MTBE and so does its RVP blending qualities. The ethanol feed stream of course is not as readily available as methanol and requires a separate production unit, often by means of fermentation of organic materials.

TAME has an average octane number of 104 and an RVP blending of 3–5 psi. Except for the lower octane value, TAME has similar blending properties to ETBE. The ether in this case is formed by the reaction of 2-methyl-2-butene and 2-methyl-1-butene olefin feed and methanol. Commercial plants operate in the UK and parts of Europe producing TAME. The compound is used in Europe as a gasoline product and not as a gasoline blend stock. The front end of a cracked gasoline stream is used in this manufacture to provide the olefin.

Use of MTBE has been phased out in the USA because of groundwater contamination (MTBE has a very unpleasant smell) but is still in use in Europe and elsewhere. However, emphasis on the use of renewable resources in Europe has prompted a gradual shift from MTBE to ETBE.

The Production of Ethers for Gasoline Blending

There are several licensed processes for the production of methyl tertiary butyl ether by the etherification of a C_4/C_5 olefin stream and methanol. These processes

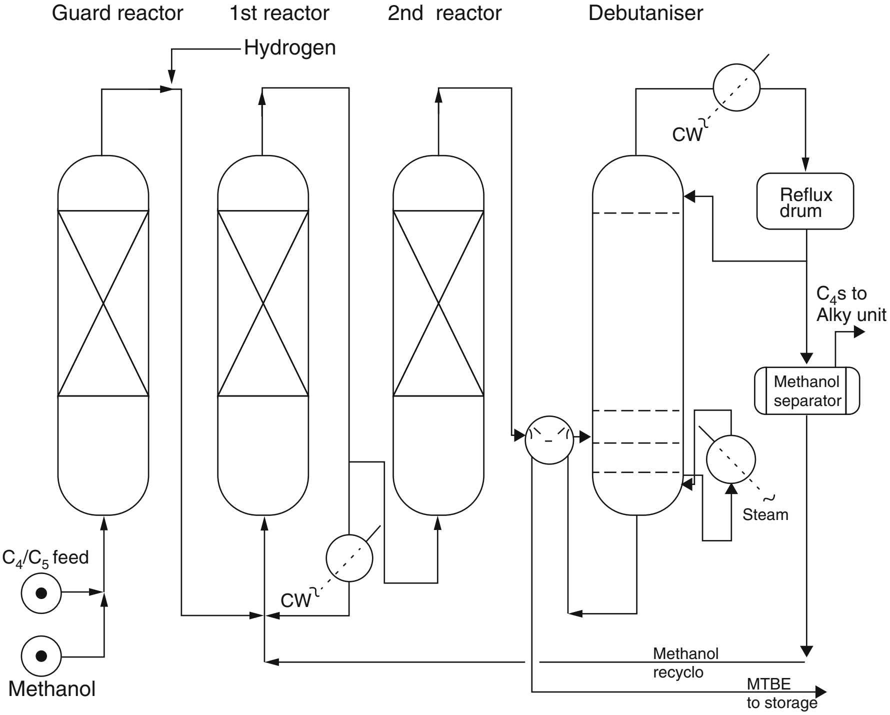


Fig. 15 Typical flow diagram for the production of MTBE

have very similar configurations and are flexible enough to be converted quite simply to the production of the other ethers. Figure 15 is a typical flow diagram for this process.

The olefin feed from a FCCU or a steam cracker is combined with a methanol stream to enter a guard reactor to remove impurities. A small hydrogen stream is added to the hydrocarbon from the guard reactor prior to entering the ether reactor. This reactor contains a special acid resin catalyst (usually a cross-linked sulfonic resin) and the reactor feed flows upward through this catalyst bed at moderate temperature and pressure and in the liquid phase. The reaction is exothermic and temperature control is maintained by externally cooling a recycle stream from the first of two reactor vessels.

The catalyst in this case performs three reactions simultaneously: etherification of branched olefins, selective hydrogenation of the unwanted diolefins, and hydroisomerization of olefin by a double-bond switch. The reactor effluent leaves the top of the second reactor vessel to be heated in a feed heat exchanger with the debutanizer bottoms product. The overheads from the debutanizer are a C_4 and methanol stream. The methanol stream is recycled to the first reactor, while the C_4s are returned to the FCCU light end unit. The bottom product is C_5+ enriched with MTBE (or TAME depending on the olefin feed used).

The production of oxygenated gasolines is described and discussed further in the chapter on "▶ Petroleum Products and a Refinery Configuration."

The Nonenergy Refineries

In addition to the energy-related refineries, which occupy most of this book, there are two major types of nonenergy-producing refineries. These are the lube oil refinery and the petrochemical refineries. These are summarized below:

The Lube Oil Refinery

The schematic flow diagram (Fig. 16) shows a typical lube oil-producing refinery configuration. In this case, the processes used involve extraction and dewaxing of conventional petroleum stocks. Only about eight or nine base lube oil stocks are produced from refinery streams. The many hundreds of commercial grades of lubricating oils used in industry and transportation are blends of these base stocks with some small amounts of proprietary additives (mostly organic acid derivatives) included to meet their required specifications. There are also two quite important by-products of lube oil. These are bitumen and waxes. Most refineries include bitumen blending in their configuration, but only a few of the older refineries process the waxes. These are exported to manufacturers specializing in wax and grease production.

Newer lube oil production processes are based on:

- High-temperature and high-pressure hydrocracking, hydrodewaxing, and hydrofinishing
- Conversion of natural gas to liquids (GTL) with subsequent hydrocracking and hydrodewaxing/finishing

While the extraction/dewaxing approach is still used for some oils, most new engine oils require the product qualities produced by the hydrocracking or GTL processes. It is still instructional to understand the needs for lube oils by reviewing the older process scheme.

Lube oil production starts with the vacuum distillation of atmospheric residue. This feedstock is usually cut into three distillate streams each meeting a boiling range which gives streams with viscosity meeting the finished blending product specifications. The lighter stream is taken off as the top side stream and is further distilled again under vacuum to three light lube oil blending cuts. These are called spindle oils and, when finished, will form the basis of light lubes used for domestic purposes such as sewing machine, bicycle, and other home lubricant requirements. Some of the heavier spindle oils are also used as blend stocks for light motor oils. These spindle oils require very little treatment for finishing. Usually, a mild hydrotreating suffices to meet the color requirement.

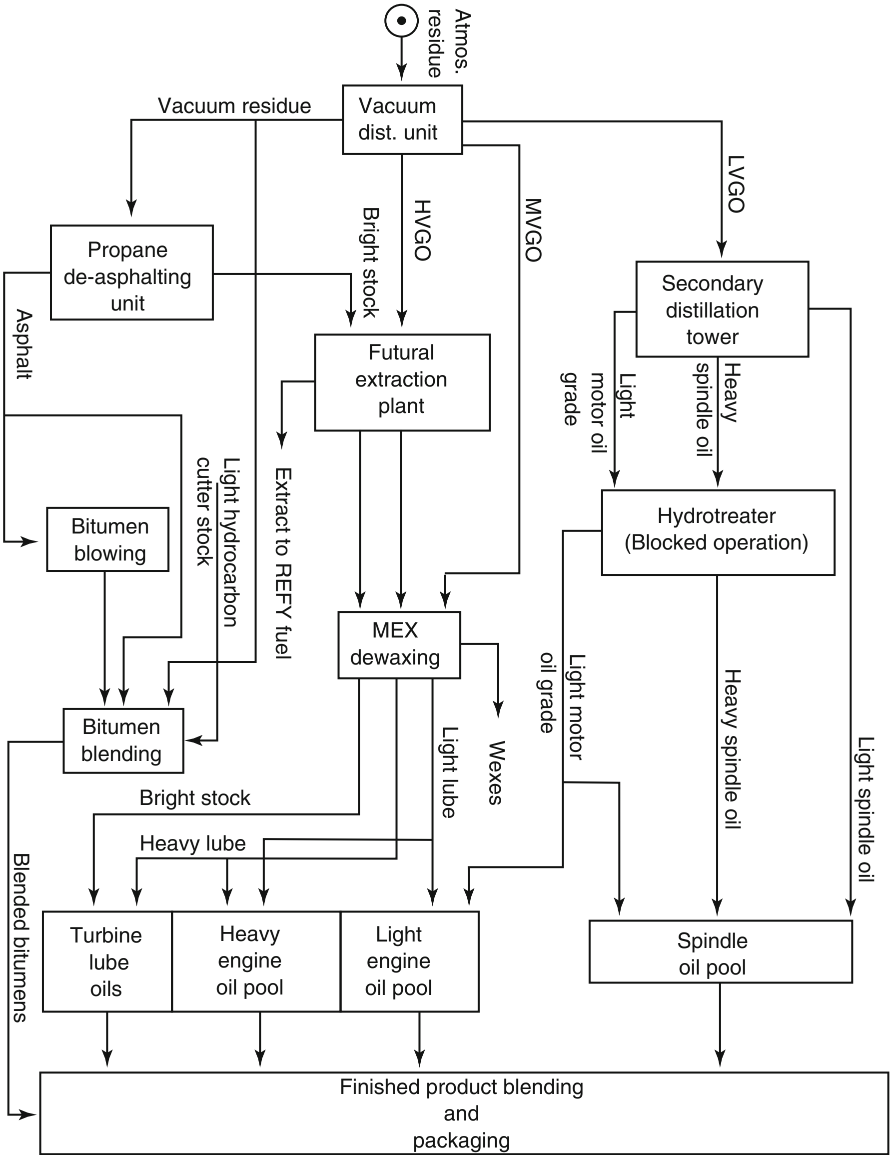


Fig. 16 A lube oil refinery configuration

The second distillate side stream is dewaxed and sent to the engine lube oil pool. It may also be blended with the heavier bottom side stream as heavy engine oil stock. The bottom side stream is one of the base blending stocks for heavy engine oils and the turbine oil stocks. To meet color and other specifications, these heavier oils must be treated for the removal of undesirable components (such as heavy aromatics and olefins) by solvent extraction. This is accomplished prior to the stream being dewaxed and routed to storage. The heavy vacuum residue from the vacuum tower is routed to a propane deasphalting unit. Here, the very thick bituminous asphaltenes are removed by extraction with liquid propane. The raffinate from this extraction process is the heaviest lube oil blending stream commonly called bright stock. This stream is also routed to the solvent extraction unit and the dewaxing process before storage.

Solvent extraction is accomplished in a trayed column by contacting the oil feed and solvent countercurrently in the tower. The lighter raffinate stream leaves the top of the tower to be stripped free of the solvent in an associated stripper column, before entering the dewaxing unit. The extracted components leave the bottom of the tower also to be stripped free of the solvent in an associated stripper column. The extract in this case may be routed to the propane deasphalting unit or simply sent to the refinery fuel supply. The solvent in modern refineries is either furfural, phenol, or a proprietary solvent based on either of these chemicals. In earlier plants oleum or liquid SO_2 was used for this purpose.

The oil streams routed to the dewaxing plant are contacted and mixed with a crystallizing agent such as methyl-ethyl-ketone (MEK) before entering a series of chiller tubes. Here the oil/MEK mix is reduced in temperature to a degree that the wax contained in the oil crystallizes out. The stream with the wax now in suspension enters a series of drum filters where the wax and oil are separated. Both streams are stripped free of the MEK in separate columns. The MEK is recycled while the dewaxed oil is sent to storage and blending. The wax may be retained as a solid in a suitably furnished warehouse or remelted and stored in special tanks with inert gas cover.

The asphalt from the propane deasphalting unit is stripped free of propane and any other light ends using inert gas as the stripping agent. It leaves the unit to proceed either directly to the bitumen pool or to be further treated by air blowing. The air-blowing process increases the hardness of the bitumen where this is required to meet certain specifications. It is accomplished either as a batch process or on a continuous basis. The hot stripped asphalt from the deasphalting unit enters the air blower reactor under level control (if the process is continuous). Air is introduced via a small compressor to the bottom of the reactor vessel and allowed to bubble up through the hot oil phase. The air removes some of the heavy entrained oils in the asphalt and reacts mildly to partially oxidize the asphaltenes. The hot oil vapors and the unused air leaves the top of the reactor to be burned in a suitably designed incinerator. The blown asphalt leaves the reactor as a side stream to bitumen storage or blending.

The production of lube oils usually takes place in a section of an energy refinery. The various grades of the oils are also produced in a blocked operation using storage facilities between the units. This is feasible as the amount of lube oils required to be produced is relatively small and normally does not justify separate treating facilities for each grade.

The lube oil refinery is further detailed in the chapter "▶ Non-energy Refineries in Petroleum Processing."

The Petrochemical Refinery

Feedstocks for the production of petrochemicals originate from refineries with processes similar to those described earlier to produce fuels. Indeed, there are only a few refineries worldwide that cater only to petrochemical requirements. Most petrochemical feedstocks are produced by changing operating parameters of the normal fuel refinery processes. In catering for the petrochemical needs, much of the refinery product streams are tailored as follows:

- *Aromatic streams* – high in benzene, toluene, and xylenes
- *Olefin streams* – high in ethylene, propylene, and C_4s

Producing the Aromatic Feedstock

The production of aromatic feedstocks originates with the catalytic reforming of a refinery stream of a heavy naphtha range (say 120–420 °F) and rich in naphthenes. A typical stream that meets these criteria would be a naphtha stream from a hydrocracker. Thus, in order to meet petrochemical needs, a hydrocracker may form part of a fuel refinery configuration. This unit would be operated to maximize naphtha production. This would mean running the unit at a low space velocity with a higher oil recycle rate (i.e., most recovered product heavier than the naphtha would be recycled back to the reactors).

Another source of high naphthene feed to the cat reformer would be hydrotreated cat cracker naphtha. Of course the hydrotreating of unsaturates has a high demand on the refinery’s hydrogen system, but this is balanced to some extent by the additional hydrogen produced in reforming the naphthenes. Should the refinery configuration include a thermal cracker and/or a steam cracker, the hydrotreating of the naphtha cut from these units also yields high naphthene catalytic reformer feedstock.

Catalytic reforming of the high naphthene-content naphtha produces aromatics, but there are also some unreacted paraffins and some naphthenes present. The downstream petrochemical units that separate and purify the aromatic reformate are expensive both in capital and operating costs. The specification for the BTX (benzene, toluene, xylene) feed is very stringent and excludes nonaromatic components as much as possible. Another process may therefore be included in the refinery configuration to “clean up” this aromatic feed stream before leaving the refinery. This is an aromatic extraction plant. This is a licensed process using a solvent to separate the paraffins and aromatics by countercurrent extraction. The rich aromatic stream is then forwarded to the BTX plant where benzene, toluene, ethyl benzene, and o-xylene are separated by fractionation while the para-xylene is usually separated by crystallization or by solid adsorption. The meta-xylene may also be recovered by super distillation, but more often than not, it is converted into *o*-xylene or *p*-xylene in an isomerization unit.

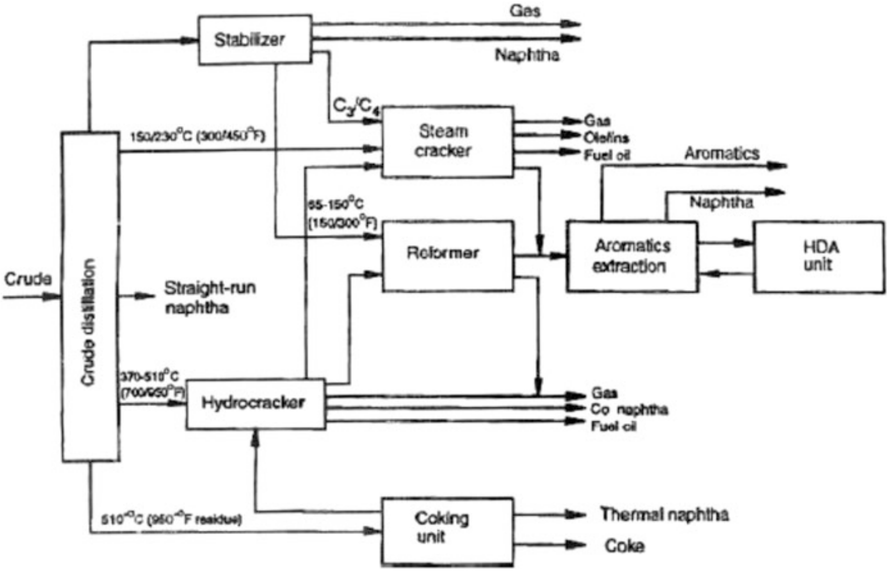


Fig. 17 A petrochemical refinery configuration

Producing the Olefin Feedstock

The source of olefins in a refinery configuration is from either the FCCU, a thermal cracker, or a steam cracker. The olefins produced as a gas are ethylene, propylene, and the C_4s, such as butylenes, butadiene, etc. Liquid olefinic products from these units are normally hydrotreated to make reformer feedstock and thus the BTX feed. All products, of course, are treated for sulfur control and cleaned up before leaving the refinery as petrochemical feedstock. The specifications for these products are stringent and usually the "clean-up" plants are dedicated to the treatment of these products.

Olefins are used mostly in the production of polymers such as the vinyl polymers (vinyl chloride, vinyl acetate, and the like), polyethylene products, and polypropylene products. The heavier C_4s are a major constituent in the production of synthetic rubbers. Figure 17 shows a configuration for a typical petrochemical refinery.

The petrochemical refinery is also further described and discussed in the chapter entitled "▶ Non-energy Refineries in Petroleum Processing."

Appendix 1 Procedure for Manual Calculation of an Equilibrium Flash

The equilibrium flash can be calculated using the composition of the feed mixture and the vapor/liquid equilibrium constant of the components in the mixture. This is expressed by the following equation:

$$L = xf/[1 + (V/L)K] \qquad (7)$$

where:

L = Total moles/hr of a component in the liquid phase
xf = Moles/hr of the component in the feed
V/L = Ratio of total moles vapor to total moles liquid
K = Equilibrium constant for each component at the temperature and pressure of the flash

The flash calculations can be done using a process simulation program employing appropriate thermodynamic models or manually using a spreadsheet. There are several publications giving values for K. Among these are the charts in Maxwell's *Data Book on Hydrocarbons* which are based on fugacities. Others may be found in engineering data books such as "Gas Processors Suppliers Association" (GPSA) which are based on convergence pressures. A rough and ready substitute for K factors is to use the vapor pressure of the component divided by the system pressure. This, however, should not be used for any definitive design work nor in systems which have azeotropes or are near their critical conditions. A method for calculating equilibrium flash vaporization to produce two, primarily, hydrocarbon, phases is given by the following steps. If significant amounts of water are present, more complex procedures are required. Such a "three-phase" flash with water is not included here.

Note that this procedure can be adapted to provide a simple and useful spreadsheet flash calculation, making use of the iterative calculation option that is available in most spreadsheets.

Step 1. Prepare a table with the first column giving the components making up the feed. The second column will be the composition of the feed in mols/hr. The third column is a listing of the equilibrium constant K for each component at the temperature and pressure of the flash condition. Allow up to three columns following for assumptions of V/L. Each of these three columns should be subdivided into two, the first giving the product of $(V/L)\ K$ and the second for listing the "L" for each component. Other columns may be added to calculate mole wt of vapor and SG of the liquid phase.

Step 2. Assume a value for V/L. This is a judged assumption, but start with 1.0 or 0.1 whichever seems to be more realistic. Calculate $(V/L)\ K$ for each component.

Step 3. Calculate "L" for each component from the equation:

$$L = xf\ /[1 + (V/L)K] \qquad (8)$$

Step 4. The calculated V/L is now obtained by adding the "L" column and subtracting this value from the total moles of feed in column 1. This subtraction is the vapor moles as calculated. Then the calculated V/L is arrived at by dividing the total V by the total of the "L" column.

Table 9

			First trial		Second trail		Third trial					
			V/L guess	0.5	V/L guess	0.2	V/L guess	0.1				
	F, mol/h	K at 127 psia, 300 °F	(V/L) K	L = F/ (1 + (V/L) K)	(V/L) K	L = F/ (1 + (V/L) K)	(V/L) K	L = F/ (1 + (V/L) K)	MW	Liquid lb/h	lb/ gal	GPH
C_2	6.4	9.100	4.550	1.153	1.820	2.270	0.910	3.351	30	101	2.97	34
C_3	43.5	5.000	2.500	12.429	1.000	21.750	0.500	29.000	44	1,276	4.69	272
iC_4	16.9	3.300	1.650	6.377	0.660	10.181	0.330	12.707	58	737	4.69	157
nC_4	67.6	2.900	1.450	27.592	0.580	42.785	0.290	52.403	58	3,039	4.87	624
iC_5	80.5	1.800	0.900	42.368	0.360	59.191	0.180	68.220	72	4,912	5.21	943
nC_5	34.6	1.600	0.800	19.222	0.320	26.212	0.160	29.828	72	2,148	5.26	408
C_6	124.9	0.850	0.425	87.649	0.170	106.752	0.085	115.115	86	9,900	5.54	1,787
C_7	140.9	0.480	0.240	113.629	0.096	128.558	0.048	134.447	100	13,445	5.74	2,342
NP260	99.8	0.212	0.106	90.235	0.042	95.741	0.021	97.728	114	11,141	6.18	1,803
NP300	99.8	0.116	0.058	94.329	0.023	97.537	0.012	98.656	126	12,431	6.37	1,951
NP340	60.4	0.063	0.032	58.556	0.013	59.648	0.006	60.022	136	8,163	6.46	1,264
NP382	29.8	0.035	0.018	29.287	0.007	29.593	0.004	29.696	152	4,514	6.56	688
Total	805.1			582.827		680.218		731.172	98.2	71,805	5.85	12,273
Calc V/L				0.276		0.155		0.092			API = 70	

lb/h liquid = 71,805
lb/h vapor = 7,260
lb/h feed = 79,065
lb/gal = 5.9
Liquid mol. wt. = 98.2

Step 5. The calculation is complete when *V*/*L* calculated is equal to *V*/*L* assumed. An answer within 5 % is usually acceptable. If the calculated *V*/*L* assumed is not within this limit, make another assumption for *V*/*L* and repeat steps 2, 3, and 4. For this second assumption try 5, or 0.5, or 0.05, whichever is most appropriate.

Step 6. If there is still no agreement between assumed and calculated *V*/*L*, plot the two trial points (assumed *V* s calculated) on log graph paper. Draw a straight line through these two points and note where on this line assumed *V*/*L* = calculated *V*/*L*. This value is the next assumed *V*/*L*. Repeat the calculation steps 2–4 using this value; this usually completes the calculation. If it does not then check that the conditions for the flash are within the boiling point and condensing point for the feed.

In the example below, it is desired to determine the amount of vapor and liquid and their compositions in a feed to a fractionator at 112 psig and 300 °F (Table 9).

Note the components NP260–NP382 are pseudo components having mid-boiling points of 260 °F, 300 °F, 340 °F, and 382 °F respectively. *K* for these components are based on their vapor pressure and system pressure relationship.

Predicting the EFV Curve from TBP Data. For crude oils and complex mixtures such as the heavy products, the equilibrium vaporization curve can be calculated from the TBP curve using empirical methods given by Edmister or Maxwell. In this work the EFV is based on the method by Maxwell in his book *Hydrocarbon Data*. This method has been described in the section "Developing the TBP Curve and the Equilibrium Flash Vaporization (EFV Curve from the ASTM Distillation Curve" of this chapter.

References

W.C. Edmister, *Applied Hydrocarbon Thermodynamics* (Gulf Publishing, Houston, 1961)
C. Good, et al., *Oil & Gas Journal*, (Pennwell Publishing, Tulsa, 1944)
J.B. Maxwell, *Data Book on Hydrocarbons* (D. Van Nostrand, London, 1968). 1950, 9th Printing
Thrift, *Oil & Gas Journal*, (Pennwell Publishing, Tulsa, 1961)

Petroleum Products and a Refinery Configuration

David S. J. Jones and Steven A. Treese

Contents

Abstract

This chapter defines the major products normally produced from the refining of crude oil. These products are the intermediates and finished products from energy refineries. The "▶ Introduction to Crude Oil and Petroleum Processing"

Steven A. Treese has retired from Phillips 66.
David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_10

chapter of this book provided a brief description of the products; this chapter expands on this with a more in-depth look at the products themselves. Their demand in the petroleum markets and also the environmental impact of the more prominent products are also discussed in this chapter. The chapter continues with a discussion of the types of refinery configurations, including yields, capabilities, economics, advantages, and disadvantages of the common configuration categories. The chapter concludes with a detailed example of the development of the process configuration for a refinery to meet a particular product slate.

Keywords
Refining • Petroleum • Configuration • Topping refinery • Hydroskimming refinery • Cracking refinery • Full conversion refinery • Complex refinery • Fuel specifications

Introduction

This chapter defines the major products normally produced from the refining of crude oil. These products are the intermediary and finished products from energy refineries only. The "▶ Introduction to Crude Oil and Petroleum Processing" chapter of this book provided a brief description of the products; this chapter expands on this with a more in-depth look at the products themselves. Their demand in the petroleum markets and the environmental impacts of the more prominent products are also discussed in this chapter. The chapter continues with a discussion of the types of refinery configurations, including yields, capabilities, economics, advantages, and disadvantages of the common configuration categories. The chapter concludes with a detailed example of the development of the process configuration of a refinery to meet a desired product slate.

The first part of this chapter describes the basic fractions obtained from the atmospheric and vacuum crude distillation units. It continues with the description of products from the most common intermediate processes used in many refineries to meet their various product requirements. This part of the chapter continues with an outline of the specifications for various finished petroleum products and discusses their salient points.

The second part of the chapter discusses the features of the motive fuels. It continues with the effect of environmental constraints and the development of changes in the content of these products.

The third part focuses on the development of a refinery's process configuration and discusses its purpose. The development of a refinery configuration is illustrated by an example. This example is compiled manually. In modern development practice however, this would be accomplished by reducing the various product properties and their relationship to linear equations and solving these with high-speed computers, a process called linear programming, which is discussed in more detail in the chapter entitled "▶ Petroleum Refinery Planning and Economics" in this handbook.

Petroleum Products

Fractions from the Atmospheric and Vacuum Distillation of Crude Oil

The most common fractions distilled from crude oil distillation processes are shown in Fig. 1.

These cut lengths will vary slightly depending on the crude oil source and the finished product slate requirements. These are the basic components which, after further processing and blending, will make the finished products in the composition and quantity required by the refinery. The cuts shown in Fig. 1 are called "straight run" products , and these are described in the following paragraphs. The crude source, in this case, is a medium Middle Eastern crude with a gravity of 33.9° API and a sulfur content of 1.9 % wt.

Atmospheric overhead distillate. This is not strictly a cut but consists of all the light material in the crude absorbed into the total overhead distillate from the crude tower. This distillate, and in most cases, together with similar distillates from other processes, forms the feed to the refinery's light ends unit (see the chapter entitled "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing"). It is in the light ends unit that the straight run LPG, light naphtha, and the heavy naphtha are separated. However, the end point of the heavy naphtha is determined by the cut point of the overhead distillate and the fractionation between it and the first side stream product from the atmospheric unit.

Refinery gas and LPGs. In many refineries, most of the C_4s and lighter are removed from the atmospheric column overhead distillate in the first column of the light ends unit. This is the unit's debutanizer column. Some refineries however choose to separate the light naphtha and lighter from the heavy naphtha first. There is no specific reason; it's really a question of the specific refinery's economic criteria. Having separated the C_4s and lighter as a distillate from the naphtha, the distillate enters a depropanizer where C_3 and lighter are separated as a distillate from the C_4s. This distillate is further fractionated in a deethanizer column where the C_3 is removed as the bottom product. There is no distillate product from this unit, but all the gas lighter than C_3 leaves the tower as a vapor usually routed to the refinery fuel gas system (see the chapter titled "▶ Refinery Gas Treating Processes").

The C_4 portion of the overhead distillate is fractionated in the debutanizer so that it meets finished product specifications with respect to its C_5 content. The fractionation in the depropanizer will be such that the C_3 content of the bottom product – C_4 LPG – will meet the butane LPG specification with respect to RVP (Reid Vapor Pressure). The fractionation in this tower will also be such that the C_4 content in the overhead

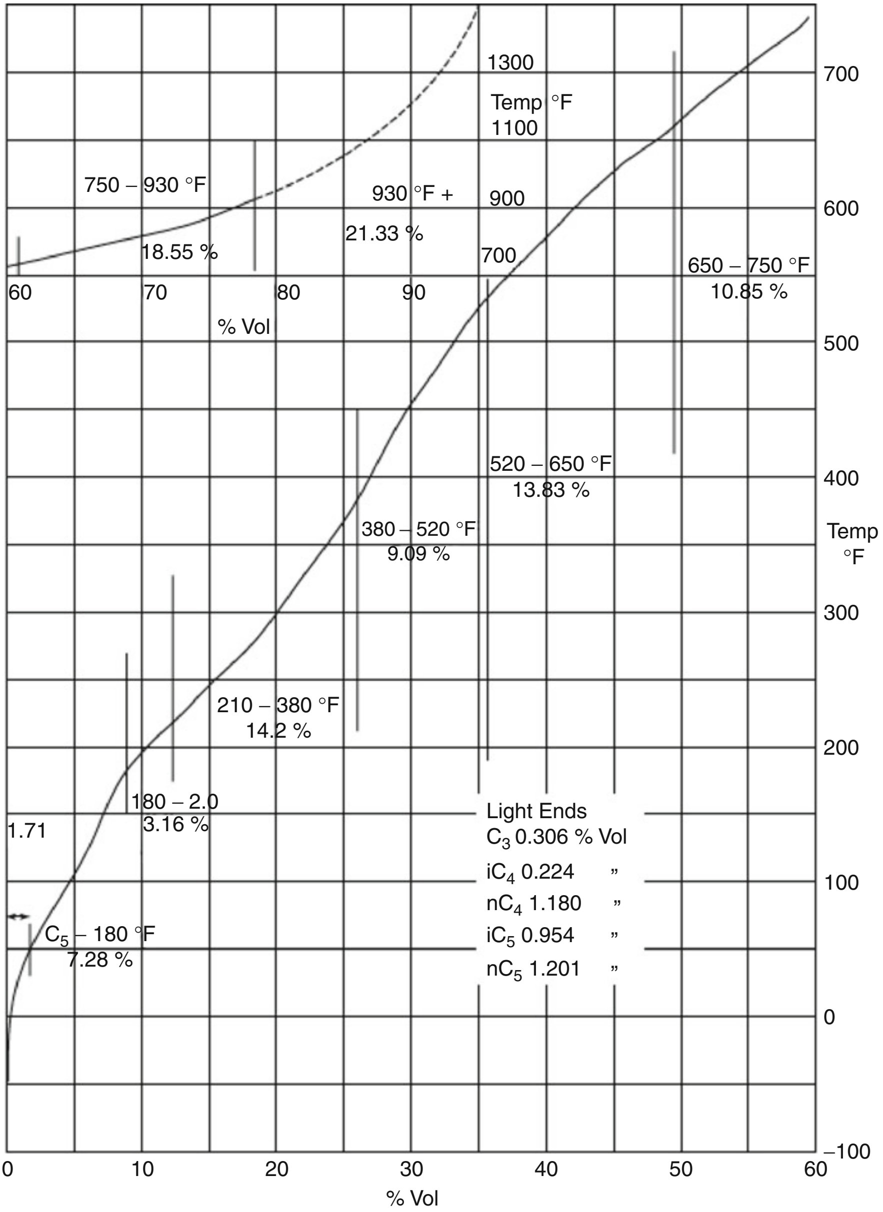


Fig. 1 Sassan crude TBP curve and product split

distillate will meet the propane LPG specification which leaves as the bottom product from the deethanizer with respect to its C_4 content. The fractionation in the deethanizer will be such as to ensure that the C_2 and lighter content of the propane LPG will meet that LPG's Reid Vapor Pressure specification.

The naphthas. There are usually two naphtha cuts produced from most crudes. These are:

- Light naphtha (sometimes called light gasoline)
- Heavy naphtha

Both these streams are the bottom product of the debutanizer unit. They are separated in a naphtha splitter tower. The light naphtha contains most of the crude's C_5s and much of the paraffin portion of the crude's C_6s. The purpose of making such a division is to produce a satisfactory heavy naphtha which will contain the heavier naphthenes and will be a suitable feed for a catalytic reformer (see the chapter on "▶ Catalytic Reforming in Petroleum Processing").

The light naphtha has a TBP distillation range of C_5 to around 190 °F. The heavy naphtha is the feed to the catalytic reformer and is a cut on crude of about 190–360 °F. This cut point of 360 °F can vary depending on the operating severity of the catalytic reformer, the volatility specification of the finished gasoline for which the reformate will be a major precursor, and the refinery's production requirements. In this latter case, for example, the refinery's operating plan may call for maximizing kerosene in which case the atmospheric distillation unit would be operated to decrease the amount of overhead distillate in order to increase the kerosene (top side stream) fraction. Of course, if the refinery plan is to maximize gasoline, the atmospheric tower would be operated to increase the overhead distillate at the expense of the kerosene fraction.

Straight run kerosene. This fraction is usually the first side stream of a conventional atmospheric distillation unit. It may be cut to meet a burning oil specification or become a component in Jet Fuel finished product. Its cut range is usually between 360 °F and 480 °F. Again this cut range may vary with the required heavy end of the naphtha and the front end of the gas oils. In most cases, this Kero fraction must meet a flash point specification after it has been steam stripped, and its end cut point is usually set to meet a smoke point specification. Usually the sulfur content restriction is met by hydrodesulfurization; in some cases too, the smoke point is reduced by other processes. These subsequent processes are aimed at removing or converting the aromatic content of the fraction. It can also be routed to the gas oil pool as a precursor for a diesel finished product.

The atmospheric straight run gas oils. Usually there will be two gas oil side streams, a light gas oil side stream and, below this take off, a heavy gas oil side stream. Both these side streams are steam stripped to meet their respective flash point specification (usually 150 °F minimum). The lighter side stream (cut of about 480–610 °F on crude) is the principal precursor for the automotive diesel grade finished product. This side stream is desulfurized to meet the diesel sulfur specification in a hydrotreater (see the chapter "▶ Hydrotreating in Petroleum Processing"). The lower gas oil stream is really a guard stream to correct the diesel distillation end point. This heavy gas oil may also be hydrodesulfurized and routed to either the fuel oil pool (e.g., as a precursor for marine diesel) or to a finished heating oil product from the gas oil pool.

The atmospheric residue. This is the bottom product from the atmospheric distillation of the crude oil. Most crude oils are distilled in the atmospheric crude oil tower to cut the atmospheric residue at a +650 °F up to a +680 °F cut point. Cutting the residue heavier than +680 °F risks the possibility of thermal cracking with heavier coke lay down and discoloring of the distillate products. Those atmospheric crude towers that do operate at higher cut points minimize the cracking by recycling the cold quench into the bottom of the tower (below the bottom stripping tray) and minimizing the residue holdup time in the tower. The atmospheric residue may be routed to the fuel oil pool as the precursor to several grades of finished fuel oil products. The other options for this stream in a modern refinery are as follows:

- Feed to a vacuum distillation unit (this is the most common option).
- Feed to a thermal cracker (visbreaker or coking unit). See the chapter on "▶ Upgrading the Bottom of the Barrel."
- Feed to a deep oil fluid catalytic cracker. Refer to the chapter "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining."
- Feed to a hydrocracker or hydrotreater. Refer to chapters titled "▶ Hydrocracking in Petroleum Processing" and "▶ Hydrotreating in Petroleum Processing."

The vacuum distillation of atmospheric residue. In modern refinery practice, the distillation of atmospheric residue is accomplished under high vacuum conditions in a specially designed tower whose internal equipment ensures a very low pressure drop. Normally the vacuum conditions in the flash zone of the tower allow about the same percentage of distillate based on the tower feed to be cut in this tower as the distillate on whole crude in the atmospheric unit. Again the flash zone temperature in the vacuum unit is kept below 700 °F. Usually there are two or three vacuum distillates from this tower. In a pure energy-related refinery, there will be two. The heavier of the two (say to a cut range of 750–930 °F) will be the feed to a distillate hydrocracker (see the chapter "▶ Hydrocracking in Petroleum Processing") or to a fluid catalytic cracker (see the chapter "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining"). In both of these cases, however, a small heavier cut is taken off and returned to the tower bottom in order to correct the bottom distillate Conradson carbon content to meet the specification required for either of the two downstream processes. This distillate product is usually titled HVGO (heavy vacuum gas oil).

For those refineries which produce lube oils as nonenergy products, this bottom distillate may be split into two side streams in order to provide the flexibility required in the production of the lube oil blending stock specifications (see the chapter on "▶ Non-energy Refineries in Petroleum Processing").

The light vacuum distillate is taken off as a top side stream and is usually routed to a hydrodesulfurizer to be sent either to the gas oil pool as heating oil stock or routed to the fuel oil pool as blending stock. This side stream is a cut range of 680–750 °F and is usually labeled LVGO (light vacuum gas oil).

The vacuum residue. This is the bottom product from the vacuum distillation unit. Just as in the case of the atmospheric residue, it has several options for its use in meeting the refinery's product slate. In the case of the energy refineries, it can be upgraded to prime distillate products by a recycling thermal cracking process (see the chapter "▶ Upgrading the Bottom of the Barrel"), coking, deep oil fluid catalytic cracking (see the chapter "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining") or hydrocracking, or a combination of these processes.

In the case of the production of lube oils, the vacuum residue can be processed to remove the heavy asphaltene portion of the stream. This deasphalted product is an excellent lube oil blending stock, commonly called "Bright Stock", which, when dewaxed and subject to other lube oil processes, becomes the precursor for a variety of lube oil products (see chapter "▶ Non-energy Refineries in Petroleum Processing"). The asphalt portion of the deasphalting process has a wide spectrum as precursor to the many grades of bitumen used in building and road paving (see chapter "▶ Upgrading the Bottom of the Barrel"). The vacuum residue itself also figures in the production of bitumen. Where nonenergy products are significant in the refinery's product slate, the vacuum residue, as produced, is the key component in bitumen production.

Typical Properties of Some Straight Run Product Streams

These cuts and stream properties are based on Arabian crude and are shown here for the light, medium, and heavy Arabian crude oil (Table 1).

Product Streams from Intermediate and Finishing Processes

Most finished marketable petroleum products are blends of some straight run product streams with the products from further processing of some of these streams (see section "Petroleum Products" of this chapter). This section deals with the intermediate or finishing product processes which provide the finished product precursors. Some of these more common intermediate products together with reference to their respective processes are described and discussed in the following paragraphs.

The LPG products. These two finished products, propane LPG and butane LPG, are products from straight run sources combined with the products from intermediate processes such as the cracking and the naphtha reforming processes. Their finished specifications, except for some mild desulfurization treating, are met by the distillation of the source streams and the central light ends units (see chapter "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing"). No further precursors are added, except for injection of odorizing chemicals for the detection of leaks and thus their safe storage. Finished LPGs are stored in spheres for propane and, usually, bullets for butane.

Butane LPG is however used extensively as a finished gasoline product precursor to correct for the volatility of the finished gasoline.

Table 1 Arabian crude straight run product streams

	Light	Medium	Heavy
Crude, °API	38.8	30.7	28.2
Sulfur, % wt	1.1	2.51	2.84
Light naphtha			
Cut range, °F	68–212	68–212	68–212
Yield, % vol	10.5	9.4	7.9
Gravity, °API	77.4	78.4	80.1
Sulfur, % wt	0.056	0.007	0.0028
RVP, Psi	6.9	7.9	10.2
Paraffins, % vol	87.4	89.7	89.6
Naphthenes, % vol	10.7	8.8	9.5
Aromatics, % vol	1.9	1.5	0.9
RON clear	54.7	48.2	58.7
Heavy naphtha			
Cut range, °F	212–302	212–302	212–302
Yield, % vol	9.4	7.4	6.8
Gravity, °API	58.8	59.6	60.6
Sulfur, % wt	0.057	0.019	0.018
Paraffins, % vol	66.3	67.8	70.3
Naphthenes, % vol	20.0	20.8	21.4
Aromatics, % vol	13.7	11.4	8.3
Kerosene			
Cut range, °F	302–455	302–455	302–455
Yield, % vol	18.4	13.5	12.5
Gravity, °API	48.0	48.9	48.3
Sulfur, % wt	0.092	0.12	0.19
Paraffins, % vol	58.9	59.9	58.0
Naphthenes, % vol	20.5	21.9	23.7
Aromatics, % vol	20.6	18.2	18.3
Freeze point, °F	−67	−72	−84
Smoke point, mm	26	23	26
Luminometer no.	57	55	60
Aniline point, °F	133	139	138
Kin cSt at –30 °F	5.09	4.63	4.74
Kin cSt at 100 °F	1.13	1.09	1.12
Light gas oil			
Cut range, °F	455–650	455–650	455–650
Yield, % vol	21.1	17.4	16.4
Gravity, °API	37.3	37.2	35.8
Sulfur, % wt	0.81	1.09	1.38
Pour point, °F	10	0	5
Aniline point, °F	166	156	156
Kin cSt at 100 °F	3.34	3.15	3.65
Kin cSt at 210 °F	1.32	1.22	1.4

(*continued*)

Table 1 (continued)

	Light	Medium	Heavy
Heavy gas oil			
Cut range, °F	650–1,049	650–1,049	650–1,049
Yield, % vol	30.6	30.5	26.3
Gravity, °API	24.8	22	21.8
Sulfur, % wt	1.79	2.87	2.88
Pour point, °F	100	75	90
Aniline point, °F	195	172	172
Kin cSt at 100 °F	49.0	62.2	62.5
Kin cSt at 210 °F	6.65	7.25	7.05
Atmos. residue			
Cut range, °F	+650	+650	+650
Yield, % vol	38.0	50.0	53.1
Gravity, °API	21.7	14.4	12.3
Sulfur, % wt	2.04	4.12	4.35
Pour point, °F	75	55	55
Con carb, % wt	4.5	10.0	13.2
Kin cSt at 100 °F	146	1,570	5,400
Kin cSt at 210 °F	12.4	54.0	106
Vacuum residue			
Cut range, °F	+1,049	+1,049	+1,049
Yield, % vol	7.4	19.5	26.8
Gravity, °API	11.5	3.8	4.0
Sulfur, % wt	3.0	5.85	5.6
Pour point, °F	80	120	120
Con carb, % wt	19	22.8	24.4
Kin cSt at 210 °F	392	19,335	13,400
Kin cSt at 275 °F	40.1	743	490
Vanadium, ppm	12	249	171
Nickel, ppm	7	55	53
Iron, ppm	36	79	28

Gasoline precursors. Gasoline is a blend of straight run naphtha (usually light naphtha) and products of intermediate processes. These are usually suitably boiling range products from:

- Catalytic reforming process (see the chapter "▶ Catalytic Reforming in Petroleum Processing")
- Fluid catalytic cracking process (see the chapter on "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining")
- Hydrocracking process (see the chapter on "▶ Hydrocracking in Petroleum Processing")

Modern refining configurations may also include processes which convert low-quality products to gasoline precursors, enhancing the gasoline's octane rating. These include the alkylation and isomerization processes (see the relevant chapters). Others which are less common are the oxygenated precursors (discussed in the chapter "▶ Introduction to Crude Oil and Petroleum Processing").

Catalytic Reforming

This is a process which converts a relatively low octane straight run naphtha into a high-octane liquid reformate which is a major precursor for finished gasoline. This process also produces a high-purity hydrogen stream; this makes the process one of the most important in a modern-day refinery configuration.

Briefly, the straight run heavy naphtha is heated and is passed over beds of platinum/rhenium catalyst contained in (usually) three or four separate reactor vessels. A recycle hydrogen stream accompanies the feed through these reactors, and the reaction temperature is controlled by heaters between each reactor. The principal reaction is the dehydrogenation of the naphthenes in the feed to their respective aromatic homologues. In so doing the excess hydrogen molecules are released as a hydrogen by-product. Other reactions also occur which enhance the octane rating of the debutanized reformate liquid product. Among these are some isomerization and, to some extent, some hydrocracking. Details of this process are given in the chapter "▶ Catalytic Reforming in Petroleum Processing."

Some typical properties of the debutanized reformate are given in Table 2. The feed to the catalytic reformer in this case includes the straight run naphtha (SRN) from the crude unit and the naphtha streams from gas oil hydrotreaters and a thermal cracker. This feed stream was also hydrotreated before entering the catalytic reformer (Table 2).

Naphtha from a Fluid Catalytic Cracking Unit

The naphtha from the FCCU is always a prime precursor for gasoline blends. There are usually two naphtha streams which are the debutanized overhead distillate from the cracker's main fractionator. This distillate is fractionated to produce a light naphtha and the heavy naphtha. As can be seen from the chapter "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining," the fluid catalytic cracker is a very flexible unit with respect to the feedstock that it can process. As a matter of fact, the only real constraints on the process are high metals and Conradson carbon contents of the feed. Even these constraints are reduced with the improved catalysts now available and some modification to the conventional process (see the topic in chapter "▶ Upgrading the Bottom of the Barrel" on deep oil cracking). The effect of the feedstock quality however is confined mostly to the severity of cracking and the resulting yields of the cracked products. The qualities of the streams from the main fractionator can be and usually are constant. Table 3 shows the properties of

Table 2 Properties of a debutanized reformate

Feed	
Crude source	Sassan
Heavy naphtha blend	
Cut range, °F	212–375
Gravity, °API	56.0
Paraffins, % vol	59.0
Naphthenes, % vol	29.6
Aromatics, % vol	11.4
Octane number (Res) clear	34.5
Reformate	
Gravity, °API	47.0
Dist ASTM D86	
IBP, °F	124
10 % vol recovered, °F	174
30 % vol recovered, °F	214
50 % vol recovered, °F	255
70 % vol recovered, °F	273
90 % vol recovered, °F	314
FBP, °F	416
Octane number (Res) clear	91.0

Table 3 Light and heavy cracked naphtha stream properties (feed is Sasson HVGO with gravity of 26.1° API)

	Light naphtha	Heavy naphtha
Gravity, °API	56.1	43.8
ASTM distillation D86		
IBP, °F	108	319
10 % vol recovered, °F	158	336
30 % vol recovered, °F	170	348
50 % vol recovered, °F	191	362
70 % vol recovered, °F	223	378
90 % vol recovered, °F	283	388
FBP, °F	330	448
Octane no. (Res) clear	94	89
Cut range, °F	C_5–300	300–420

the two naphtha streams from the catalytic cracker, which in this case is operated on Sasson Heavy Vacuum Gas Oil at a 70 % severity conversion.

Alkylation Plant

The other most common precursor for the gasoline products is the liquid alkylate from the alkylation process. This process is described in some detail in the chapter titled "▶ Alkylation in Petroleum Processing," and its part in the gasoline blending pool is shown in section "Petroleum Products" of this chapter (Table 4).

Table 4 Alkylate

	Alkylate
Gravity, °API	49.5
ASTM distillation D86	
IBP, °F	211
10 % vol recovered, °F	237
30 % vol recovered, °F	266
50 % vol recovered, °F	289
70 % vol recovered, °F	296
90 % vol recovered, °F	304
FBP, °F	394
Octane no. (Res) clear	97

Because of the high-octane product and the clean paraffinic nature of the alkylate, this is the preferred gasoline blending component from an environmental viewpoint.

There are other processes that produce precursors for gasoline and diesel motive fuels, among these are the products from olefin condensation and other polymer processes. These are not so common however, but details of the olefin condensing process are discussed in the chapter "▶ Olefin Condensation."

The Middle Distillate Products

Finished products derived from the middle distillate boiling range include:

- Kerosene for illumination
- Kerosene as a precursor for aviation turbine gasoline (ATG)
- Kerosene for tractor vaporizing oil (TVO)
- Kerosene as a precursor for automotive diesel
- Kerosene for asphalt cutback
- Light gas oil for diesel fuel
- Heavy gas oil for domestic heating oil
- All middle distillates for fuel oil blending

The straight run kerosene products. Most straight run kerosenes are desulfurized and routed directly to the finished product blending pools. The exception is in the case of the aviation turbine gasoline (ATG) which requires the kerosene precursor to be treated for aromatics reduction or removal to meet the strict smoke point specifications associated with this finished product. In present-day refineries, this is accomplished by hydrotreating the kerosene using a nickel catalyst. In older refineries, the aromatics contained in the cut were removed as an extract in a process using SO_2 as a solvent. In some cases also, the specification for the tractor vaporizing oil (TVO) requires the kerosene, which is the major component of this finished product, to be dearomatized also. Some details of the dearomatization

Table 5 General specifications of kerosene finished products

Parameters	Reg kero	ATG	TVO	ASTM method
Flash point, °F	100	<66	100	D-56
Aromatics, % vol	–	20	–	D-1319
Temperature at 20 % max		293 °F	–	D-86
Temperature at 50 % max		374 °F	–	D-86
Temperature at 90 % max		473 °F	540 °F	D-86
Final boiling point	572 °F	572 °F	–	D-86
Sulfur max, % wt	0.04	0.04	0.3	D-1266
Smoke point, min	–	25 mm	25 mm	D-1322
Freeze point, °C	–	−47	–	D-2386

hydrotreating process are given in the "▶ Hydrotreating in Petroleum Processing" chapter. The straight run kerosene product destined for fuel oil and asphalt blending is not necessarily desulfurized before routing to the respective blending pools.

Some general specifications for the various finished products containing predominately kerosene are given in Table 5.

Straight run light gas oil. This cut is always desulfurized and routed to the automotive diesel blending pool or to No. 2 Fuel Oil. It is the major component of this finished product. Its four major specifications are:

- Cetane number
- Pour point
- Sulfur content
- Flashpoint

Another important requirement is its volatility as defined by the ASTM distillation analysis. Except for the sulfur content, these specifications are met by the set points established in the atmospheric crude unit. Some kerosene may be blended to lighten the front end of the finished product, if required, and some heavy gas oil or light vacuum gas oil (LVGO) may be added to maximize the finished product yield, but limited to the product's ASTM distillation and the other specifications.

Note: Where the refinery configuration contains a thermal cracker, the gas oil cut from this unit may, depending on the unit's fractionator cut points, be added to the light straight run gas oil as feed to the hydrotreater and its subsequent routing to the diesel blending.

Straight run heavy gas oil. This cut could be a heavy side stream from the atmospheric crude distillation tower, or, if there is a vacuum unit in the configuration, it could be one or more of the gas oil distillate cuts from this tower. Most refineries that maximize motive fuels would have a cracking unit of some kind in their configuration. More often than not, this would be a fluid catalytic process taking as feed the heavy vacuum gas oil stream. Hydrocrackers are becoming more common however, since they can make ultralow sulfur fuels directly.

Table 6 General specifications for gas oil finished products

Parameters	Auto diesel	Heating oil	ASTM tests
Color	2.0 max	1–1/2	D-155
Specific gravity, °API	37.0–33.0	41.1–36.0	D-1298
Viscosity sus at 100 °F	32.0–43.9	37.5 max	D-88
Flash point, °F	150 min	150 min	D-93
Pour point winter, °F	5.0 max	5.0 max	D-97
Pour point summer, °F	15.0 max	15.0 max	
Sulfur content, ppm wt	10–500 (*)	10–500 (*)	
Diesel index	54 min	57 min	IP-21
Cetane number	45 min	50 min	D-613
Distillation			D-158
Recovered at 446 °F % vol	–	10 min	
Recovered at 464 °F % vol	50 max	50 max	
Recovered at 482 °F % vol	–	40 min	
Recovered at 572 °F % vol	–	70 min	
Recovered at 619 °F % vol	–	80 min	
Recovered at 657 °F % vol	50 min	–	
Recovered at 675 °F % vol	90 min	90 max	
FBP, °F	725 max	725 max	

(*) or as required

The heavy gas oil from the atmospheric distillation unit would be hydrotreated before being routed to the heating oil blending pool or partly to heating oil and partly to fuel oil pool. If there is a catalytic cracker in the refinery, the cycle oil from this unit would be blended with the straight run heavy gas oil to be desulfurized and routed as described. This cycle oil as a cracked product will be rich in olefins, and these would be saturated by the hydrodesulfurization process to meet heating oil specifications. Some traditional product specifications for the various gas oil finished products are given in Table 6. With the advent of low-sulfur and ultra-low sulfur diesels, these specifications are being modified considerably, with sulfur levels as low as 10 wt-ppm (0.001 wt%) and cetane numbers in excess of 50 required.

Products from the Residues

The residues from the atmospheric and vacuum distillation of crude oil open a spectrum of saleable products which constitute a major source of revenue for many refineries. These are listed in order of their importance as follows:

- The fuel oils
- Petroleum coke
- The lube oil products
- The asphalt products

Table 7 General specifications for fuel oil products

Parameters	Marine diesel	No. 6 fuel oil	ASTM tests
Specific gravity °API	39–40	11.4 max	D1298
Viscosity Redwood 1 at 100 °F, sec	30–40	2,400 max	D445
Pour point summer, °F	25 max	65 max	D97
Winter, °F	10 max	–	
Flash point, °F	150 min	160 min	D93
Calorific value (gross) Btu/lb	19,200 min	18,300 min	D240
Sulfur content, % wt	1.0 max (*)	2.0 max (*)	D129
Diesel index	45 min	–	IP21
Ash, % wt	0.01 max	0.1 max	D482
Sediment, % wt	0.01 max	0.1 max	D473
Water, % wt	0.05 max	1.0 max	D95

(*) or as required

The fuel oil products. There are two common fuel oil products in use today. The first and perhaps the second most common product is the marine diesel. As the name suggests, it is the fuel used by heavy marine diesel engines. It is the least viscous of the three grades and is usually a blend of a middle distillate (kerosene and/or gas oil) with atmospheric residue. It has a general specification as shown in Table 7.

The most common fuel oil used in industry is the No 6 fuel oil which is either a suitably cut atmospheric residue or a vacuum residue blended with a distillate cut back. It may mean also that a cutback distillate has been desulfurized to meet the product sulfur specification of the fuel oil. A general specification for No 6 fuel is shown in Table 7. Again, depending on use, sulfur specifications are being lowered in many instances. The trend is toward much lower sulfur specifications for fuel oil.

Several other fuel oil grades are often produced by blending one or other of the distillation residues with suitable distillate streams. These however are customized for clients' specific needs. For example, a No 5 fuel oil grade was once produced in some quantity for the steel industry. This is a product less viscous and of a lower gravity than No 6 fuel oil. It is now seldom produced.

Petroleum coke. This is not found in crude oil but is formed by the thermal cracking of the residues from both atmospheric and vacuum distillation of the crude. The coke is really formed by the thermal conversion of these heavy products which contain the resins and asphaltenes from the crude. The major purpose of the "coking" processes is to upgrade the residues by producing lighter marketable products in the gasoline and middle distillate range. The coke becomes the by-product of these thermal cracking mechanisms (see the chapter titled "▶ Upgrading the Bottom of the Barrel" for more details on these processes). The coke as produced in the refinery processes is called *green coke*, and this may be subclassified as *sponge coke* from a delayed coking process and *needle coke*, normally from a fluid coking process. Approximately one half of the green coke (both needle and sponge) is further calcined to make the calcined coke product.

Table 8 Typical sponge coke specification

Parameter	Green coke	Calcined coke
Fixed carbon, % wt	86–92	99.5
Moisture, % wt	6–14	0.1
Volatile matter, % wt	8–14	0.5
Sulfur, % wt	<2.5	<2.5
Ash, % wt	0.25	0.4
Silicon, % wt	0.02	0.02
Nickel, % wt	0.02	0.03
Vanadium, % wt	0.02	0.03
Iron, % wt	0.01	0.02

Uncalcined coke has a heating value of around 14,000 Btu/lb and is primarily used as a fuel. High-sulfur uncalcined sponge coke is particularly popular in the cement industry since the sulfur reacts to form sulfates. Low-sulfur, low-metals sponge coke may be calcined to remove volatiles and is used mostly for anodes in the aluminum industry, while needle coke is calcined for anodes in the steel industry. Table 8 defines the general specification for green coke and calcined coke.

Lube oil production. The second most important products from the residue of crude oil are the lube oil products. Details of the lube oil production processes are given in the chapter on "▶ Non-energy Refineries in Petroleum Processing." The development of the industrial revolution gave a big incentive for the production of high-quality lubricants from the processing of crude oil. A further boost to these processes followed the rapid development of the automotive industry, particularly in the Western world. More and more sophisticated processes were developed for the purpose of this growing demand and an increasing quality requirement. This has culminated in the use of the hydroprocesses used extensively in today's modern refineries.

Still higher quality demands are driving a trend toward synthetic lube oil processes, such as gas-to-liquids and poly-alpha-olefins.

Through the years, the lubricant market has developed its own lexicon of terms. Some of these are:

A lube oil base stock – This refers to a base lube oil product from a lube oil process which meets all the requirements for blending to make a spectrum of lube oil finished products.

A lube oil slate – This is a set of lube oil base stocks that makes up a particular finished product. Usually there are between three and five such stocks.

Neutral lubes – These are lube oil streams obtained as side cuts from the vacuum distillation of the crude oil atmospheric residue.

Bright stock lubes – These are processed as deasphalted oil from vacuum residues. (*Note*: deasphalted oils are also used as feedstock to fluid catalytic crackers and more commonly to heavy oil hydrocrackes).

Table 9 SAE viscosity specification for single-grade motor oil grades

Grade	Max viscosity (SS) at 0 °F	Max viscosity (SS) at 210 °F	Min viscosity (SS) at 210 °F
5 W	6,000	–	–
10 W	12,000	–	–
20 W	48,000	–	–
20	–	58	45
30	–	70	58
40	–	86	70
50	–	110	85

Paraffinic lubes – These are all grades, both neutral and bright stock, with a finished viscosity index of more than 75.

Naphthenic lubes – These are all grades with finished viscosity index of less than 75.

The important properties of lube oils are:

- Kinetic viscosity (centistokes)
- Color
- Pour point
- Flashpoint
- Volatility
- Oxidation stability
- Thermal stability

Although kinematic viscosity is measured in centistokes, it is usually specified in Saybolt Seconds (SS). Specifications for lube oils are established by the Society of Automotive Engineers who also perform research on a wide range of automotive topics. One very well known motor oil specification is the SAE viscosity. This is given in Table 9. Multigrade oils (10–20, 10–30, 10–50, etc.) prevail in today's markets.

There are a great many specifications covering all grades and uses for the lube oil products. Many of these, particularly for the motor lube oils, are customized within certain basic maximum and minimum constraints (such as viscosity), for the local climate, motor type, and legislative requirements.

The asphalt products. Asphalt is the heaviest boiling point product that can be produced in the processing of crude oil. Contrary to common beliefs, asphalts can only be made from crude oils that contain asphalt. That is, they contain the right amount of the carbon and the resin that allows the formation of asphalts. A full description of the types and the production of asphalt is given in the chapter on "▶ Upgrading the Bottom of the Barrel." Briefly, most grades of asphalt are produced from the deep-cut vacuum residue of suitable crudes. The asphalt extract from the lube oil deasphalting process may also be included with the residue for the production of certain asphalt grades. The finished product is often treated by air blowing to achieve the required hardness and ductility of the product. Asphalt becomes an important product because of its wide use in road and other building industries.

A Discussion on the Motive Fuels of Gasoline and Diesel

Of all the petroleum products that are marketable, motive fuels are the ones that are most common to the general public. Because of this, they are continually in the public focus with respect to their performance, their availability and cost, and their effect on the environment. This section of the current chapter continues with a closer look at the makeup, manufacture, and the environmental impact of these two motive fuels. It begins with the gasolines.

The Parameters of Gasoline

Parameters Affecting Engine Performance

The following parameters are the major criteria in the production of finished gasoline with respect to its performance: These are:

- Octane number
- Thermal efficiency
- Volatility of the gasoline
- Engine deposits

Octane number. Among the most important parameters in the manufacture of gasoline is its resistance to “knocking.” This resistance is expressed as an “octane number.” A definition of octane number and its measurement has already been given in the introductory chapter of this book.

Knocking limits the power that can be developed by the engine/fuel combination. Detonation is the spontaneous explosion of the residual fuel (after almost complete combustion) and the air in the combustion chamber as the normal mechanism of combustion nears its end. It’s a very fast oxidation reaction which sets up its own flame front. The knocking occurs when this front and that of the normal combustion collide, creating a pressure wave.

Another, and perhaps, more destructive form of engine knock is “preignition”. This is the spontaneous ignition of the fuel/air mixture before the ignition spark. This in turn is caused when the unburned gases are compressed in the cylinder and the resulting temperature reaches the auto ignition point before the ignition spark occurs. This preignition usually causes major engine damage in just a few seconds or minutes.

Increasing humidity, cooler ambient air temperatures, and altitude reduce requirements for antiknock.

Thermal efficiency. As may be expected, fuel economy is a factor in determining the thermal efficiency of the auto engine. The engine's efficiency increases with the increase in compression ratio. However, with the increase in compression ratio, there is an increasing need for fuels that do not knock. Since the 1980s, engine manufacturers have been incorporating knock sensors to the engine electronic management system to continuously adjust the ignition timing. This development allows the timing of the spark to occur in advance of the piston reaching the top of its travel. The maximum engine efficiency is produced with this timing control measured and adjusted by the computer control of fuel-to-air ratio. Further development and testing of individual engine design sets optimum criteria for fuel octane number of the fuel and air ratio for lean mixture combustion.

Volatility of the gasoline. Another important property of gasoline is its volatility. The gasoline must be volatile enough to enable the engine to start at the lowest temperature expected in its service. At too low a volatility, the engine would have difficulty starting and would be prone to stalling in service. On the other hand, too high a volatility would cause excessive vapor which in turn would cause vapor lock in the fuel lines and fuel pump.

Engine deposits. Engine deposits affect fuel efficiency and emissions. Deposits are of particular concern in the carburetor, fuel injectors, inlet valves, and combustion chamber. These deposits are essentially fine carbon granules which are formed by high inlet valve temperatures, airflow inconsistencies, and minor oil contamination.

Parameters Affecting Pollution by Emission

Air pollution is an important factor in motive fuel design and manufacture. There are two main types of air pollutants that affect the manufacture of motive fuels. These are:

- Hazardous air pollutants (HAPs)
- Criteria air pollutants

Hazardous Air Pollutants

These are air pollutants that have been shown statistically to cause major health disorders such as cancer, neurological damage, respiratory irritation, and reproductive disorders. In general these pollutants are believed to have no threshold and are harmful even in small doses or concentrations. The Environmental Protection Agency (EPA) has been regulating these pollutants since the 1977 Clean Air Act. There are more than 189 hazardous air pollutants including benzene, formaldehyde, and 1,3-butadiene which are formed by combustion of motive fuels such as gasoline.

Criteria Air Pollutants

These are pollutants that can injure health, harm the environment, and cause property damage. These pollutants do have a threshold level however, below which they are relatively harmless. The EPA labels these pollutants as *criteria air pollutants* because the basis for setting standards is developed from health-based criteria. There are six primary air pollutants that affect the design and manufacture of gasoline. These are:

- Lead
- Carbon monoxide (CO)
- Sulfur dioxide (SO_2)
- Nitrogen dioxide (NO_2)
- Particulate matter
- Ozone (O_3)

Lead. This emission from gasoline engines has been known to be toxic for several decades. It adversely affects the kidneys, liver, and other organs and leads to neurological impairment, learning deficits, and behavioral disorders. The reduction of lead programs conducted in the 1970s and 1980s have made leaded gasoline (TEL added) unavailable for on-road vehicles since the 1990s.

Carbon monoxide (*CO*).This is a colorless, odorless, and poisonous gas produced from the incomplete combustion of carbon in fuels. Elevated exposures are serious for those suffering from cardiovascular disease and lead to visual impairment, loss of manual dexterity, and the ability to perform complex tasks. At high enough levels, it depresses cardiac activity and respiration and causes convulsions and ultimately death. Over half the carbon monoxide emissions are from motor vehicles.

Sulfur dioxide. This is formed during burning of sulfur-containing fuels. Motor vehicles are a minor source of SO_2 due to the desulfurizing processes used in the production of motive fuel components. Short-term exposure to high concentrations leads to reduced lung function, while longer exposures are associated with chronic respiratory problems. Sulfur dioxide mixed with nitrogen oxide is a major contributor to the formation of *acid rain*. This in turn causes acidification of lakes, rivers, and waterways. It damages crops and trees and accelerates the corrosion of building materials and coatings.

Nitrogen dioxide. Also known as nitrogen peroxide, nitrogen dioxide is a brown gas formed by high-temperature combustion of fuels. It is one of a family of nitrogen oxides which are often treated as one species under the term NO_x. Nitrogen dioxide is a severe irritant to the lungs and can cause respiratory infections, pneumonia, and bronchitis. Nitrogen dioxide coupled with volatile organic compounds (VOC) and ozone are the main components of smog.

Particulate matter. Dust, dirt, smoke, and liquid droplets form the particulate matter in motor emission and pollutants. Some of the liquid droplets are formed in the atmosphere by the condensation of sulfates, nitrates, and hydrocarbons. Fine particles with diameter less than 2.5 μm are emitted by motor vehicles. Gasoline-driven vehicles, however, do not emit significant levels of particulate matter compared with diesel-driven engines. Particulate matter aggravates existing respiratory and cardiovascular disease, damages lung tissue, and may cause cancer. Fine particles of 2.5 μm or less are considered more serious since they can penetrate easily into the respiratory tract and are retained longer. Particulate matter also contributes to haze.

Ozone. This photochemical oxidant is found in the atmosphere from ground level to 6 miles above the ground and again in the stratosphere 6–30 miles above the earth. At ground level, ozone, together with nitrogen oxides, volatile organic compounds, and sunlight are the major constituents of “smog.” Ozone is a strong oxidant that damages lung tissue and reduces lung function.

Meeting the Gasoline Parameters

Prior to 1990, the performance and emission characteristics of motor fuels were mainly the responsibility of the engine manufacturers with some notable changes imposed on the gasoline manufacturers. Notable among the restrictions imposed on the refineries in the gasoline manufacture was the restriction on the use of TEL (tetra ethyl lead) as an octane enhancer. The EPA (Environmental Protection Agency) had, as early as 1970, enforced a program to reduce the addition of lead so that even before 1990, there was available only “no lead” or “unleaded” gasoline for road vehicles. The “Clean Air Act” of 1990 however put the onus on the gasoline manufacturers for meeting the act’s requirements. In North America, programs to introduce reformulated gasoline were launched. This RFG allowed the performance of the gasoline to be retained while reducing the harmful emissions caused by the traditional octane enhancers such as aromatics (from reformates) and olefins (from cracked naphtha).

Reducing aromatics in gasoline. The most stringent environmental restriction imposed on aromatics in gasoline is on benzene. This component in benzene has now been reduced to levels below 1.0 % vol in the product. Refining processing philosophy has undergone some extensive changes to meet this single requirement. The following steps have been taken in part or as a whole to meet this change:

- Reducing reformer severity. This also reduces the quantity of the heavier aromatics.
- Reducing the final boiling point of the gasoline. This essentially reduces the amount of the heavier aromatics in the gasoline.
- Increasing the quantity of isoparaffin. This is accomplished by saturating the benzene ring and isomerization of the naphthenes to isoparaffins.
- Reducing the aromatics in the cracked naphtha stock. Catalytic cracker naphtha is high in olefins in the front end but high in aromatics in the back end. The reduction of aromatics from this source is accomplished by lowering the cut’s final boiling point.
- Aromatic extraction using an extraction process similar to that used in producing the petrochemical aromatic complex feed (e.g., the sulfolane process). Only about 20 of the largest refineries in North America have this extraction facility however.

Reducing the olefins in gasoline. Almost all the olefins and sulfur in the gasoline pool come from the catalytic cracker naphtha with a relatively small amount from thermal crackers. The following methods again in part or as a whole are used to reduce this olefin content:

- Alkylation and etherification. The light olefins of C_5 can be fractionated out, and, following a simple sulfur removal step, are fed to an alkylation process to produce good high-octane C_9 alkylate. Alternatively, the light fraction from the cracked naphtha can be processed to the oxygenate TAME (tertiary-amyl methyl ether).
- Isomerization of the C_6 and C_7 fractions. These two olefin components of cracked naphtha may be hydrogenated and isomerized to provide a good octane rating. The two olefin components are only small in quantity in gasoline but they are highly reactive, and their removal and conversion is necessary to meet the present restrictions in gasoline manufacture.

Meeting the gasoline sulfur content. Almost all of the sulfur in gasoline comes from the catalytic cracker and other thermal crackers. The RFG program is expected to reduce sulfur in gasoline to around 10 ppm by weight; European specifications are also lowered to 10 wppm. To meet these new criteria, refiners are taking the following approaches:

- Route the heavy end (about 20 % vol) of the catalytic naphtha into the middle distillate pool. This does not reduce the sulfur, but it moves a large portion of it and the heavy aromatics into other parts of the product slate, reducing the sulfur and aromatic content of the gasoline.
- Either hydrotreat and/or caustic treat the lighter portion of the cracked naphtha. This is rich in olefins and sulfur. Hydrotreating does reduce the octane value of the naphtha in that it saturates the olefins to lower octane paraffin or naphthene. Treating with sulfur extraction wash (e.g., UOP's Merox process) is the often preferred route; however, caustic treating is often inadequate to reach 10 ppm.
- The back end of cracked naphtha is high in sulfur, aromatics, and olefins. This may be hydrogenated using a catalyst selective in removing sulfur and leaving the aromatics essentially as they were.
- Hydrotreating of the catalytic cracker gas oil feed is quite common. This significantly reduces the sulfur content of all the cracked products from the catalytic cracker unit and increases the product yields from the FCC.

Manufacturing Gasoline

The requirements of the Clean Air Act of 1990 and later additions have changed the refining requirements to meet this product's need quite significantly. Prior to this date, much of the gasoline finished product recipe consisted of normal light naphtha, reformate, usually some cracked naphtha, and possibly alkylate; some butane may be included if required to meet volatility. The Clean Air requirement and its subsequent additions force a reduction of both reformate and the cracked stock (see Tables 10 and 11).

Table 10 A gasoline recipe prior to 1990

Component	% vol	Aromatics % vol	Olefins % vol	ON res clear	ON ratio
Butane	3.75	0	0	92	3
LSR	12.5	10	2	69	8
Reformate	24.39	89	0	91	18
Lt crack naphthas	12.5		35	89	18
Hy crack naphthas	21.19	53		90	19
Alkylate	25.67	0	0	95	24
Total	100.00	31.0	12.0		90

SG at 60 °F 0.7749
RVP 7.0 psig

Table 11 A gasoline recipe post 1996

Component	% vol	Aromatics % vol	Olefins % vol	ON res clear	ON ratio
Butane	1	0	0	92	0.9
LSR	15	0	0	69	10.0
Reformate	30	60	0	80	24.0
Cat naphthas	32	25	35	82	26.0
Alkylate	20	0	0	95	27.0
MTBE	2	0	0	110	2.1
Total	100	26	11.2		90.0

Table 12 Oxygenates commonly used in gasoline (except for ethanol, subject to phase out in the USA)

Name	Formula	RON	RVP psig	Oxygen % wt	Water solubility %[a]
Methyl tertiary butyl ether (MTBE)	$(CH_3)_3COCH_3$	110–112	8	18	4.3
Ethyl tertiary butyl ether (ETBE)	$(CH_3)_3COC_2H_5$	110–112	4	16	1.2
Tertiary-amyl methyl ether (TAME)	$(CH_3)_2(C_2H_5)COCH_3$	103–105	4	16	1.2
Ethanol	C_2H_5OH	112–115	18	35	100

[a]wt% soluble in water

Using the oxygenates. Oxygenates were used originally simply as an additive to improve octane number. However, because of their oxygen content, they are now added also to reduce carbon monoxide and hydrocarbon in the emission gases. There are a number of oxygenates now used in gasoline manufacture; some of the more common are given in Table 12.

The EPA has established limits for the use of each oxygenates in gasoline blends. For example, MTBE may be blended up to 15 % vol subject to an overall limit of 2.7 % wt oxygen content. The role of MTBE and other oxygenates in the USA was discontinued in 2002 after it was discovered that underground storage tanks had not been upgraded to retain reformulated gasoline. As a consequence, tanks were leaking gasoline that contained MTBE into the ground and drinking water systems. In the USA, ethanol is the primary oxygenate used for blending.

Diesel Fuel

The policies in place to control emissions from motive fuels have moved from gasoline engines to diesel engines. Similar to the gasoline fuels, diesel has also changed in composition to meet these environmental constraints while still maintaining a required performance standard. These changes have imposed a major impact on the refining industry at a time when the demand for diesel is increasing. Again, as in the case of the gasoline fuel, reformulated diesel fuel becomes part of the modern diesel specification and composition. These are described and discussed in the following sections.

The Diesel Engine

Before dealing with the diesel fuel, it may be advantageous to review briefly the principles of the diesel engine itself: diesel engines have historically been preferred in many applications because of their simplicity of design, power, durability, and higher fuel efficiency. Diesel engines fit into three categories and these are:

- Low-speed engines
- Medium-speed engines
- High-speed engines

Low-speed engines. These operate at less than 300 revolutions per min (rpm) and are used for applications that require sustained heavy loads at constant engine speed. Examples are the main propulsion engines in marine vessels and engines used in electric power generation.

Medium-speed engines. These operate at speeds between 300 and 1,000 rpm and are used for applications with fairly high loads and relatively constant speeds. Engines used in auxiliary power plants on marine vessels and in smaller power generation plants are examples of this type of diesel engine.

High-speed engines. Operate at speeds above 1,000 rpm and are designed for frequent and wide variations in load and speed. This is the type of engine used for road transport and diesel locomotives.

Almost all diesel engines use a standard four-stroke design which are intake, compression, power, and exhaust. During the intake stroke, air alone enters the cylinder, and during the compression stroke, the air is compressed by the upward movement of the piston. The final temperature and pressure reached in the cylinder is a function of the compression ratio, engine speed, and engine design. Pressures of 450 psig and temperatures of 500 °F are typical. Shortly before the end of the compression stroke, one or more jets of fuel are injected into the cylinder. The fuel pump introducing these jets is usually cam-driven type and operates at pressures between 1,800 and 30,000 psig. The fuel does not ignite immediately. There is a delay period when the fuel droplets vaporize and reach their ignition temperature. The extent of this time delay is affected by the design of the engine, the temperatures of the inlet air and fuel, and the degree to which the injected fuel is atomized on entering the cylinder. This ignition delay must be kept as short as possible to avoid accumulation of fuel in the cylinder before ignition. Such a situation causes diesel knock when this large quantity of fuel detonates.

After ignition, fuel injection continues for a portion of the power stroke. This fuel burns almost instantaneously with the remaining air and combustion products in the cylinder. This more controlled burning period is referred to as diffusion combustion. Fuel injection is stopped part way through the power stroke. Finally the exhaust stroke purges the combustion products from the cylinder, and the cycle begins again.

Design Improvements to the Basic Diesel Engine

Fuel injection improvements. Most diesel engines built in the 1980s were equipped with indirect fuel injection system (IDI). Modern engines are equipped with direct fuel injection (DI) which is designed for the geometry of the combustion chamber and is significantly more efficient. (Note: This can be compared with the direct injection concept in gasoline engines which was introduced around this time also.)

Four-valve cylinder heads. This promotes better movement of both combustion air and exhaust gases. This causes high turbulence of the fuel and air in the combustion chamber, resulting in good distribution of the fuel and increased flame speed which reduces the ignition delay time.

Electronically controlled fuel injection timing. This allows for the injection of a small quantity of fuel before the main charge into combustion chamber. The result is a quieter combustion, minimizing the amount of premixed combustion and maximizing the more controlled diffusion combustion.

Increasing the amount of air introduced into the cylinder. Using a turbocharger, which is an air compressor driven by a turbine using exhaust gas energy, the mass of air introduced into the cylinder is increased. This enables the engine to burn more fuel, thus increasing its power output. Using this concept, the power output for a diesel engine can be increased by as much as 50 % for the same engine displacement.

The Parameters of Diesel Fuel

The following are the major parameters in meeting the diesel fuel specification with respect to engine performance and/or emissions:

- Cetane number
- Aromatic content
- Density
- Sulfur content
- Distillation

- Viscosity
- Cold properties
- Flashpoint

Most of these parameters have been defined elsewhere in this book. This section then deals with the effect these parameters have on the performance of the diesel engine or the emission of undesirable components from the engine or both. Where the definition of the parameter is not dealt with in detail elsewhere in the book, then definition is included here.

Cetane number. This is the result of an engine test that compares the ignition delay for a fuel. For this test, two reference fuels are chosen. The first is normal cetane (n-C_{16}) and the second is an isomer of cetane which is heptamethylnonane. The normal cetane is arbitrarily given the cetane number of 100, while the isomer as the second reference fuel is assigned a cetane number of 15. The fuel being tested is run in a standard test engine. The cetane number is derived by comparing the ignition delay of the test diesel with a blend of the two reference fuels. The cetane number is then calculated using the equation:

$$\text{Cetane number} = \%\ \text{normal cetane} + 0.15 \times \%\ \text{heptamethylnonane}. \qquad (1)$$

Higher cetane numbers indicate that the fuel has a shorter ignition delay. A higher cetane number also results in less CO and unburnt hydrocarbons in the engine emission gases. This has a greater effect in older diesel engines. Modern engines are equipped with retarded ignition timing, and increasing the cetane number has a smaller effect on these more modern engines.

Aromatics. The aromatic content of diesel fuel can be measured for single-ring aromatics, multi-ring, or poly-aromatic hydrocarbons (PAH). Some studies show that reducing the aromatics results in the reduction of all regulated emissions, but other studies have indicated reduction of emissions of unburned hydrocarbons, NO_x, and particulates can only be achieved by reducing multi-ring aromatics.

Density. As density is a measure of the mass per unit volume, diesel fuels of low density require a longer injection time to deliver the same mass of fuel into the cylinder. The longer the injection time, the lower is the peak temperatures which, in turn, results in lower NO_x formation. At high loads and engine speeds, the longer injection interval causes some incomplete combustion, resulting in a high emission of unburnt hydrocarbons and CO. When the load is being increased, however, the lower density fuel results in less over-fueling, which actually decreases the emission of particulates, hydrocarbons, and CO.

Sulfur. The sulfur in diesel fuel is burned to SO_2, a portion of which is further oxidized to sulfates. This binds with water to generate acid rain and to form a portion of the particulate matter. Because only a small percent of the total sulfur in fuel is oxidized to sulfates, the contribution of sulfates to the total particulates is quite small. However, if an oxidation catalyst is used to reduce emission of hydrocarbons, CO, and particulate matter, a significant amount of the SO_2 is converted to sulfates and consequently makes a significant contribution to the particulates in the emission gases.

Distillation. The distillation range of diesel fuel has a significant influence on engine performance. This is especially so in medium- and high-speed engines. If the fuel is too volatile, the engine loses power and efficiency because of vapor lock in the fuel system or poor droplet penetration into the cylinder. On the other hand, if the volatility of the fuel is too low, the engine will lose power and efficiency as a result of poor atomization of the fuel. Both the front end and the back end of the distillation are important. If the 10 % vol point is too high, the engine will have difficulty starting. A low 50 % point reduces particulate emissions and odor. Because heavier molecules are more difficult to burn, both soot and the soluble organic fraction (SOF) of the particulate emissions are increased if the 90 % point is too high; the emission of unburned hydrocarbons will also increase.

Viscosity. Fuel viscosity has an important effect on the fuel pump and injector system. The shape of the fuel spray is affected by viscosity. If this is too high, the fuel will not be properly atomized into the cylinder, which will result in poor combustion, loss of power, and efficiency, with an increase in CO and hydrocarbon emission. Another effect of poor atomizing of the fuel will be to allow the fuel to impinge on the cylinder walls and remove the lubricating film. This results in excessive wear and increase of hydrocarbon emissions.

If the viscosity of the fuel is too low, the injection spray is too soft and will not penetrate far enough into the cylinder. A loss of power and efficiency will occur due to this. Where the fuel system is also lubricated by the fuel, as is the case in some engine designs, increased wear to the system will result through low fuel viscosity.

Cold properties (cloud and pour point). Cold weather performance of diesel fuel is a key consideration for users. Actual specifications for cold flow properties are based on expected temperature extremes, and different test methods are used in different parts of the world. In the USA, cloud point is used as an indicator of the cold flow properties of the fuel. Cloud point is the temperature at which wax begins to precipitate out of the fuel. The longer paraffin molecules in the fuel precipitate as a wax when the temperature falls below the cloud point. This wax clogs unheated fuel lines and filters. The more paraffinic a fuel, the higher will be its cloud point. In some parts of the world, pour point is used as an indication of the lowest temperature at which a fuel can be pumped. Pour points are generally 4–5 °C lower than the cloud point. Increasingly, the Cold Filter Plugging Point (CFPP) test is replacing or supplementing the other cold property specifications, since it directly measures cold weather problems with fuels.

Flash point. The flash point of a fuel is the temperature that the fuel must be heated to produce an ignitable mixture of vapor and air above the surface of the liquid. This property is only important for safe handling and storage of the fuel. It has no effect on the performance of the fuel or its emission properties. If the flash point is too low, fire or explosion could occur when it is handled.

Meeting the Diesel Fuel Parameters

There are various solutions for meeting the parameters of diesel fuel in the design of the fuel. These solutions range from fractionation, adding improvers, and more complex hydroprocessing. Using modern developments in hydroprocessing, it is

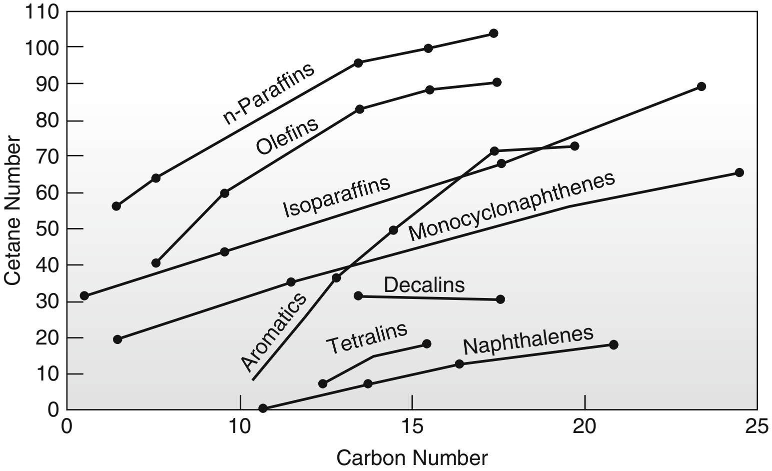


Fig. 2 Cetane number of hydrocarbon types

possible to convert low-grade blend stocks, such as FCCU or thermal cracker product streams, to good diesel precursors. Among the more important parameters to be met both from the performance and the emission aspects of the fuel are discussed below.

Increasing cetane value. The simplest way to improve cetane number is to use an appropriate ignition improvement additive. These are mainly alkyl nitrates. The effectiveness of cetane improvement additives tends to be linear with addition rate; however, the improvement can vary with different diesel blend stocks. Paraffins which already have high cetane value respond best to the additives. Aromatics, on the other hand, which have a low cetane number, have a poorer response. About 500 wppm of standard alkyl nitrate will increase the cetane value by 2–5 numbers. Another way to increase cetane number is to modify the hydrocarbon type in the diesel blend. Figure 2 shows the relationship between molecular types and cetane number.

Straight chain paraffin molecules have the highest cetane numbers, while multiple ring aromatics have the lowest. Cetane number improvement also occurs during the hydrotreating of the gas oil fractions used as blend components in the diesel product. During hydrotreating to remove the organic sulfur and nitrogen species found in these untreated gas oil fractions, the molecules containing these items are opened and saturated to form paraffins and naphthenes. At the same time, some of the aromatic molecules contained in the gas oils are also opened and saturated increasing the paraffin/naphthene content of the hydrotreated product. As a result of this ring opening and saturation, a cetane number improvement of between 3 and 5 numbers can be expected. Hydrocracking of heavy gas oil fractions and hydrotreating of thermal cracked gas oils and FCC gas oils significantly increase product cetane numbers from those processes.

Meeting sulfur content. Sulfur content of 0.05 % wt or less is now on its way out as a common requirement for diesel fuel around the world. The current common standard is between 10 and 20 wppm in many areas. In most cases, this level of sulfur can only be met by extensive hydrotreating or hydrocracking to remove the sulfur from the middle distillates that will be used to blend the diesel product. Some refineries select their crude slate with low-sulfur crudes to reduce the hydrotreating demand. The impact on refiners to meet this parameter extends beyond the severity of hydrotreating that may exist. It impacts the availability of hydrogen in the front end and the capacity for handling the sour gases (H_2S in particular) in the back end of the process. It is likely that the legislative sulfur content in diesel may be reduced still further. Ultralow sulfur diesel (ULSD) is now the norm in many areas of the world. This makes the selection between crude slate demand for low-sulfur crude and a modified refinery configuration and operation a critical one.

Reducing aromatic content. With the increasing demand for diesel fuel, particularly in North America and Europe, refiners will need to use streams normally routed to heating oils as components for the diesel product blend. These streams are of lower quality and, in particular, contain higher quantity of aromatics than will be acceptable as diesel blend stocks without severe treating to improve their blending characteristics. High-severity hydrotreating to remove sulfur and nitrogen helps in reducing aromatics in acceptable diesel blend stocks, it will not be sufficient to improve the quality of the heating oil and fuel oil blend stocks to meet the diesel pool requirement. Hydrotreating using nickel molybdenum catalyst (dearomatization process) is used for the purpose of upgrading these poorer blend stocks. This dearomatization process usually consists of two stages. The first is processing over a conventional Co–Mo hydrotreating catalyst to remove sulfur and then to process over the Ni–Mo catalyst. The nickel catalyst is poisoned by sulfur, thus the two stages. The economics of using the dearomatization process must be carefully evaluated because the metal content of the nickel catalyst represents a significant investment. The process however operates at a higher space velocity and lower pressure than the conventional Co–Mo hydrotreating process.

Improvement of cold flow properties. Problems with meeting the cold flow properties of diesel fuel are associated with the presence of straight chain paraffins. Although these have higher cetane numbers, they pose cold flow limitations because they tend to precipitate as a wax at low temperatures. The simplest and probably the best solution to this cold flow property of these paraffins is the use of additives. These additives are however costly, ranging from below $50 per thousand bbls for pour point reduction to as high as $250 per thousand bbls for cloud point reduction (these are year 2000 dollars). Another alternative is to reduce the diesel FBP and add kerosene. This action removes the heavier paraffinic molecules, which tend to precipitate at higher temperature. Reducing the cut point from 700 °F to 640 °F reduces the yield of diesel by, perhaps, 6 % vol on crude. Solvent dewaxing is another option. In this process, the wax-forming components are selectively removed from the diesel product. This is only considered however for stocks from high paraffin crudes. Selective hydrocracking of the straight chain paraffins to smaller paraffin molecules is an option. This, however, is accompanied by a reduction in yield and cetane number. Finally isomerization of the straight chain paraffins to branched paraffins minimizes cetane and yield loss as a viable option. However, these isomerization catalysts contain noble metals and are therefore quite expensive and require the two-stage process, desulfurization followed by the isomerization stage.

A Refinery Process Configuration Development

There are many steps necessary to meet a refining company's marketing strategy and production objectives. These steps may culminate in building new processing facilities or revamping existing ones. The course of action that will ultimately be adopted will, almost invariably, be decided on an economic basis reflecting the company's future profitability picture. Among the most important of these steps however will be the development of several refining scenarios and processing configurations.

A process configuration and its accompanying block flow diagram is a blue print and a basis for economic study and decision making. The final and accepted configuration will also be the foundation for the design of new facilities or the revamping of existing ones. The block flow diagram shows the calculated results of process plant design capacity, the quantity of process streams to and from each process plant, the sequence of the plants relative to one another in the refining scheme, and, finally, the blending recipes (streams and their quantities that make up the finished product blends). Such a development requires the in-depth knowledge of the refining industry and relies, in no small measure, on the expertise of those companies that license processes and their technology.

Refinery Configurations and Categories

It is useful to classify refineries by their processing capability for economic analyses. Four general categories or configurations of refineries are normally recognized:

- Topping
- Hydroskimming
- Cracking
- Full conversion/complex

These definitions describe facilities that are progressively more complex, more capable, and able to use increasingly worse crudes to make products efficiently.

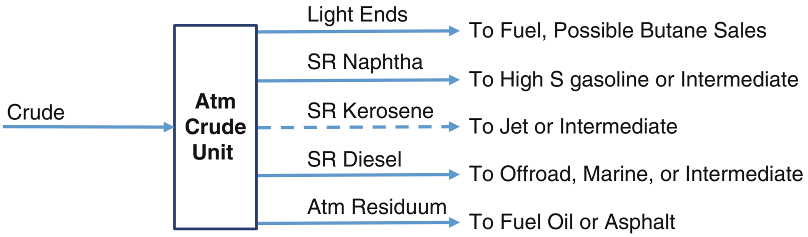


Fig. 3 Simple topping refinery flowsheet

While these categories apply to refineries in general, a given refinery may have aspects of more than one configuration as a result of history or market decisions. Hence, the categories are not hard and fast.

The following discussion will describe each type of refinery and the implications of the refinery configuration. More detailed discussion of economics can be found in the chapter "▶ Petroleum Refinery Planning and Economics."

Topping Refinery

A topping refinery is the simplest configuration. The refinery processing scheme primarily consists of a crude unit making light ends (C_1–C_4), naphtha, kerosene, and some diesel. The atmospheric residue from the crude unit is normally sold as fuel oil or an intermediate. The flowsheet for such a refinery is shown in Fig. 3.

Products from a topping refinery do not undergo much additional treatment. Specifically, they do not undergo chemical processing to change their boiling range (cracking, coking) or to improve the products' characteristics (like reforming or hydrotreating).

As a result of the limited process capabilities of this refinery, these facilities are usually found in locations where environmental regulations are lax, where there is a use for the intermediates, or at oil field processing facilities to stabilize the crude.

One example of this type of facility has been in the Alaskan pipeline where topping units are installed at pump stations to extract enough fuel from the crude to power the pumping station. Some small refiners also top crude to recover the heavy oil for asphalt production – this is where the definitions blur some.

Crude fed to a topping refinery is generally light, sweet material to get the most value from the equipment. This limits crude options and flexibility.

The advantages of topping refineries lie in their simplicity and low cost. It is relatively easy to operate a crude column. Compared to more complex refineries, these are cheap to build, with flexibility in size.

The key disadvantages of topping are in the limited crude slate, products that will not meet most environmental specifications and must be sold as intermediates,

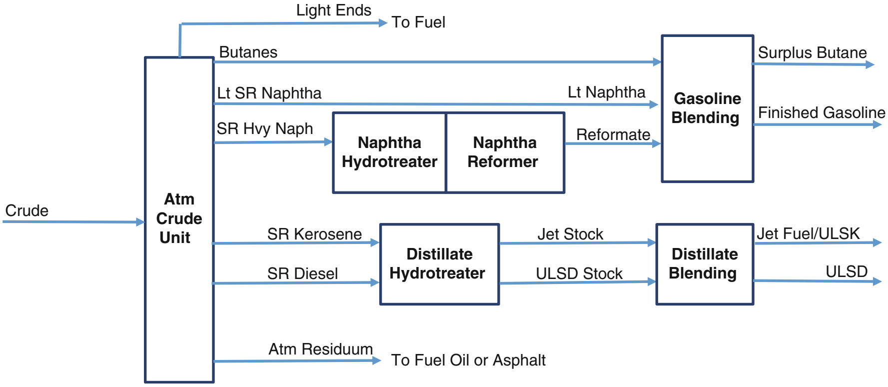


Fig. 4 Simple hydroskimming refinery flow sheet

and production of a lot of low value product (like fuel oil). This type of refinery is usually not economically viable in low margin periods.

Hydroskimming Refinery

The next most complex and capable refinery is the hydroskimming facility, illustrated in Fig. 4. In this configuration, the diesel and lighter products from the crude unit are processed to meet final product specifications. There is still no cracking involved.

Products from a hydroskimming refinery could include light ends (C_1–C_4), finished gasoline, finished jet fuel, and ultralow sulfur diesel. The light ends may also be upgraded to improve their value (e.g., isomerizing butanes).

This configuration gains some crude flexibility, but still wants a light crude. The crude does not have to be sweet. It is still fairly inexpensive to build and easy to operate. Hydrogen produced by naphtha reforming opens several doors to upgrading.

The key disadvantages of hydroskimming are that you still are producing a lot of fuel oil and you are limited to relatively light crudes.

Cracking Refinery

A cracking refinery begins to chew into the atmospheric resid to convert it to more valuable products. Figure 5 shows two block flow configurations for cracking refineries. Compared to hydroskimming, a cracking refinery adds a vacuum tower and (a) a fluid catalytic cracking (FCC) unit plus an alkylation unit or (b) a hydrocracker to convert the vacuum gas oil. Some refineries may have both. Additional feed or product treating is needed to meet the most stringent specifications, such as US Tier III gasoline. The vacuum resid is still sold as fuel oil (usually high sulfur) or made into asphalt. On-purpose hydrogen production may be needed.

A cracking refinery with a high gasoline market will favor an FCC route. Some resid conversion may also be accomplished by feeding resid to the FCC, with

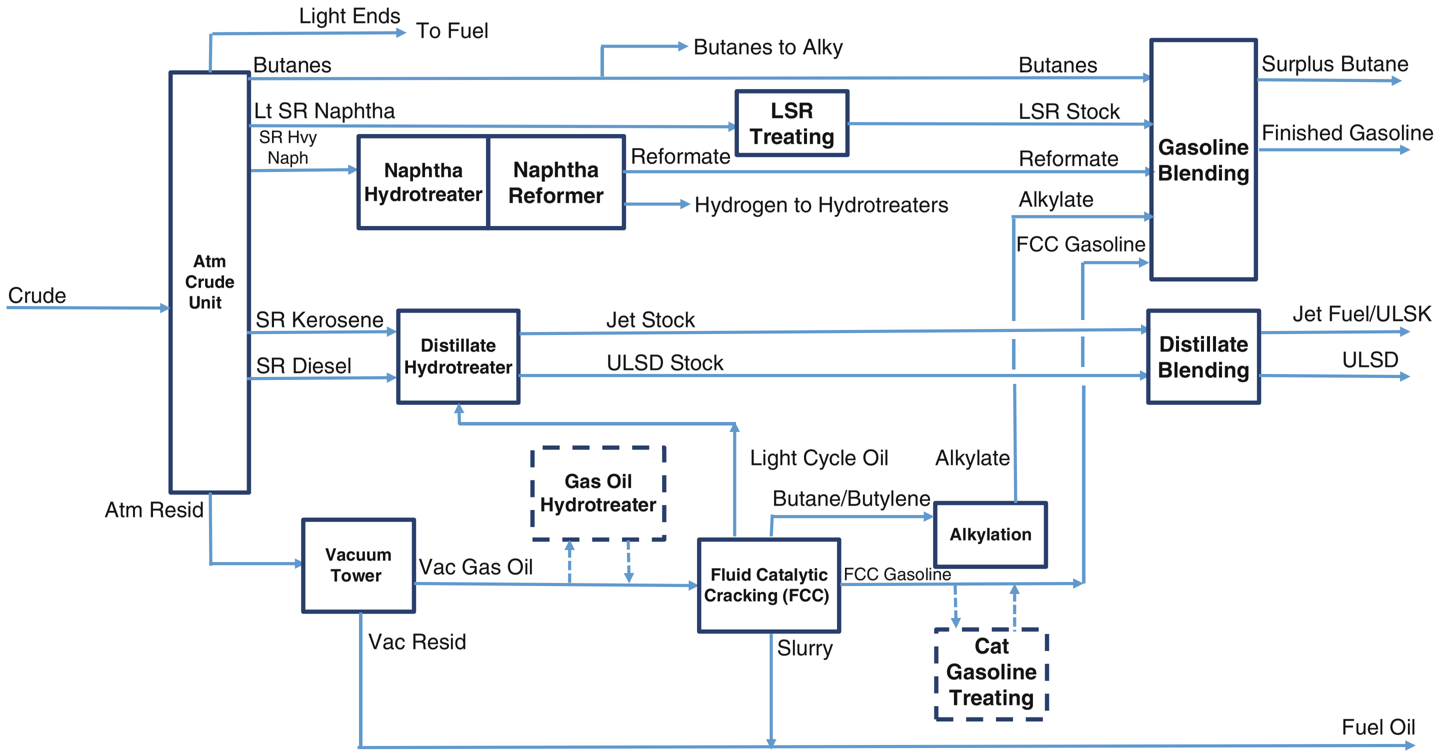


Fig. 5 (continued)

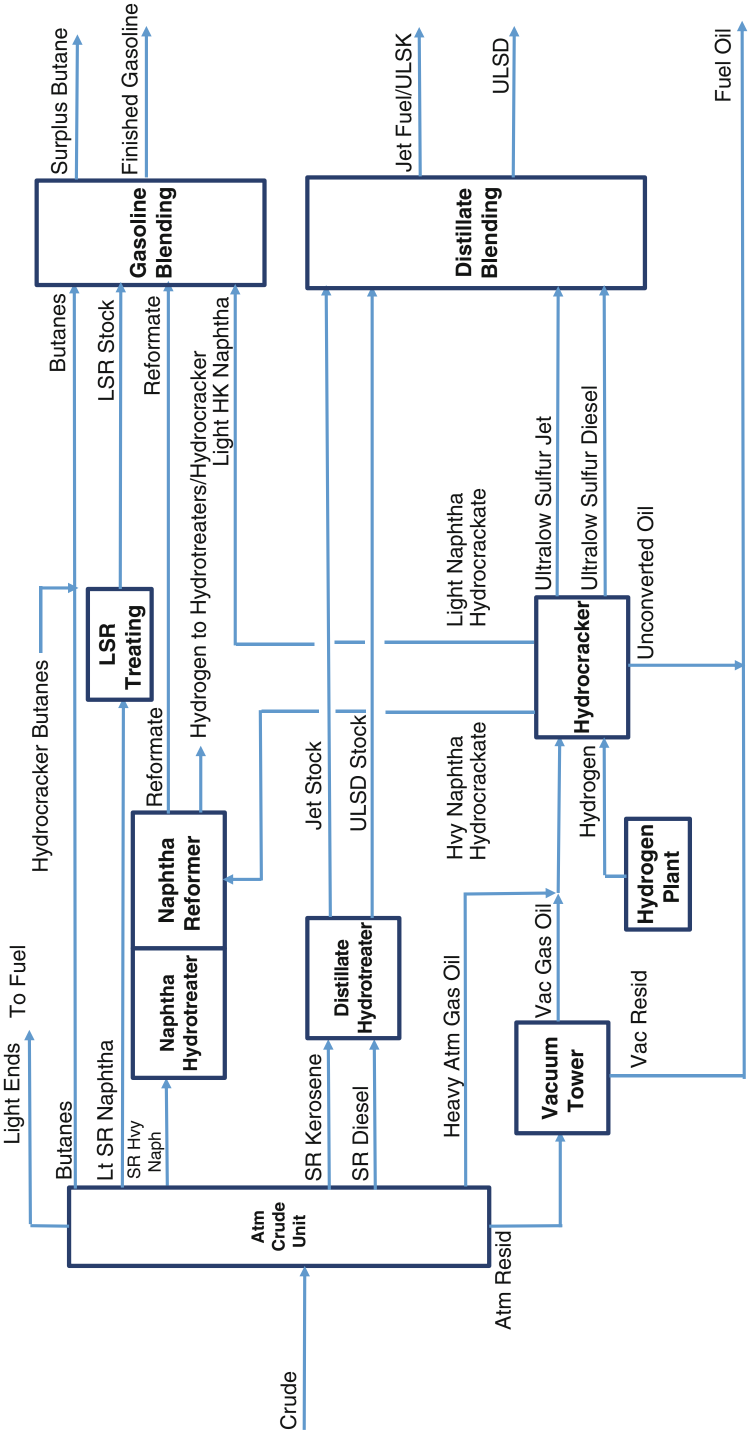


Fig. 5 Two possible configurations for a cracking refinery

associated operating penalties. In a diesel market, the cracking refinery would favor hydrocracking over FCC.

The advantages of a cracking refinery are greatly increased crude flexibility and the production of more high-value products per barrel of crude. This type of facility can weather more variation in margins than either topping or hydroskimming.

To obtain the advantages, this type of refinery takes on greater operating complexity, as well as higher capital and operating costs.

Full Conversion/Complex Refinery

The final category for refinery configurations is the full-conversion/complex refinery. You will also hear these facilities referred to as "coking" or "high-conversion" refineries. The key feature distinguishing these facilities is the conversion of the remaining vacuum resid to high-value products. These plants may incorporate chemical production into the refinery, as well as fuels.

Two possible flowsheets for a full-conversion refinery are shown in Fig. 6. The refinery pretty much looks like a cracking refinery up to a point. The key changes from the cracking refinery flowsheet are the addition of coking, heavy oil cracking (like a resid FCC), deasphalting, and/or resid hydrocracking (like LC-fining or H-oil). The top configuration would focus on a gasoline-driven market, whereas the bottom sheet would apply more to a diesel-driven market.

A full-conversion refinery has the greatest flexibility possible in crude slate and seeks to make the maximum amount of high-value products from the crude charge with a minimum of by-product. The products can meet more severe specifications. Some facilities incorporate power cogeneration for additional value. Because of their flexibility, these facilities can operate profitably through low margin periods.

On the downside, these facilities cost significantly more than the other types of refineries and add operating complexity. A problem in a downstream unit (which is more likely because there are more downstream units) can back up to the crude unit and greatly impair economics. There are still some by-products that are of low value, such as petroleum coke, that must be managed.

Geographic Trends in Refinery Configurations

The refinery configuration chosen for a given facility depends on the crudes and markets available for that facility. For example, in a region where crude, operating, environmental, and transportation costs are high, it will make sense to build a facility that maximizes the amount of product made from every barrel and minimizes the by-products and other wastes. A region where the corresponding costs are lower allows some flexibility in product slate and reduced complexity.

As a region develops, the dominant refinery configurations move from topping toward full conversion. North America, with a fairly mature industry, is dominated by full-conversion facilities. The Middle East has less local market, so focus is on refining for export. This leads the Middle East refineries to be dominated by cracking, with less need for vacuum resid conversion. Where does the resid go now? Some is actually cracked along with VGO. A lot ends up in fuel oils. The international movement toward lower sulfur fuel oils for ships will eventually push

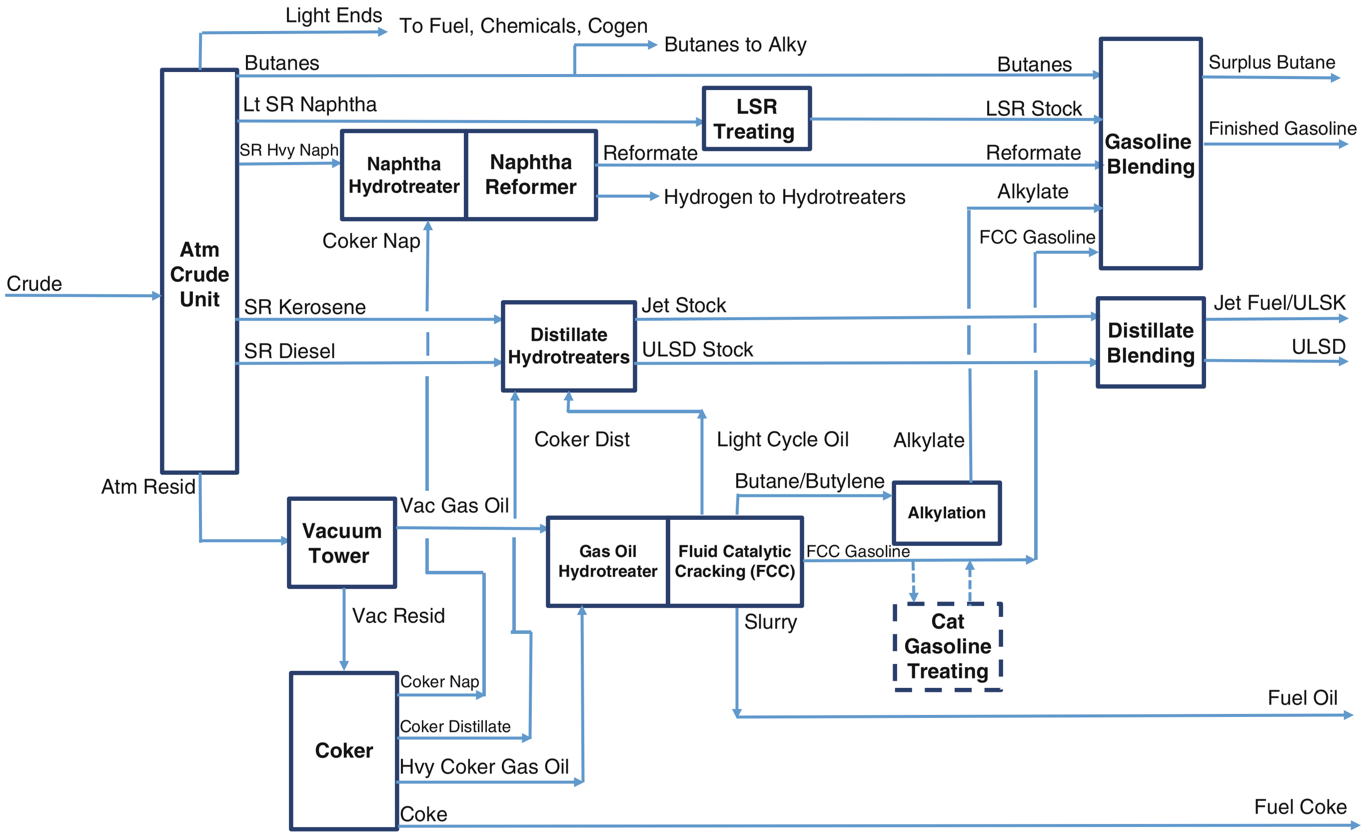


Fig. 6 (continued)

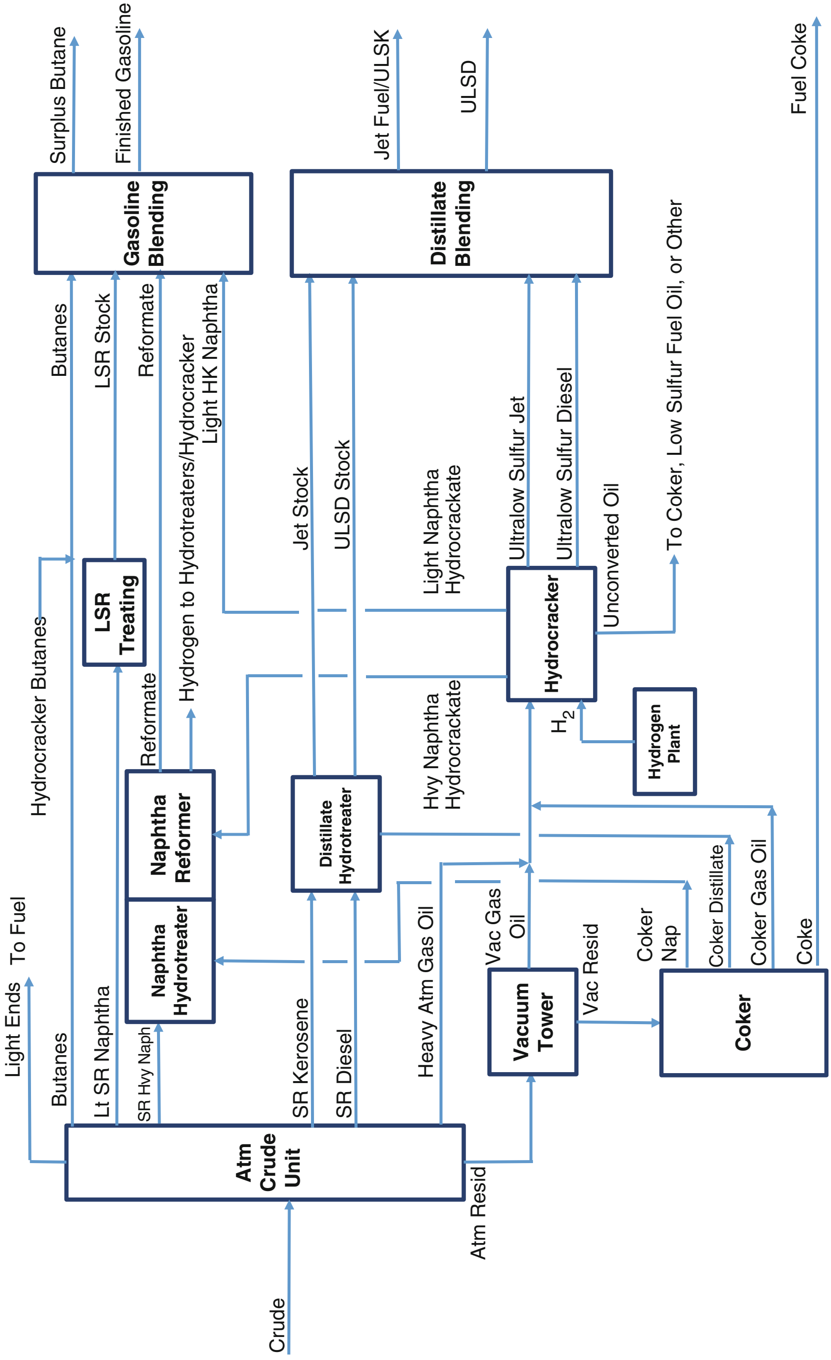


Fig. 6 Two possible complex refinery configurations

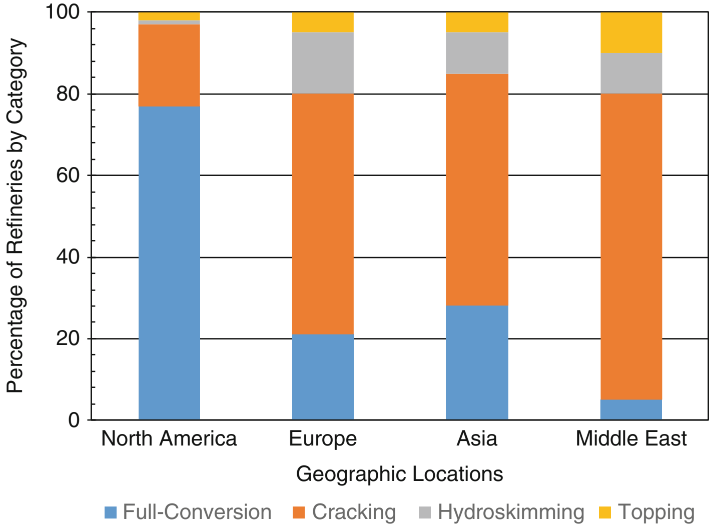


Fig. 7 Geographic trends in refinery configuration

refineries toward full conversion Fig. 7 illustrates how the general types of refineries are distributed among different geographic areas of the world.

Side-by-Side Comparison of Refinery Configurations

If you can sell whatever products you make from a simple facility, why would you ever go to a more costly and complex refinery? The key drivers for increasing conversion are economic:

- More product can be made for each barrel of crude. There is less by-product.
- Higher conversion means more "clean product." The products can meet more stringent standards.
- Cleaner products are more valuable. The by-products are normally less valuable, so less by-product means less drag on the economics.
- Higher complexity and deeper conversion capability provide more crude flexibility. You can pick worse crudes that are available at a discount from better crudes.
- You can integrate production of chemicals and other very high-value products into a more complex refinery.

The drivers all translate into larger *potential* margins for more complex refineries. Offsetting this potential, however, are increased operating costs. The more you work on refining an oil, the more it is going to cost to process.

Table 13 illustrates how the economics of the four types of refineries we've been describing mesh together, just focusing on making clean fuels. The crude and

Table 13 Comparison of potential margins by refinery category. Multiple data sources. See references

Refinery category	Topping		Hydroskimming		Cracking		Full conversion	
	vol% crude	$/bbl crude	vol% crude	$/bbl crude	vol% crude	$/bbl crude	vol% crude	$/bbl crude
Same crude basis								
Refinery input								
Type of crude	West Texas intermed		West Texas intermed		West Texas intermed		West Texas intermed	
Crude	100	97.65	100	97.65	100	97.65	100	97.65
Refinery products								
Clean products								
Gasoline	0	0.00	26	31.05	48	57.81	54	64.86
Jet fuel	0	0.00	15	18.65	17	20.51	17	20.51
Diesel	0	0.00	20	27.09	22	29.66	22	29.66
Other products								
Naphtha	26	27.82	0	0.00	0	0.00	0	0.00
Distillate	39	44.07	0	0.00	0	0.00	0	0.00
Fuel oil	34	30.60	37	33.30	10	9.00	1	0.90
Other (FOE)	1	0.25	2	0.50	3	0.80	6	1.58
All products	100	102.74	100	110.59	100	117.78	100	117.51
Potential margin		5.09		12.94		20.13		19.86
(Ignores Op cost and transportation)								
Better-fit crude basis								
Refinery input								
Type of crude	Generic light sweet		West Texas intermed		West Texas intermed		Generic heavy sour	
Crude	100	99.30	100	97.65	100	97.65	100	76.00
Refinery products								
Clean products								
Gasoline	0	0.00	26	31.05	48	57.81	59	70.23
Jet fuel	0	0.00	15	18.65	17	20.51	10	11.93
Diesel	0	0.00	20	27.09	22	29.66	26	35.08
Other products								
Naphtha	30	31.57	0	0.00	0	0.00	0	0.00
Distillate	46	52.21	0	0.00	0	0.00	0	0.00
Fuel oil	24	21.87	37	33.30	10	9.00	1	0.90
Other (FOE)	0	0.00	2	0.50	3	0.80	5	1.18
All products	100	105.64	100	110.59	100	117.78	100	119.32
Potential margin		6.34		12.94		20.13		43.32
(Ignores Op cost and transportation)								

product pricing basis is December 2013. FOB points vary, affecting transportation costs. The economics are based on US pricing.

In the upper set of numbers, we look at how the yields and product values change with increasing refinery conversion using a single marker crude: West Texas Intermediate (WTI). You can see that the potential margin increases significantly with increasing conversion. These margins do not include operating costs or transportation, which reduce the actual realized margin for each type; but the trend toward more profitability for a more complex facility still remains, even after factoring in the costs.

The lower set of numbers in the table illustrates how improving crude selection for each type of refinery can help optimize the margin. For a topping facility, selection of a sweeter, lighter crude means more product with lower sulfur per barrel of crude. Value of the products is a little better. You pay for this with a higher crude cost. WTI is a pretty good fit for the hydroskimming and cracking refineries. For the full-conversion refinery, however, we would pick a heavy, sour crude, like Western Canadian Select, which has a large price discount. Compared to running WTI, the potential margin is more than twice as large by picking a crude to fit the facility capabilities. Of course, expect higher processing costs.

Key Points in Refinery Configuration

Refineries are generally classified into four categories based on their conversion capability: topping (no conversion), hydroskimming (product treatment), cracking (heavier oil conversion), and full conversion (maximum conversion).

As the conversion capability is increased from none to full conversion, the potential product value from a refinery increases and the crude flexibility expands. The net result is that the potential margin increases with conversion capability. The selection of configuration for a specific refinery has to consider the available market and crudes. There is an economic optimization among the factors to select a refinery configuration that has the best margin potential with appropriate crude flexibility. This evaluation must be made for each facility. Expect the economics to change as a region develops and global economic forces change.

Refinery Configuration References

1. Article: The sweet and sour economics of refining, (2013), http://www.investingdaily.com/16229/the-sweet-and-sour-economics-of-refining/, accessed February 2014.
2. Hauge, K. (Statoil, 2010), Article: Refining ABC, http://www.statoil.com/en/investorcentre/presentations/, accessed February 2014.
3. MathPro (2011), Article: An introduction to petroleum refining and the production of ultralow sulfur gasoline and diesel fuel, International Council on Clean Transportation, October 2011, accessed 2014.

4. Canadian Crude Quality Monitoring Program, www.crudemonitor.ca.
5. Crude prices and trends
    (a) Index Mundi, http://www.indexmundi.com/commodities/, accessed 2014.
    (b) CME Group, Chicago, http://www.cmegroup.com/trading/energy/crude-oil/, accessed 2014.

An Example of Refinery Configuration Development

The configuration example described here would be one of many that would be examined meeting the production and economic objectives of a particular refinery operation. In this example, a refining company wishes to examine a new "grass-roots" configuration that will produce the following products from a medium Middle East crude, whose assay TBP curve is given as Fig. 1.

The product specifications are given in the respective text, and the production limits are as follows:

Crude feed	50,000 BPCD
LPG	3,289 BPCD (max)
Gasoline	22,170 BPCD (max)
	20,390 BPCD (min)
Kerosene	No target
Auto diesel	8,830 BPCD (max)
	3,000 BPCD (min)
Gas oil	8,553 BPCD (max)
	2,630 BPCD (min)
Marine diesel	3,000 BPCD (max)
	2,300 BPCD (min)
Heavy fuel	8,500 BPCD (max)
	6,500 BPCD (min)
Bunker fuel	No restrictions

A Solution

For this configuration, the following processes will be examined:

- Atmospheric crude distillation unit (CDU)
- Vacuum distillation unit (VDU)
- Light ends distillation units
- Naphtha hydrotreater (Nap HDS)
- Catalytic reformer
- Light gas oil hydrotreater (LGO HDS)
- Heavy gas oil hydrotreater (HGO HDS)

- Fluid catalytic cracker (FCCU)
- Isomerization/alkylation plant
- Thermal cracker (TC)
- Gas treating and sulfur recovery processes

The stream quantities to each of these units will be developed as follows:

The atmospheric crude distillation unit. The crude is split to satisfy the quantities and distillation characteristics of the finished products required. For this example, these are as follows:

Gas to C_5	1.71 % vol on crude	
C_5 to 210 °F	10.44 % vol on crude	Light naphtha (LSR)
210–380 °F	14.20 % vol on crude	Heavy naphtha (HSR)
380–520 °F	9.09 % vol on crude	Kerosene
520–650 °F	13.83 % vol on crude	Diesel
650 °F+	50.73 % vol on crude	Residue (to vacuum unit)

Then from the cut points corresponding to the stream's volume % on crude, the Table 14 ASTM and TBP distillation of the streams leaving the unit are calculated. The ASTM curves (starting at the C_5 + level) are developed using the 50 % point of each cut and the 70 % point converted to ASTM (using the Edmister correlation) and a straight line drawn through them to give the ASTM distillation. These are then converted to TBP (again, using the Edmister correlation) and are shown in Table 14.

These curves are given in Fig. 8.

From these curves, Table 15 gives a component breakdown of the distillate streams.

The properties of these distillate cuts are determined using the component mid vol% on crude multiplied by its volume on the respective cut or by use of indices as previously described.

Table 16 gives the component properties from the assay data.

Using the methods described earlier in this chapter, the products from the atmospheric crude distillation unit (CDU), including their salient properties, are shown in Table 17.

The vacuum distillation unit, *VDU*. The feed to the vacuum distillation unit will be the atmospheric residue from the CDU. This stream will be treated in the same manner as the distillate streams shown above for the CDU. Thus, the distillate streams and the vacuum residue stream including their salient properties are shown in Table 18.

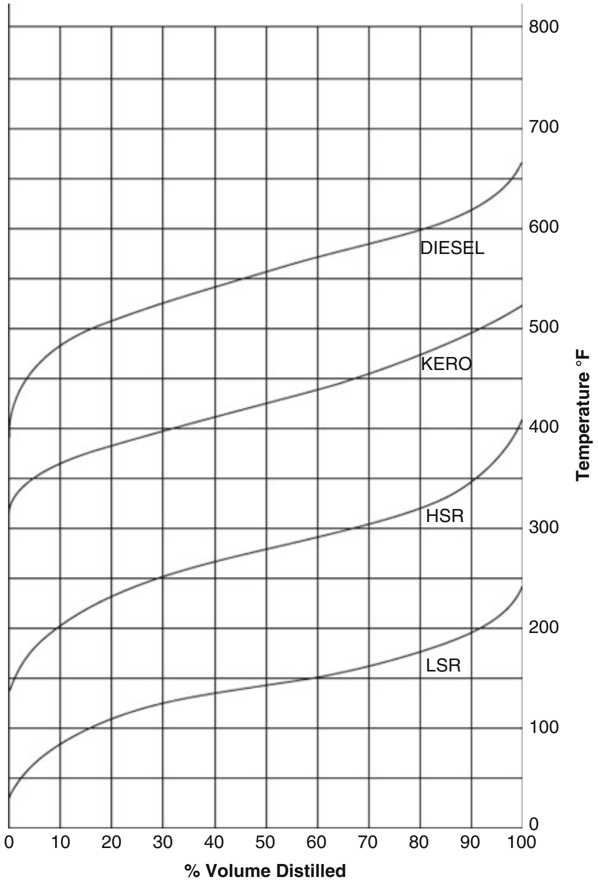
The product streams from this unit are:

LVGO (light vacuum gas oil) – 650–750 °F (49.27–60.12 % vol on crude)
HVGO (heavy vacuum gas oil) – 750–930 °F (60.12–78.67 % vol on crude)
Vacuum residue – +930 °F (21.33 % vol on crude)

Table 14 ASTM and TBP of the crude distillate cuts

	C_5 to 210 °F		210–380 °F		380–520 °F		520–650 °F	
	ASTM°F	TBP°F	ASTM°F	TBP°F	ASTM°F	TBP°F	ASTM°F	TBP°F
IBP	90	30	198	132	363	310	451	392
10 % vol	115	78	235	196	387	357	507	480
30	135	116	260	242	407	395	533	527
50	148	140	280	276	424	425	551	558
70	162	163	301	308	440	451	567	583
90	182	191	332	349	462	481	593	618
FBP	225	238	390	412	493	515	622	650

Fig. 8 Distillate products TBP curves



These streams totally, or in part, will be routed as follows:

- LVGO via the gas oil hydrotreater to gas oil blending pool
- HVGO via the gas oil hydrotreater to FCCU
- Gas oil hydrotreater will be on block flow operation

Examination of the remaining units in this configuration now follows:

The thermal cracker. The yields and properties in Table 19 have been developed from empirical correlations. These are presented and discussed in the chapter on "▶ Upgrading the Bottom of the Barrel." Such correlations are acceptable for use in configuration development, particularly those that will be used in study work. For any definitive design work, however, it is essential that the data used be obtained from pilot plant runs using samples of the actual residue as feed.

Table 15 Component split of the distillate cuts

Component	Range °F	LSR % vol	HSR % vol	Kero % vol	Diesel % vol
1	C_5	21.6			
2	C_5–125	15.4			
3	150	23.0	1.0		
4	175	20.0	4.0		
5	200	13.0	6.0		
6	230	7.0	14.0		
7	250		9.0		
8	275		16.0		
9	300		15.0		
10	325		15.0	2.0	
11	350		11.0	6.0	
12	412		9.0	29.0	1.0
13	450			30.0	4.0
14	480			23.0	5.0
15	515			10.0	14.0
16	550				19.0
17	575				20.0
18	600				19.0
19	650				18.0
Total		100.0	100.0	100.0	100.0

The property curves are developed from pilot plant runs on a similar feed stock. These are based on total product % volume. Refer to Tables 20 and 21; Figs. 9, 10, and 11.

The gas to 380 °F stream will be routed as the overhead distillate from the thermal cracker syncrude fractionator to the naphtha hydrotreater and the saturated light ends unit.

The gas oil stream will be routed to the straight run diesel hydrotreater.

The cracked residue will be routed directly to the fuel oil pool.

The HyGO hydrotreater on cat cracker (FCCU) feed operation. The feed to the heavy gas oil hydrotreater will be the HVGO stream from the vacuum distillation unit (VDU) to meet the feed requirements of a FCCU. This hydrotreater will operate on a blocked operation with the LVGO. That is, it will operate so many days processing HVGO and the remainder of the “stream” year processing LVGO.

Details of the HVGO operation are in Figs. 9, 10, and 11, with the following specifics:

Feed to the hydrotreater = 9,275 BPCD
SG at 60 = 0.9218
Pounds/gal = 7.678
Pounds/CD = 2,990,965
% wt sulfur = 3.10

Table 16 Component properties

Component	Mid vol on crude	°API	SG at 60 °F	Sulfur % wt	Viscosity at 100 °F cSt	Viscosity at 210 °F cSt	Pour point °F
1	1.31	12	0.5811	0.04			
2	3.56	105	0.5983	0.05			
3	5.96	87.5	0.6461	0.05			
4	8.92	71.0	0.6988	0.06	0.27		
5	11.49	65.0	0.7201	0.06	0.33		
6	14.28	60.5	0.7370	0.07	0.45		
7	16.34	57.3	0.7495	0.07	0.48		
8	18.12	55.5	0.7567	0.08	0.52		
9	20.32	53.0	0.7669	0.09	0.70		
10	22.54	51.5	0.7732	0.10	0.78		
11	24.75	49.0	0.7839	0.12	0.90	0.60	−88.0
12	27.19	46.5	0.7949	0.14	1.25	0.68	−76.0
13	30.22	44.5	0.8040	0.20	1.82	0.78	−60.0
14	33.25	41.5	0.8178	0.26	1.95	0.90	−48.5
15	36.06	40.0	0.8251	0.40	2.23	1.13	−34.0
16	38.8	38.5	0.8324	0.62	2.85	1.25	−22.0
17	41.56	37.0	0.8398	0.89	4.00	1.52	−0.08
18	44.26	35.5	0.8473	1.16	5.20	1.70	2.0
19	46.85	34.5	0.8524	1.48	6.25	1.85	16.0

Table 17 CDU product streams

Product stream	BPCD	SG at 60 °F	MM lbs/CD	Sulfur % wt	Visc at 100 °F cSt	Visc at 210 °F cSt	Pour point °F
Gas + LSR	6,075	0.6512	1.383	0.053			<−100
HSR	7,100	0.7550	1.863	0.091	0.58	0.43	<−100
Kero	4,545	0.8048	1.279	0.21	1.60	0.80	−58
Diesel	6,915	0.8420	2.036	0.869	4.0	1.5	0
Atmos residue	25,365	0.9485	8.405	3.92	>100	9.8	>100
Total	50,000	0.8565	14.966	2.35	8.00	2.20	−5.0

Table 18 The VDU product streams

Product stream	BPCD	SG at 60 °F	MM lbs/CD	Sulfur % wt	Visc at 100 °F cSt	Visc at 210 °F cSt	Pour point °F
LVGO	5,425	0.8789	1.667	2.18	13.0	3.0	15
HVGO	9,275	0.9218	2.990	3.10	49.0	6.4	52
Vac res	10,665	1.007	3.748	5.35	>100.0	28.5	>100
Total	25,365	0.9485	8.405	3.92	>100.0	9.8	>100

Table 19 Yield of thermal cracker product streams

Streams	% vol on feed	% vol on total products	Mid vol% on total product
H_2S	0.18	0.17	–
Gas to C_6	7.81	7.40	3.87
Naphtha C_6 –380 °F	9.51	9.02	12.08
Gas oil 380–650 °F	13.91	13.19	23.12
Cracked resid +650 °F	74.08	70.22	71.49
Total	105.49	100.00	–

Table 20 Cracked product properties

Stream	BPCD	SG	Sulfur % wt	Vis at 100 °F	Vis at 210 °F
Gas to C_5	852	0.465	3.47[a]	–	–
Naphtha	1,014.2	0.724	1.58		
Gas oil	1,483.5	0.825	2.55	5.4	0.2
Residue +650 °F	7,900.6	1.046	6.19	110	12.5
Total	11,250.3	0.944	5.35		

[a] Includes 3,362 lbs/CD sulfur as H_2S

Table 21 Sulfur balance over the thermal cracker

Streams	BPCD	lbs/gal	MM lbs/CD	% Sulfur	lbs sulfur/CD
Feed in	10,665	8.38	3.756	5.35	200,964
Streams out					
Gas to C_5	852	4.21	0.151	3.47	5,243.7
Naphtha	1,014.2	6.03	0.257	1.58	4,058.3
Gas oil	1,483.5	6.87	0.428	2.55	10,914.0
Cracked res	7,900.6	8.80	2.920	6.19	180,748.0
Total	11,250.3	7.94	3.756	5.35	200,964.0

$$\begin{aligned}\text{Total sulfur in feed} &= 9{,}275 \times 42 \times 7.678 \times 0.031\\ &= 92{,}720 \text{ lbs per calendar day.}\end{aligned}$$

85 % wt of the sulfur is to be removed. This amounts to 78,812 pounds of sulfur or 2,462.9 mol/CD.

Hydrogen required for sulfur removal in the gas oil is estimated as follows:

$$\begin{aligned}\text{Hydrogen contained in } H_2S \text{ only} &= 92{,}720 \times 0.85/32 = 2{,}462.9 \text{ mols/CD.}\\ &= 2{,}462.9 \times 379\\ &= 933{,}439 \text{ Scf (standard cuft at 60 °F and 14.7 psia).}\end{aligned}$$

Hydrogen is also required for nitrogen removal and to close ruptured hydrocarbon rings due to the sulfur removal. This reaction also produces light ends at the

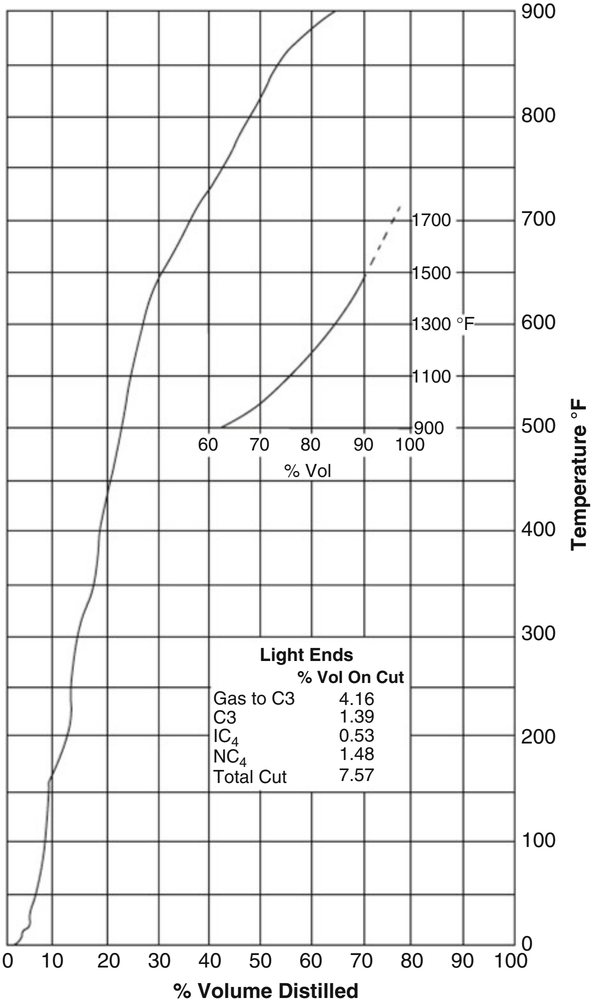


Fig. 9 Thermal cracker effluent TBP curve

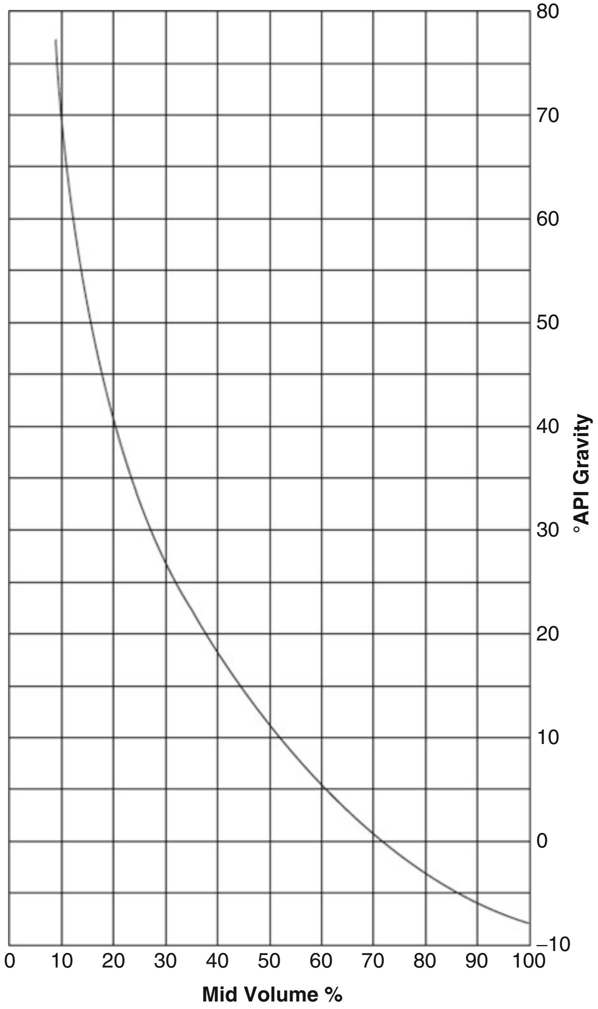
expense of the treated gas oil yield. These reactions double the hydrogen used in this case. Hence:

Total chemical hydrogen required = 1,866,878 Scf/CD (this is from the licensor's data).

There will also be a loss of hydrogen from the system (mostly due to the flash drum operation and purge (see the chapter entitled "▶ Hydrotreating in Petroleum Processing" for more details)). This "purge and dissolved hydrogen loss" amounts to 186,689 Scf (again from Licensor data).

$$\begin{aligned}\text{Total hydrogen makeup required then} &= 1{,}866{,}878 + 186{,}689 \\ &= 2{,}053{,}567 \ \text{Scf/CD}.\end{aligned}$$

Fig. 10 Thermal cracker effluent gravity curve



Assume the hydrogen makeup stream (usually from the naphtha reformer) is 92 % mole pure.

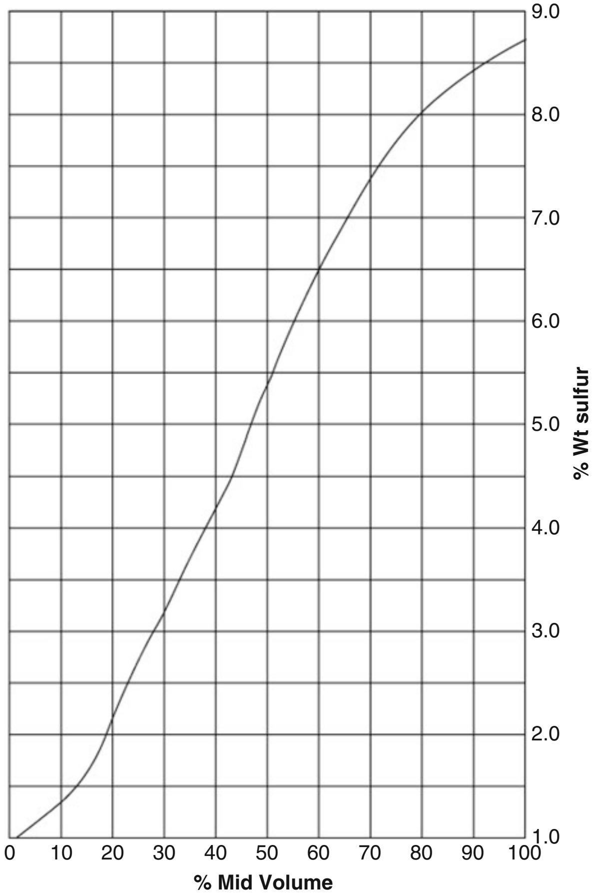
The makeup gas stream required $= \frac{2{,}053{,}567}{0.92} = 2{,}232{,}000\ \text{Scf/CD}$ or, as usually expressed, about 240 scf per bbl of feed.

The material balance over the unit is shown in Tables 22, and 23.

Heavy gas oil hydrotreater on LVGO operation. Feed to hydrotreater is as follows:

LVGO = 5,425 BPCD
SG at 60 °F = 0.8789
Pounds/gal = 7.309

Fig. 11 Thermal cracker effluent sulfur curve



Sulfur % wt = 2.18
lbs feed per CD = 5,425 × 42 × 7.309 = 1,665,356
lbs/CD sulfur in feed = 1,665,356 × 0.0218 = 36,305 lbs
Sulfur removed at 85.0 % = 30,859 lbs/CD
Sulfur in finished product = 5,446 lbs/CD

Hydrogen makeup required to make $H_2S = \frac{30,859}{32} = 964$ moles/CD
Hydrogen makeup required for cracking reactions = 1,079 mol/CD (Licensor)
Hydrogen purge and solution losses = 204 mol/CD (Licensor)

$$\begin{aligned}\text{Total hydrogen makeup} &= 2{,}247\ \text{moles/CD}\\ &= 851{,}613\ \text{Scf/CD}\end{aligned}$$

$$\begin{aligned}\text{Reformer gas as makeup} &= 851{,}613 \div 0.92\\ &= 925{,}666\ \text{Scf/CD}\end{aligned}$$

Table 22 HVGO desulf material balance

Stream	BPCD (Scf/CD)	SG60 °F (MW)	lbs/CD	Routing
In				
Hydrogen MU	(2,232,000)	(11)	64,781	
HVGO	9,275	0.9218	2,990,965	
Total in	9,275 + MU		3,055,746	
Out				
H_2S (+LE)	(933,439)	(34)	23,739	Gas treating
Naphtha	566	0.786	154,518	Nap hydrotreater
Gas oil	8,811	0.898	2,756,987	FCCU
H_2S vent	(162,777)	(28)	120,502	Fuel gas via GT
Total out	9,377 (+ gases)		3,055,746	

Table 23 Desulfurizer sulfur balance

Streams	MM lbs/CD	% wt sulfur	lbs sulfur/CD
Feed in			
HVGO	2.991	3.1	92,720
Mu gas	0.065	Neg	Nil
Total in	3.056		92,720
Products out			
H_2S + light ends	0.024	41.0[a]	9,840
Naphtha	0.155	0.08	125
Gas oil	2.756	0.5	13,908
Vent gas	0.121	57.0[a]	68,847
Total out	3.056		92,720

[a] Sulfur in the form of H_2S from purge and stripper overheads

Material balance for the unit in this service is shown in Table 24.

The FCCU process. From licensor data, the following are the expected yields from the desulfurized feed:

Gas C_2 to C_3	8.1 % vol on feed
C_3	2.3 % vol
C_3=	5.6 % vol
iC_4	2.8 % vol
nC_4	1.4 % vol
C_4=	7.6 % vol
C_5 + naphtha	59.0 % vol
Lt cycle oil	15.5 % vol
Slurry	14.0 % vol
Total	116.3 % vol on feed

In terms of BPCD:

Gas to C_3 = 714
C_3 to C_4s = 1,736

Table 24 LVGO hydrotreater material and sulfur balance

Stream	BPCD (Scf/D)	lbs/Gal (MW)	MM lbs/CD	Sulfur % wt	Sulfur lbs/CD	Routing
Feed in						
LVGO	5,425	7.32	1.665	2.18	36,305	
MU gas	(925,666)	(11)	0.027	Neg	Nil	
Total in	5,425 (+ MU)		1.692		36,305	
Out						
Gas to C_5	(102,375)	(48)	0.013	84.4[a]	10,783	Gas treating
Naphtha	239		0.063	0.08	51	Nap HDS
Gas oil	5,295		1.592	0.34	5,446	Gas oil pool
Vent gas	(394,435)	(23)	0.024	84.1[a]	20,025	Gas treating
Total out	5,534 (+ gases)		1.692		36,305	

[a] Sulfur in the form of H_2S from purge and stripper overheads

Naphtha = 5,198
Lt cycle = 1,366
Slurry = 1,234
Total = 10,248

The overall FCC unit balance is given in Table 25.

Lt gas oil hydrotreater. The LGO hydrotreater will operate on two blocked operations to desulfurize diesel feed and secondly to desulfurize kerosene.

i. *Diesel operation*. The feed in this case will consist of straight run diesel from the CDU and the diesel cut from the thermal cracker. Thus:
   The licensor guarantees 75 % wt sulfur removal. Therefore:

$$\text{Sulfur removed} = 21{,}536 \ \text{lbs/CD}$$

$$\text{Sulfur in product} = 7{,}179 \ \text{lbs/CD}$$

$$\begin{aligned} H_2 \ \text{consumption for sulfur removal} &= 157{,}664 \ \text{Scf/CD for SR diesel} \\ &= 97{,}415 \ \text{Scf/CD for cracked feed} \\ &= 673 \ \text{moles/CD} \end{aligned}$$

$$\begin{aligned} H_2 \ \text{cons. for ring saturation} &= 384{,}474 \ \text{Scf/CD for SR(includes losses)} \\ &= 735{,}322 \ \text{Scf/CD for cracked feed} \\ &= 2{,}954 \ \text{moles/CD} \end{aligned}$$

Table 25 FCCU material and sulfur balance

Stream	BPCD	SG at 60 °F	MM lbs/CD	S % wt	S lbs/CD	Routing
Feed						
Des HVGO	8,811	0.898	2.757	0.50	13,908	FCCU
Products out						
Gas to C_3	714	–	0.13	2.19	2,850	Gas treating
C_3–C_5	1,736	0.560	0.341	–	Neg	Alkylation
C_5 to 300 °F	3,503	0.7856	0.929	–	Neg	Gasoline pool
300–420 °F	1,695	0.8251	0.489	0.05	262	Gasoline pool
Lt cycle oil	1,366	0.9159	0.438	0.54	2,380	Gas oil blending
Slurry	1,234	0.990	0.428	2.0	8,416	Fuel oil
Total out	10,248		2.757	0.5	13,908	

Table 26 Diesel hydrotreater material and sulfur balance

Stream	BPCD (Scf/D)	lbs/gal (MW)	MM lbs/CD	% wt sulfur	lbs/CD sulfur	Routing
In						
Diesel	8,399	7.0	2.470	1.16	28,652	
MU gas	(1,495,000)	(11)	0.043	Neg	Nil	
Total in	8,399 (+ MU)		2.513			
Out						
Gas to C_5	(42,037)	(55)	0.006	69.5	4,168	Gas treating
Naphtha	459	6.55	0.126	0.08	101	Nap HDS
Diesel prod	8,036	6.98	2.356	0.30	7,068	Diesel pool
Vent gas	(255,067)	(37)	0.025	69.4	17,315	Gas treating
Total out	8,495 (+ gases)		2.513		28,652	

$$\text{Total hydrogen makeup} = 1.375 \text{ MM Scf/D for Total Feed}$$

$$\begin{aligned}\text{Reformer gas makeup} &= 1.495 \text{ MM Scf/CD}\\ &= 3,945 \text{ moles/CD}\end{aligned}$$

The diesel operation is summarized in Tables 26 and 28.

ii. *Hydrotreater on Kero operation*
Kero feed ex CDU = 4,545 BPCD
SG at 60 °F of Kero = 0.8048 and then MM lbs/CD = 1.280
Sulfur content = 0.21 % wt so sulfur make = 2,685 lbs/CD

Licensor guarantees middle of run sulfur removal as 99 % wt.

Then lbs/CD sulfur removed = 2,631 lbs/CD. This generates 2,795 lbs/CD of H_2S.

There is no significant amount of naphtha made, nor is there significant amount of hydrogen needed for saturation. The hydrogen makeup required is 82 mol/CD or 82 ÷ 0.92 = 89 mol/CD reformer gas. This amounts to 33,780 Scf/CD.

iii. *Summary of Kero operation*

In		
Kero feed	4,545 BPCD	1.280 mm lbs/CD
Hydrogen	89 moles/CD	979 lbs/CD ref gas
Total		1,280,979 lbs/CD
Out		
Kero product	4,539 BPCD	1,277,342 lbs/CD
Hydrogen sulfide	82 mol/CD	2,788 lbs/CD
Losses from stripper		813
Total		1,280,166 lbs/CD

Naphtha consolidation and treating. Summary of naphtha and light ends streams to treating processes.

From	Stream	BPCD
CDU	Gas to C_5	855
	Lt naphtha to 212 °F	5,219.5
	Hvy naphtha to 380 °F	7,100
Thermal cracker	Gas to C_5	852
	Lt naphtha to 212 °F	436.5
	Hvy naphtha to 380 °F	577.7
The hydrotreaters	Gas to C_5	Mostly H_2S to treating
	Lt naphtha to 212 °F	323.5
	Hvy naphtha to 380 °F	940.5
Unstabilized naphtha feed to naphtha hydrotreater	Gas to C_5	1,707
	Light naphtha	5,981
	Heavy naphtha	8,618
	Total	16,306
Light naphtha to gasoline pool	Total	5,970
Heavy naphtha feed to cat reformer	Total	8,618

The naphtha hydrotreater (HDS) material balance is in Table 33.

Catalytic reformer operation. The reformer will operate at a severity of 91 RON and at a reactor pressure of 350 psig.

Table 27 Material balance over the reformer

Stream	BPCD (MM Scf/CD)	SG at 60 °F (MW)	MM lbs/CD	Routing
In				
Hy nap ex CDU	7,100	0.755	1.863	
Hy nap ex TC	578	0.752	0.152	
Hy nap ex Hds	940	0.793	0.261	
Total in	8,618	0.7543	2.276	
Out				
Reformer gas	(7.33)	(11)	0.224	To naphtha Hds
Light ends	837	0.521	0.152	To sat Lt ends
Reformate	6,852	0.7927	1.900	To gasoline pool
Total out	7,689		2.276	

Table 28 Diesel feedstocks

	BPCD	SG at 60 °F	#/Gal	MM #/CD	S % wt	S/CD
Straight run	6,915	0.842	7.013	2.04	0.87	17,748
Cracked	1,484	0.825	6.87	0.43	2.55	10,967
Total	8,399	0.841	7.00	2.47	1.16	28,715

Licensor data for these conditions are:

Yield of reformate = 79.5 %LV
Reformate make = 6,851.5 BPCD
Hydrogen made = 5.13 MMscf/CD purity is 70 mol%
Then reformer gas is 5.13 ÷ 0.7 = 7.33 MMscf/CD

Mol Wt of reformer gas is 12 as given by the licensor. Then MM lbs/CD of the gas is 0.237.

C_5 = reformate = 6,851 BPCD and at an SG of 6.604 lbs/gal lbs/CD of reformate = 1.9 MM lbs/CD.

Light ends leaving the reformer stripper will be in accordance with the following balance:

lbs per CD of fresh feed = 2.276 MM lbs
lbs per CD of reformate = 1.900 MM lbs
lbs per CD of reformer gas = 0.237 MM lbs
By difference Lt ends = 0.152 MM lbs/CD routed to reformate stabilizer.

The reformer material balance is shown in Table 27.

Table 29 Reformer light ends analysis

	% wt	lbs/CD	BPCD
Gas to C_3	9.8	14,896	122
C_3	33.1	50,312	284
iC_4	22.0	33,440	170
nC_4	35.1	53,352	261
Total	100.0	152,000	837

Table 30 Reformer light ends net yields

	%mol	Moles/CD	lbs/CD	BPCD
Gas to C_3	8.2	453.1	6,797	56
C_3	37.3	2,061.2	90,693	514
iC_4	20.1	1,110.8	64,422	328
nC_4	34.4	1,900.9	110,255	540
Total	100.0	5,526	272,167	1,438

Analysis of the reformer light ends stream is given in Table 29:

The associated naphtha hydrotreater receives the fresh reformer feed and desulfurizes it using the reformer off gas on a once through basis. In this process, the hydrotreater consumes 6 vol% of the hydrogen and absorbs light ends from the reformer gas to upgrade the off gas to 92 mol% hydrogen.

Hydrogen consumed in the hydrotreater = 0.308 MMscfd
Hydrogen leaving in off gas = 5.13 – 0.308 = 4.822 MMscfd
Volume of off gas from the hydrotreater = 4.822 ÷ 0.92 = 5.241 MMscfd

By difference the volume of light ends (LEs) gas absorbed into the hydrotreater stabilizer feed will be 7.33 – 5.241 = 2.089 MMscfd or 5,526 mol/CD. This absorbed gas will be slightly heavier than that for the gas absorbed in the reformate. This will have the molar composition shown in Table 30.

Saturated light ends consolidation. Although the LEs from the thermal cracker contain a significant amount of unsaturated hydrocarbons, it is usually blended with the CDU overhead distillate, hydrotreated, and then split into its components. Thus, the LEs are considered saturated for the study here.

The isomerization and alkylation processes. The fresh feed to the alkylation reactor is the C_3 and C_4 streams from the FCCU. The volumetric and mass composition of this stream is in Table 31.

From licensor data:

$$\text{Alkylate from propylene} = 1.76 \times 493 = 868 \text{ BPCD}$$

$$\text{Alkylate from butylene} = 1.77 \times 670 = 186 \text{ BPCD}$$

The volumetric composition of the alkylate is shown in Table 32.

Table 31 Alkylation unit feed composition

Component	% vol	BPCD	lbs/Gal	lbs/CD
C_3	11.7	203	4.22	35,980
C_3-	28.4	493	4.34	89,864
iC_4	14.2	247	4.68	48,550
nC_4	7.1	123	4.86	25,107
C_4-	38.6	670	5.00	140,700
Total	100.0	1,736	4.67	340,201

Table 32 Alkylate product composition

	From propylene				From butylene			
	% wt	lbs/ Gal	vol factor	% vol	% wt	vol factor	% vol	
C_5	9.0	5.25	1.71	9.9	4.0	0.8	4.75	
C_6	4.0	5.53	0.72	4.16	2.0	0.4	2.37	
C_7	68.0	5.73	11.87	68.55	2.0	0.3	1.78	
C_8	10.0	5.89	1.69	9.76	80.0	13.58	80.65	
C_9+	9.0	6.8	1.32	7.63	12.0	1.76	10.45	
Total	100.0	5.78	17.31	100.0	100.0	16.84	100.0	lbs/Gal = 5.93

$$\text{Total alkylate} = 2{,}054\ \text{BPCD} = 506{,}101\ \text{lbs/CD}$$

$$\begin{aligned}\text{iC}_4\ \text{Consumption} &= 1.34 \times \text{propylene} + 1.15 \times \text{butylene}\\ &= 1.31 \times 493 + 1.15 \times 670 = 1{,}416.3\ \text{BPCD}\\ &= 278{,}000\ \text{lbs/CD}.\end{aligned}$$

iC_4 available in FCCU light ends = 48,550 lbs/CD.

Required from other sources = 229,500 lbs/CD or 1,167 BPCD.

A butane isomerizer is included in the process to provide the necessary isobutane stream. In this process, 50 % wt of the normal butane contained in a saturated butane stream is converted to isobutane.

Thus, from Table 33, total butanes available from saturate LE are made up as follows:

Isobutane	670 BPCD	131,695 lbs/CD	=29.2 % wt
Normal butane	1,559 BPCD	318,223 lbs/CD	=70.8 % wt

50 % of the normal butanes are isomerized giving an isomerate 29.2 + 35.4 lbs isobutane per 100 lbs feed and 35.4 lbs normal butane (Table 34). Feed to the isomerizer will be 229,500 ÷ (0.292 + 0.354) = 355,263 lbs/CD or 528 BPCD iC_4 and 1,232 BPCD of nC_4.

The combined material balance for alkylation and isomerization is in Table 36.

Table 33 Material balance over naphtha HDS

Stream	BPCD (MM Scf/CD)	SG at 60 °F (MW)	MM lbs/CD	Routing
In				
Gas to C_5	1,707	0.320	0.313	
Lt naphtha	5,970	0.661	1.379	
Hy naphtha	8,618	0.756	2.276	
Reformer gas	(7.33)	(11)	0.224	
Total in	16,295		4.192	
Out				
Deb overheads	2,817	0.436	0.398	To sats lt ends
Splitter feed	14,588	0.716	3.655	To nap splitter
Rich H_2 gas	(5.241)	(10)	0.139	To H_2 system
Total out	17,296		4.192	

Table 34 Saturated light ends summary

	BPCD				
Source	Gas to C_3	C_3	iC_4	nC_4	Total
Crude distillation unit	51	103	112	590	856
Thermal cracker	468	156	60	168	852
Cat reformer	122	284	170	261	837
Naphtha HDS	56	514	328	540	1,438
Total	697	1,057	670	1,559	3,983

Product Blending and Properties

i. *Gasoline blending*. Both grades of gasoline will be blended to a “no give away” on octane value. These grades and their blending specifications are given in Table 35.

ii. *Premium grade gasoline*. The blend of gasoline precursor streams shown in Table 37 meets the octane specifications and quantity for the premium grade gasoline.

The remaining properties of this product are developed in the following:

iii. *The distillation curves*. The TBP curves for each precursor making up the blend are divided into components of the same boiling range and combined to produce the composite TBP curve for the blend. Refer to Tables 38 and 39 for these data. RVP blending factors are in Table 39.

The TBP and the derived ASTM curves are given in Fig. 12.

The component breakdown will now be used to determine the SG of the product and the quantity of C_4 that will be added to the blend to meet the RVP spec.

Table 35 Gasoline grades and blending specifications

	Premium grade	Regular grade
Octane research clear	90	82
Ried vapor pressure (min)	7 psia	7 psia
Volatility ASTM		
50 % vol distilled (min)	275 °F	175 °F
60 % vol distilled (max)	300 °F	210 °F
95 % vol distilled (max)	400 °F	325 °F

Table 36 Balance over isom/alky plants

Stream	lbs/CD	lbs/Gal	BPCD	Routing
In				
Unsats ex FCCU	340,201		1,736	
Butanes ex sats	355,263		1,760	
Total in	695,464	4.74	3,496	
Out				
C_3 ex FCCU	35,980		203	LPG pool
nC_4 ex Sats	125,763		616	Gasoline/LPG
nC_4 ex FCCU	25,107		123	Gasoline/LPG
Alkylate	506,101		2,054	Gasoline
Total out	692,951	5.51	2,996	

Table 37 Premium gasoline grade blend

	BPCD	% vol	ON(RES) clear	Octane factor
Alkylate	2,054	26.7	97	0.26
Heavy cracked naphtha	1,695	22.0	89	0.20
Light cracked naphtha	1,000	13.0	94	0.12
Reformate	1,951	25.3	91	0.23
Light str run naphtha	1,000	13.0	69	0.09
Total	7,700	100.0	90	0.90

Refer to Table 40. The RVP of the finished product is determined by a bubble point calculation in which the C_4 is an unknown x and the RVP is set at 7 psia and 100 °F. Thus:

Calculating for butane addition to make 7 psia RVP:

$$\begin{aligned} 6.287 + x &= 3.804 + 8.57x \\ x &= 0.328 \\ &= 0.328 \div (6.287 + 0.328) \\ &= 0.0495 \end{aligned}$$

C_4 will be 4.95 mol% or 4.0 vol% of total product gasoline.

Table 38 Gasoline blend component properties

Comp	Temp, °F	LSR		Reformate		Lt-cracked naphtha		Hy-cracked naphtha		Alkylate		Total BPCD
		% vol	BPCD	% vol	BPCD	% vol	BPCD	% vol	BPCD	% vol	BPCD	
1	45–100	20	200	6	117	5	50					367
2	125	15	150	4	78	5	50					278
3	150	15	150	7	137	19	190					477
4	175	30	300	8	156	14	140			2	41	637
5	200	10	100	8	156	15	150			8	164	570
6	250	10	100	17	331	19	190			2	41	662
7	175			20	390	8	80			30	616	1,086
8	300			12	234	5	50	5	85	45	925	1,294
9	350			12	234	10	100	42	712	13	267	1,313
10	400			3	59			43	728			787
11	475			3	59			10	170			229
Total		100	1,000	100	1,951	100	1,000	100	1,695	100	2,054	7,700

Table 39 Gasoline RVP blend factors

Comp	Mid Bpt	#/ gal	Mol Wt	VP at 100 °F psia	% vol	Wt factor	Mol factor
1	75	5.96	72	22	4.77	28.43	0.395
2	115	6.03	73	11	3.61	21.77	0.298
3	135	6.09	75	6.2	6.19	37.70	0.503
4	155	6.17	81	5.0	8.27	51.03	0.630
5	185	6.25	90	2.5	7.41	46.31	0.515
6	225	6.39	100	}	8.61	55.02	0.550
7	260	6.49	110	}	14.11	91.57	0.832
8	285	6.56	119	}1.8	16.79	110.14	1.08
9	315	6.64	128	}	17.06	113.28	0.885
10	375	6.83	148	}	10.22	69.80	0.471
11	420	6.95	162	}	2.96	20.57	0.127
Total		6.45	103		100.00	645.62	6.287

Then blended premium gasoline will have the following properties:

SG at 60 °F 0.7749
RVP 7.0 psia
50 % ASTM vol distilled = 275 °F
60 % ASTM vol distilled = 290 °F
95 % ASTM vol distilled = 380 °F
Octane number research clear = 90

These meet the required specifications for the product.

iv. *Regular gasoline*. It is proposed only to include the component breakdown for the regular gasoline precursors here. The remainder of the blending recipe for the product will follow that for the premium grade. Thus, the component breakdown for regular grade is shown in Table 41.

Following the same calculation route as that for premium grade, the TBP and ASTM distillation curves are also given in Fig. 12. The calculation for RVP shows the blend requires an input of 0.36 % vol C_4 to meet the RVP of 7 psia. Regular grade gasoline therefore has the following properties:

SG at 60 °F 0.7531
RVP 7 psia
50 % ASTM vol distilled = 185 °F
60 % ASTM vol distilled = 200 °F
95 % ASTM vol distilled = 310 °F
Octane number research clear = 82

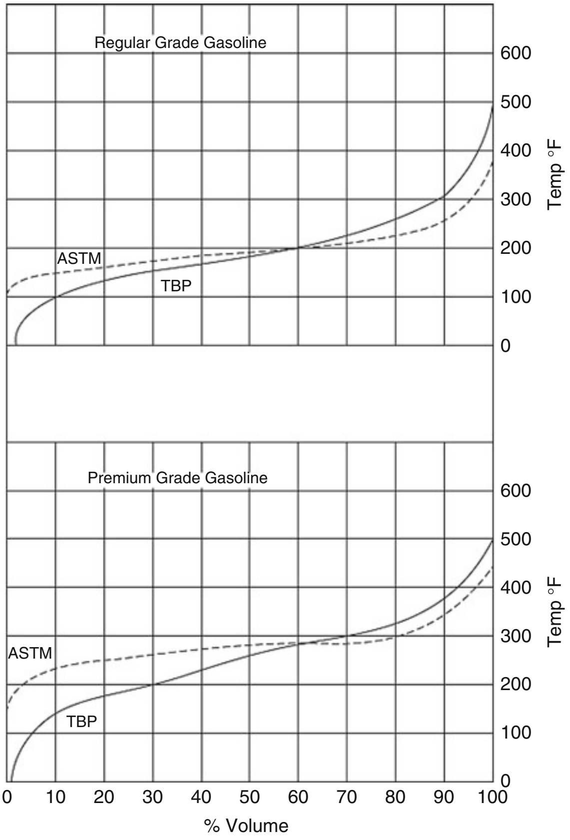


Fig. 12 Premium and regular grade TBP and ASTM curves

Table 40 Butane addition to meet RVP spec for premium gasoline

Comp	mid Bpt °F	VP @ 100°F psia	K = VP/7	moles liq	moles vap
C_4		60	8.57	x	$8.57x$
1	75	22	3.14	0.395	1.241
2	115	11	1.57	0.298	0.469
3	135	6.2	0.89	0.503	0.445
4	155	5.0	0.71	0.630	0.450
5	185	2.5	0.36	0.515	0.184
6	225	│	│	│	│
7	260				
8	285	1.8	0.26	3.946	1.015
9	315	│	│	│	│
10	375				
11	420				
Total				$6.287 + x$	$3.804 + 8.57x$

Table 41 Regular grade gasoline blend

		LSR		Reformate		Lt crack naptha		
Comp	Temp °F	% vol	BPCD	% vol	BPCD	% vol	BPCD	Total BPCD
1	45–100	20	993.9	6	294	5	125.2	1,413.1
2	125	15	745.4	4	196	5	125.2	1,066.6
3	150	15	745.4	7	343	19	475.6	1,564.0
4	175	30	1,490.8	8	392	14	350.4	2,233.2
5	200	10	497	8	392	15	375.4	1,264.4
6	250	10	497	17	833	19	475.5	1,805.5
7	275			20	980	8	200.2	1,180.2
8	300			12	588	5	125.2	713.2
9	350			12	588	10	250.3	838.3
10	400			3	147			147
11	475			3	147			147
Total			4,969.5	100	4,900	100	2,503	12,372.5

Total butanes to gasoline pool will be 310 BPCD to premium grade and 45 BPCD to regular grade totaling 355 BPCD. The gasoline product make will be:

Premium grade 8,010 BPCD
Regular grade 12,418 BPCD

- *The LPG pool*
  The LPG make from the refinery will essentially be the net make from the depropanizer, deethanizer, and the alkylation process, thus,

C_3 ex deethanizer	1,057 BPCD
C_3 ex alky process	203 BPCD
Total C_3 LPG	1,260 BPCD
C_4 ex depropanizer (net)	469 BPCD
C_4 ex alky process	739 BPCD
C_4 to gasolines	−355 BPCD
Total C_4 LPG	853 BPCD

The respective processes will operate to meet LPG specification.

- *Fuel oil pool*
  Three fuel oil products will be produced:
  - Marine diesel
  - Heavy fuel oil
  - High-sulfur bunker oil

Marine diesel specification:
SG at 60 °F 0.830 min
Viscosity Redwood at 100 °F 40 s min
Pour point 45 °F max
Flash point 150 °F min
Sulfur % wt 1.0 max

Heavy fuel oil specification:
SG at 60 °F 1.00 max
Sulfur % wt 5.0 max
Viscosity at 122 °F Cst 170 max
Flash point °F 160 min
Pour point °F 65 max

High-sulfur bunker fuel:
SG at 60 °F = 1.05 max
Viscosity cSt at 122 °F = 370 max
Flash point = 160 °F min
Sulfur % wt = 6.22 max

Blending to meet marine diesel spec:

This will be a blend of desulfurized LVGO and thermal cracker residue.

50 % of available LVGO will go into this blend = 2,648 BPCD = 796,306 lbs/CD.

Calculating amount of TC residue in blend to meet sulfur spec.

Let x lbs be the wt of residue in blend. Then

$$\begin{aligned}(796{,}306 \times 0.0035) + 0.0619x &= 0.01(796{,}306 + x)\\ x &= 99{,}730\ \text{lbs/CD}\\ \text{Total blend} = 796{,}306 + 99{,}730 &= 896{,}036\ \text{lbs}\\ \text{or } 2{,}648 + 270 &= 2{,}918\ \text{BPCD; SG at } 60\,^\circ\text{F} = 0.877.\end{aligned}$$

This meets SG and sulfur spec. Checking for pour point is in Table 42.

LVGO pour point = 15 °F (no adjustment is made for changes due to hydrotreating).

Approx ASTM 50 % point = 700 °F
TC Residue pour point is 65 °F
Approx ASTM 50 % point = 900 °F

Heavy fuel oil blending:

Eighty percent of thermal cracker residue will be routed to heavy fuel. Thus:

BPCD = 6,320
% wt sulfur = 6.19

Table 42 Fuel oil pour point blending

	Composition		ASTM 50 %		Pour point		
Components	BPCD	Fraction	50 %	Factor	Pour point °F	Index	Blend
		A	B	A × B		C	A × C
LVGO	2,648	0.91	700	637	15	5	4.6
Tc res	270	0.09	920	82.8	65	22[a]	2
Total	2,918	1.00		719.8			6.6

[a] The pour point corresponding to a 50 % ASTM point of 720 °F and an index of 6.6 is 22 °F. Therefore, blend meets spec for marine diesel

Viscosity at 122 °F = 75 cSt
SG at 60 °F = 1.046
Pour point = 55 °F

The product does not meet specification with respect to sulfur or specific gravity. The product will be blended with hydrotreated gas oil for sulfur.

$$\text{Total sulfur in thermal cracker residue } 6{,}320 \times 42 \times 8.8 \times 0.0619 = 144{,}541 \text{ lbs.}$$

Let x be lbs of hydrotreated LVGO in blend.

$$\begin{aligned}\text{Then } 144{,}541 + 0.0035x &= 0.05(2{,}335{,}072 + x)\\ x &= 597{,}578 \text{ lbs/CD of desulfurized LVGO.}\\ \text{Total fuel oil blend} &= 2{,}335{,}072 + 597{,}578 = 2{,}932{,}650 \text{ lbs/CD}\\ &= 6{,}317 + 1{,}990 \text{ BPCD} = 8{,}306 \text{ BPCD}\end{aligned}$$

SG at 60 °F of fuel oil product = 0.998 which is within spec.

Pour point of thermal cracker residue is 55 °F and, blended with LVGO, will have a pour point <55 °F, which meets fuel oil spec of 65 °F max.

Blending for high-sulfur bunker fuel.

Uncommitted Thermal Cracked Residue amounts to 1,314 BPCD. This meets all the criteria for high-sulfur bunker fuel without further blending. Decanted FCCU Slurry will also be routed to this product. Then the total product = 923,000 lbs/CD or 2,548 BPCD.

- *The gas oil pool*

Automotive diesel specification:
SG at 60 °F, 0.83–0.86
Visc at 100 °F, 1.6–5.5 cSt
Flash PM 150 °F min
Pour point 15 °F max
Sulfur 0.35 % wt max

Table 43 Diesel blending specification check

	BPCD	lbs/Gal	MM lbs/CD	Pour point °F	% wt S
Gas oil	655	7.163	0.197	15	0.35
Diesel	8,101	6.98	2.374	0	0.31
Total	8,756	6.7	2.572	<15	0.313

Table 44 Diesel product distillation check

% vol	Temp, °F
0	460
10	515
30	540
50	561
90	615
FBP	685

ASTM dist:
50 % recovered at 464 °F min; 657 deg F max
90 % recovered at 615 °F min
FBP 725 °F max
Diesel index 54 min

All the diesel stream and the remaining LVGO will be blended to meet this product spec. Some desulfurized kerosene may be added if required to make up gravity or distillation spec. The diesel index, pour point, and flash point are easily met. Viscosity spec will also be checked.

The sulfur and pour point specification checks are shown in Table 43.

Distillation:

ASTM distillation of the blend is calculated to give the results in Table 44.

This meets the spec required.

The viscosity check is shown in Table 45.

Index of blend = 4,725 ÷ 100 = 47.25, with a corresponding viscosity = 4.8 cSt which meets spec.

This completes the blend recipe calculation for the automotive diesel product.

Gas oil – (Heating oil)

Specification:

SG at 60 °F 0.840–0.860
Flash pt °F 150 min

Distillation ASTM:
10 % vol Rec at 400 °F min
50 % vol Rec at 475 °F max

Table 45 Diesel product viscosity estimate

	% vol	Visc at 100 °F cSt	Visc index	Factor (index × % vol)
Gas oil	7.5	13.0	38	285
Diesel	92.5	4.0	48	4,440
Total	100.0			4,725

Table 46 Heating oil blend recipe

Stream	MM lbs/CD	lbs/gal	BPCD
Lt cycle oil	0.438	7.63	1,366
Kerosene	0.440	6.70	1,563
	0.878	7.13	2,929

90 % vol Rec at 675 °F max
FBP 750 °F max
Sulfur 0.3 % max

Gas oil recipe:

It is proposed to route all the FCCU's Lt cycle oil make to this blend and sufficient Kero to meet the sulfur specification, thus:

Let x lbs/CD be the amount of Kero in the blend, then:

lbs/CD sulfur in cycle oil = 2,380
lbs/CD sulfur in the Kero = $0.00004x$

$$2{,}380 + 0.00004x = 0.003(438{,}000 + x)$$
$$x = 439{,}527 \text{ lbs/CD.}$$

The resulting blend is shown in Table 46.

SG of blend = 0.856, which is within spec

ASTM distillation of blend is as follows:

10 % rec at 401 °F
50 % rec at 473 °F
90 % rec at 571 °F
FBP 647 °F

This meets the distillation spec.

$$\begin{aligned}\text{Checking flash point: Kero flash point} &= 0.77(\text{ASTM 5 \% temp} - 150)\\ &= 0.77(370 - 150) = 169.4\,^{\circ}\text{F}\end{aligned}$$

The Lt cycle oil has an ASTM 5 % point higher than 370 °F; therefore, blend flash point will be >150 °F which makes it within spec.

Table 47 The calculated product slate and sulfur make

Item	Stream In	BPCD (MMScf/CD)	lbs/gal (MW)	MM lbs/CD	% wt S	Sulfur lbs/CD
1	Crude feed	50,000	7.13	14.973	2.35	351,701
2	Hydrogen gas	(7.33)	(11)	0.224	Neg	Nil
3	Total in out in LE	50,000		15.197		351,701
4	Ex Nap HDS			0.272	4.65	11,273
5	Ex Kero HDS			0.004	65.78	2,631
6	Ex LGO HDS			0.031	69.30	21,483
7	Ex LVGO HDS			0.037	83.26	30,808
8	Ex HVGO HDS			0.144	54.64	78,687
9	Ex FCCU			0.13	2.19	2,850
10	Ex reformer			0.152		Nil
11	Total ex LE			0.770		147,732[a]
						[a]As H_2S
	LE products					
12	Fuel gas	1,334		0.224		
13	LPG	2,113		0.398		
14	Sulfur			0.139	(or 62 tons)	
	Liquid products					
15	Gasolines			5.440	Neg	Nil
16	Kero			0.837	0.004	36
17	Auto diesel			2.572	0.96	8,049
18	Gas oil			0.878	0.27	2,383
19	Motor diesel			0.896	1.00	8,960
20	Heavy fuel oil			2.933	5.0	146,633
21	Bunker oil			0.923	4.17	38,469
15–21	Total liq products			14.479		204,530
12–21	Overall prod slate			15.240	2.32	352,262

Overall Product Slate Balance and Sulfur Make

Refer to Table 47 for the overall refinery yield and material balance.

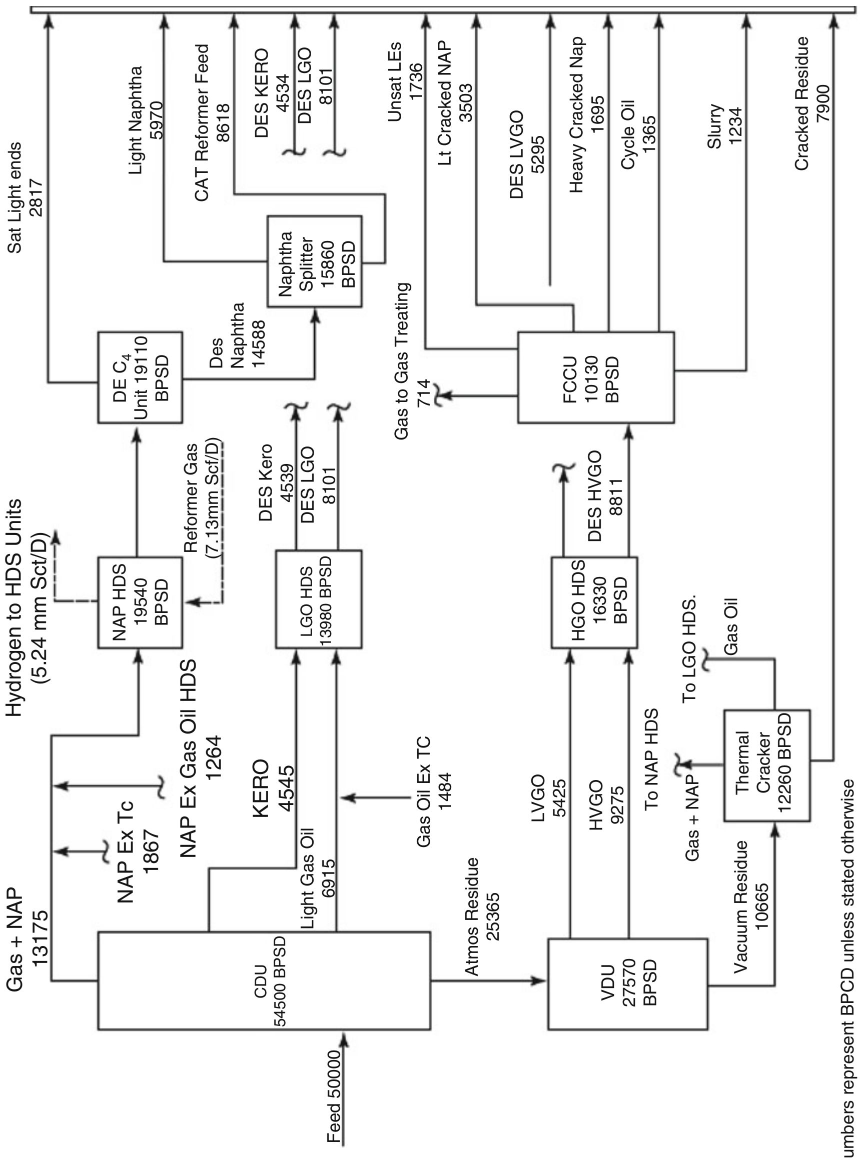
$$\text{Deviation between In and Out} = \text{lbs/CD} = +0.2\,\%$$
$$\text{Sulfur/CD} = +0.1\,\%$$

Both are within the acceptable error range for this type of calculation.

Table 48 Unit design capacities

Unit	BPCD	Service factor %	Operating days per year	BPSD	Remarks
CDU	50,000	92	336	54,500	
VDU	25,365	92	336	27,570	
Naphtha HDS	17,583	90	330	19,540	Inc Gas ex Ref
Debutanizer	17,583	92	336	19,110	Inc O/H ex TC
Nap splitter	14,589	92	336	15,860	
Depropanizer	39,60	92	336	4,310	
Deethanizer	1,774	92	336	1,930	
Cat reformer	8,618	87	318	9,910	On 97 ON Sev
Thermal cracker	10,665	87	318	12,260	
LGO HDS		90		13,980	
On kero	4,545		119		
On LGO	8,036		211		
Heavy gas oil HDS		90		16,330	
On LVGO	5,425		122		
On HVGO	8,036		208		
FCCU	8,811	87	318	10,130	Inc Gas Conc
Isom/alky	3,496	90	330	3,880	
Gas treating	2,167	95	347	2,280	
Sulfur recovery	62 (tons)	95	347	(70 tons)	

Unit capacities. The unit capacities required to meet this product slate will be based on a service factor for each unit. This service factor takes into consideration the downtime required for each type of process which has been based on statistical operating experience. This factor may be different for different operating companies based on their experiences, their maintenance philosophy, and design features of these units that they wish to consider. The latter case, for example, will consider their current pump sparing philosophy, the sophistication of their plant control system, and the like. Those service factors used in Table 48 are taken for the purpose of this exercise, but they are somewhat typical. Application of the service factor to calculate unit design capacity or stream-day rates from calendar rates is illustrated in Table 48. The block flow diagram showing this configuration is Fig. 13.



Numbers represent BPCD unless stated otherwise

Fig. 13 (continued)

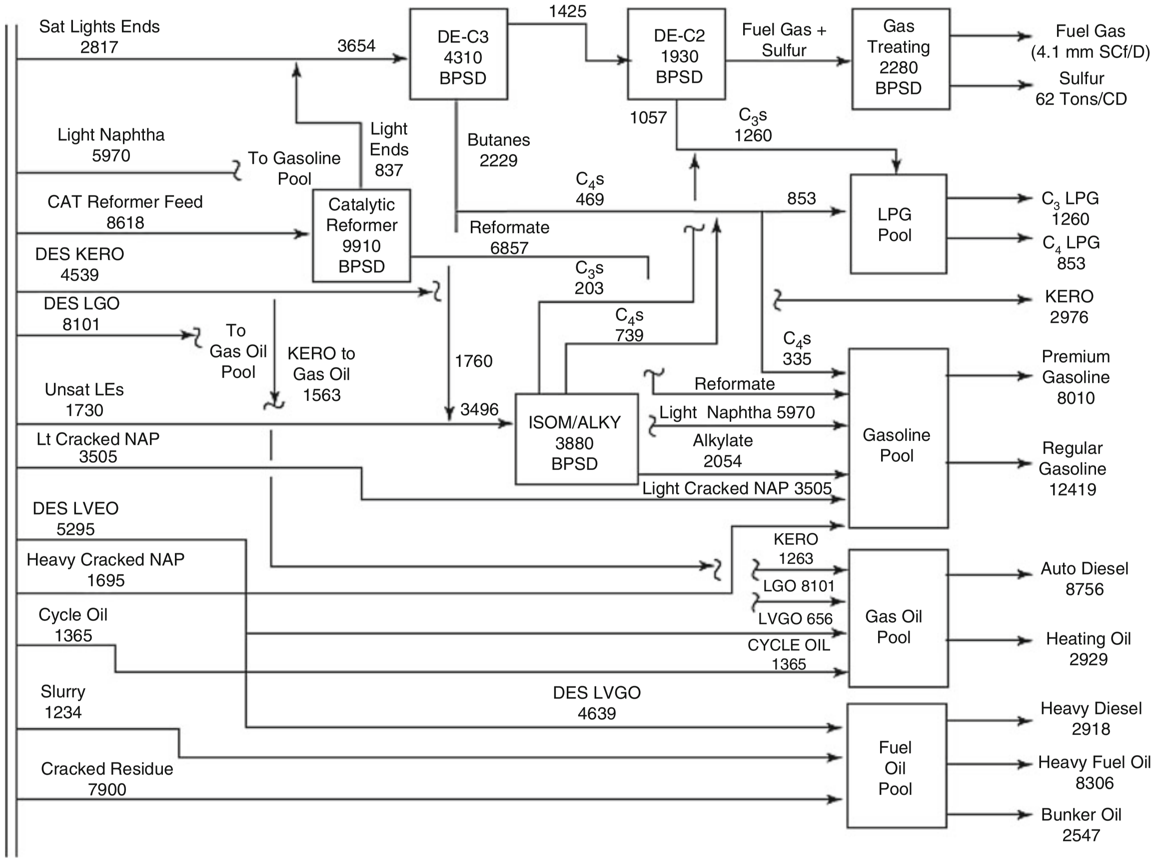


Fig. 13 The refinery configuration block flow diagram

Conclusion

This completes a very cursory look at the nature and refining of crude oil. The remainder of this first part of the Handbook continues with a more detailed examination of the various processes, the economic aspect of the refining industry, and the impact the industry has on modern living. It also describes and discusses modern techniques used in the industry and other allied industries (such as engineering and construction) to improve and optimize the design and operation of the refining processes.

Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries

David S. J. Jones

Contents

Abstract

Crude oil received by a refinery is initially distilled or fractionated into multiple "cuts" by boiling range. These cuts are further processed into final products in

---

David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_25

the refinery units. This chapter describes the initial crude fractionation process in both atmospheric and vacuum distillation units and how these units are designed. Detailed example design calculations are provided.

Keywords
Crude unit • Vacuum unit • Distillation • Refinery • Petroleum • Fractionation

Introduction

The distillation of petroleum products from crude oil has long been practiced. The ancient Egyptians, Greeks, and Romans had some form of extracting a flammable oil from, probably, weathered crude oil seepage. It was not though until the turn of the nineteenth and twentieth century that crude oil well drilling was first discovered and commercialized. Originally the crude oil was refined to produce essentially kerosene (lamp oil) and a form of gasoline known then as "benzine" (as opposed to "benzene" already being produced from coal) and the residue used as pitch for calking and sealing. The lamp oil or kerosene was produced to provide a means of illumination; later a lighter cut known as naphtha was produced for the same purpose but used in special pressurized lamps.

The production of these early distillates was made by cascading the crude oil through successive stills, each operating at successively higher temperatures. This is shown in the following diagram, Fig. 1.

The crude enters the first still to be heated to a temperature that vaporizes the light components. The residue from this still enters the second one and is heated to a higher temperature to vaporize the "benzine" fraction. The residue enters the third still and is

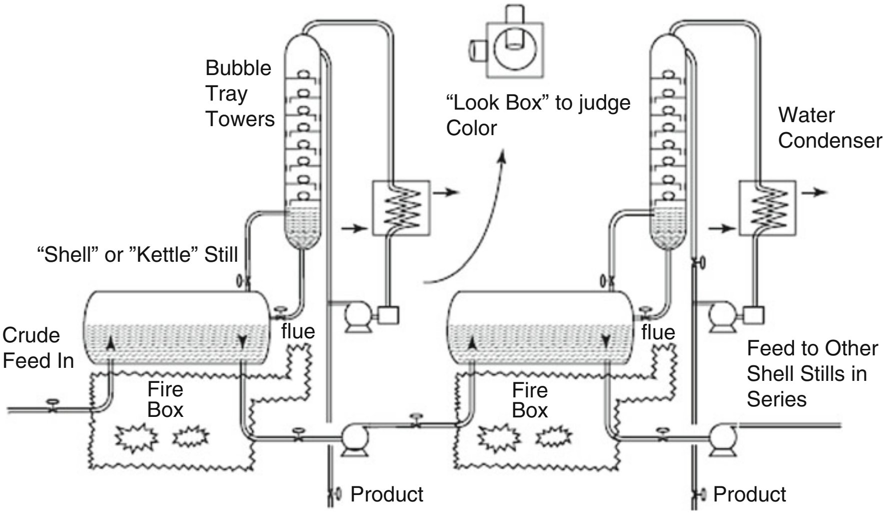


Fig. 1 Early continuous pipestill schematic

heated to remove the “kerosene” fraction. The residue from this still is a very light fuel oil which may be further heated and partially vaporized to give a pitch of sorts as a residue and a distillate which could be used as fuel. This distillate would later become the diesel or gas oil fraction and be used in the development of the diesel engine.

The vapor from each still passes through a small packed wash section before being condensed and collected in a condensate drum. A portion of the condensate is returned to the top of the wash section as the wash liquid, similar to the reflux stream in modern distillation towers. Usually steam was injected through the liquid phase of each still to facilitate vaporization and to strip out the light ends.

This type of crude distillation was superseded by the continuous fractionation tower used in modern petroleum refining. This type of crude “still” remained in operation well after World War II in some oil refineries. The author recalls such a still in operation as late as 1956 in the refinery where he was employed, although there were also in operation three other modern crude oil fractionating units. Indeed, one major oil company even today calls the crude distillation unit a “pipestill.” This chapter now continues with the description of a present-day atmospheric and vacuum crude oil distillation units. It will be divided into two parts:

- The atmospheric crude distillation unit (CDU)
- The vacuum crude distillation unit (VDU)

Both parts will contain a process description with a schematic flow sheet, a discussion on the development of the material balance, a description and discussion on the design characteristics of the units, and finally a worked design example.

It is common to use process simulation software (HYSYS, Pro/II, and others) to perform the design calculations for crude and vacuum units. This allows case studies to optimize the process design. The details of the computer simulations are beyond the scope of this Handbook.

The manual approach to the calculations is described here. It is helpful to understand this approach to establish the background and limitations behind the computerized calculations.

The Atmospheric Crude Distillation Unit

Process Description

The first process encountered in any conventional refinery is the atmospheric crude distillation unit. In this unit the crude oil is distilled to produce distillate streams which will be the basic streams for the refinery product slate. These streams will either be subject to further treating downstream or become feedstock for conversion units that may be in the refinery configuration. A schematic flow diagram of an atmospheric crude unit is shown in Fig. 2.

Crude oil is pumped from storage to be heated by exchange against hot overhead and product side streams in the Crude Unit. At a preheat temperature of about

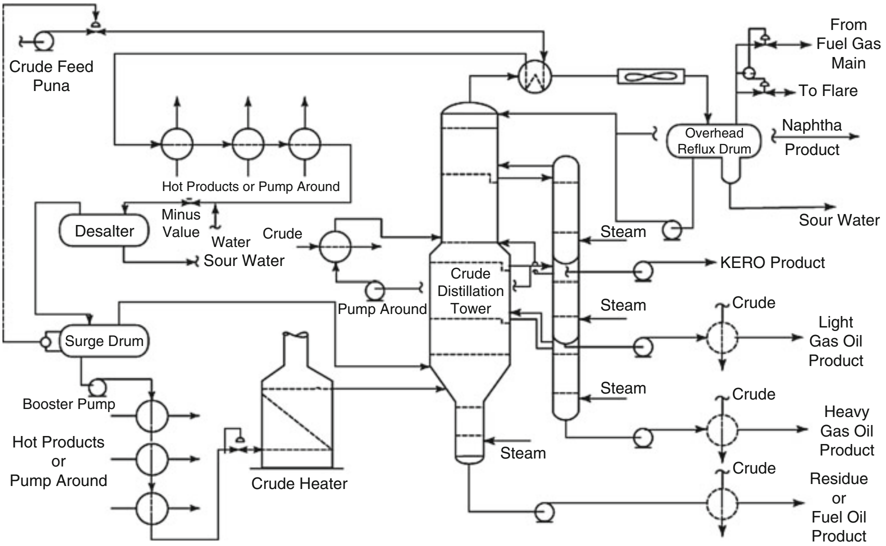


Fig. 2 A typical atmospheric crude distillation unit

200–250 °F, water is injected into the crude to dissolve salt that is usually present. The mixture enters a desalter drum usually containing an electrostatic precipitator. The saltwater contained in the crude is separated by means of this electrostatic precipitation. The water phase from the drum is sent to a sour water stripper to be cleaned before disposal to the oily water sewer.

It must be understood however that this "desalting" does not remove the organic chlorides which may be present in the feed. This will be discussed later when dealing with the tower's overhead system.

The crude oil leaves the desalter drum and enters a surge drum. Some of the light ends and any entrained water are flashed off in this drum and routed directly to the distillation tower flash zone (they do not pass through to the heater). The crude distillation booster pump takes suction from this drum and delivers the desalted crude under flow control to the fired heater via the remaining heat exchange train.

On leaving the heat exchanger train, the crude oil is heated in a fired heater to a temperature that will vaporize the distillate products in the crude tower. Some additional heat is added to the crude to vaporize about 5 % more than required for the distillate streams. This is called overflash and is used to ensure good reflux streams in the tower. The heated crude enters the fractionation tower in a lower section called the flash zone.

The unvaporized portion of the crude leaves the bottom of the tower via a steam stripper section, while the distillate vapors move up the tower countercurrent to a cooler liquid reflux stream. Heat and mass transfer take place on the fractionating trays contained in this section of the tower above the flash zone. Distillate products are removed from selected trays (drawoff trays) in this section of the tower. These streams are stream stripped and sent to storage. The full naphtha vapor is allowed to leave the top of the tower to be condensed and collected in the overhead drum. A portion of this stream is returned as reflux, while the remainder is delivered to the light end processes for stabilizing and further distillation.

The side stream distillates shown in the diagram are:

- Heavy gas oil (has the highest boiling point)
- Light gas oil (will become diesel)
- Kerosene (will become jet fuel)

A "Pumparound" section is included at the light gas oil drawoff. This is simply an internal condenser which takes heat out of that section of the tower. This in turn ensures a continued reflux stream flow below that section. The product side streams are stripped free of entrained light ends in separate stripping towers. These towers also contain fractionation trays (usually four but sometimes as many as ten), and the side stream drawn off the main tower enters the top tray of its respective stripper. Steam is injected below the bottom tray and moves up the tower to leave at the top, together with the light end stripout, and is returned to the main fractionator at a point directly above the side stream drawoff tray. These side stream stripper towers are often stacked one above the other in a single column in such a way as to allow free flow from the side stream drawoff tray to its stripper tower. On a few occasions, where the particular side stream specification requires it, the stripping may be effected by reboiling instead of using steam. One such requirement may be in the Kero side stream if this stream is to be routed directly into jet fuel blending and therefore must be dry.

The residue (unvaporized portion of the crude) leaves the flash zone to flow over four stripping trays countercurrent to the flow of stripping steam. This stripping steam enters the tower below the bottom stripping tray. Its purpose primarily is to strip the residue free of entrained light ends. The fact that this steam enters the flash zone also enhances the flashing of the crude in this zone by creating a reduced partial pressure for the liquid/vapor separation. This becomes an important factor in the design and operation of the atmospheric crude distillation unit. The stripped residue leaves the bottom of the unit to be routed either through the unit's heat exchanger system and either to product storage or to some downstream processing unit such as a vacuum distillation unit or a thermal cracker.

Development of the Material Balance for the Atmospheric Crude Distillation Unit

The knowledge of the material balance in any refining process is important both for ensuring its proper design and later for its proper operation. Because of the relative number of streams involved, this is particularly so in the case of the atmospheric crude distillation unit. The operation of this unit also is critical to the performance of downstream units such as catalytic crackers and catalytic reformers. The material balance for any specific operation required of the unit (e.g., maximizing naphtha feed to the catalytic reformer) from a particular crude feed source also sets the performance parameters of the unit. This includes the amount of reflux to be generated, at which section this reflux is to be generated, distillate drawoff temperatures, tower overhead conditions, flash zone conditions, and the like.

Whole Crude TBP Curve and Assay Data

The development of the unit's material balance begins with an "in-depth" examination and analysis of the crude oil feed assay. The first step in doing this activity is to break up the crude feed TBP distillation curve into its pseudo components and to assign the product characteristics relative to each component's mid boiling point or mid volume point on crude.

The properties of each pseudo component are provided either by the assay data giving the gravity versus mid volume percent (or mid boiling point) and by the application of Fig. 3. This chart gives the component's molecular weight based on

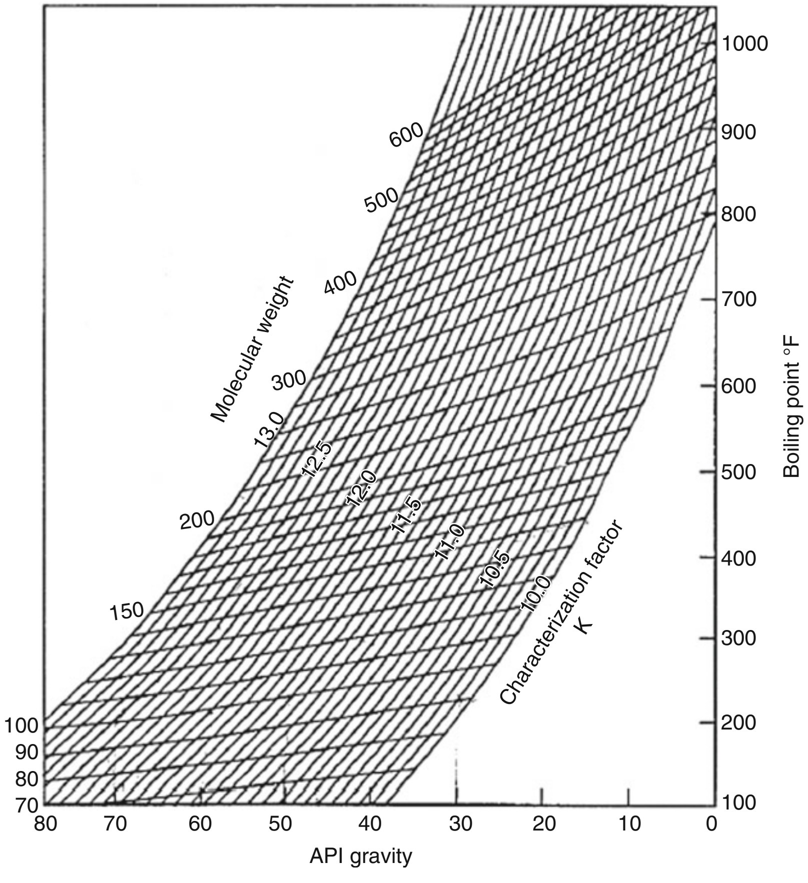


Fig. 3 Boiling points versus molecular weight and gravity (°API)

boiling point (i.e., mid boiling point) and its gravity in °API. Care must be made to establish these properties as accurately as possible. It will form the basis of any design process or definitive study work that may be carried out on this unit.

Developing the Side Stream Product TBPs

The first step is to divide the crude feed TBP curve into the product yield (in percent volume) and in terms of that product temperature cut range. This starts with establishing the cut point of the residue, that is the temperature on the TBP curve at which it is intended to separate the total distillate from the residue. Then the distillate portion of the TBP is divided into its product cuts such as gas oils, kerosene, and the total overhead naphtha or some other combination of products. The volumes of these cuts and temperature ranges represent the yield of each product that will be produced as a percentage of the whole crude.

From the cut points of each of the products, their ASTM curves are developed using the method described in the "Introduction" chapter to this handbook. The initial boiling point (IBP) of each cut (except the overhead naphtha) is fixed by the fractionation capability of the distillation unit. This term "fractionation capability" for a crude oil distillation unit is measured as the difference in temperature between the 95 % volume point of the lighter cut's ASTM distillation and the 5 % volume point of the adjacent heavier cut. This difference may be positive (gap) or negative (overlap). A gap indicates good separation while the overlap indicates poor separation. The ability to separate the fractions efficiently decreases as the products become heavier. Thus, one can expect an ASTM gap between the overhead product and the first side stream to be around 25 °F, while that between the third and fourth side stream may have an ASTM gap around – 10 °F (an overlap of 10 °F).

The side stream TBP curves are now developed using these concepts and following these stepwise procedures.

Step 1. Establish the cuts and cut ranges on the crude TBP that represent the products that will be produced in this unit. For example, the overhead product will be a full-range naphtha and will contain all the gas in the crude and the distillate to a cut point of 400 °F. The first side stream will be a kerosene cut beginning at 400 and ending at 500 °F on the crude TBP curve. The next side stream will be a gas oil boiling between 500 °F and 650 °F on the TBP curve. These will have yields as % volume on crude from the TBP curve. As an example, typical cuts are given as Fig. 4.

From this figure:

Naphtha (gas to 400 °F) = 30 %vol on crude.
Kerosene (400–500 °F) = 10.5 %vol on crude.
Gas oil (500–650 °F) = 14.5 %vol on crude.
Residue (+650) = 45.0 %vol on crude.

Step 2. Predict the ASTM end point and the ASTM 90 % point using the figures given in the chapter "▶ Introduction to Crude Oil and Petroleum Processing" of this handbook for the full-range naphtha (i.e., the overhead product).

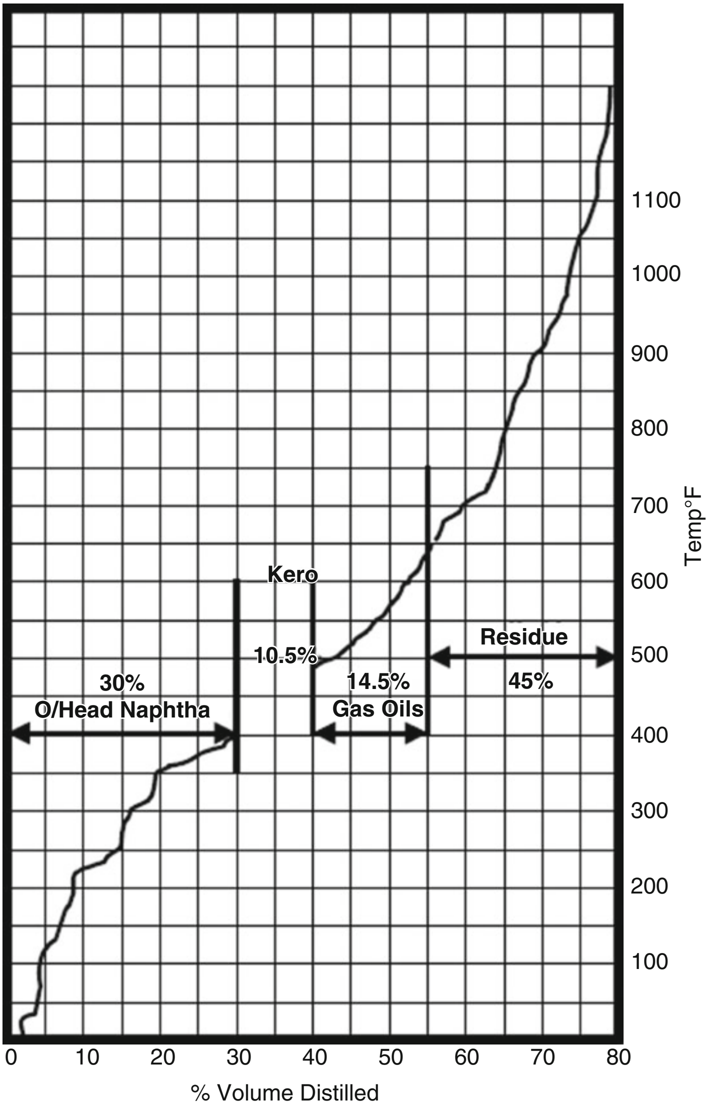


Fig. 4 TBP and product cut points for a typical mid-east crude

Step 3. Plot these on the probability chart, also given in the “Introduction” chapter, and draw the straight line through the 30 vol% point. This will be sufficient to determine a meaningful ASTM curve from which a TBP curve can be produced.

Step 4. The ASTM curves for the remaining side stream products are developed using the curves in the introductory chapter of this Handbook for fixing their ASTM end points. The 5 % points on both ASTM curves are then fixed using a reasonable ASTM gap or overlap between the products, thus:

Step 5. The 5 % ASTM point for the kerosene cut will be the 95 % point of the full-range naphtha plus a 25 °F gap. Similarly the 5 % ASTM point for the gas oil will be the 95 % point of the kerosene plus a 0 °F gap.

Step 6. The ASTM curves for the side streams are drawn as straight lines on the probability chart between their respective end points and their predicted 5 % points.

Step 7. Convert the developed ASTM curves to TBP curves using the Edmister correlations and as described in the "Introduction" chapter.

Step 8. Extend the front end of the full naphtha to include the gas portion and the light distillate below the 30 %vol point. Step this section off in mid boiling points to simulate real hydrocarbon components such as C_5's, C_6, C_7, etc. This will become important later in establishing the reflux drum pressure and temperature.

An example of this method is given later in the worked example of an atmospheric crude distillation unit process design.

Developing the Product Volume, Mass, and Mole Balance

Using the component breakdown (pseudo components) and the product TBP curves, calculate each product volume rate, mass rate, and mole rates using the following steps:

Step 1. Establish the crude feed flow rate in terms of volume (usually BPSD), and then calculate its mass flow (say in lb/h) and molal flow, using the crude feed breakdown table described in the previous section.

Step 2. Develop each product specific gravity using its component composition and each component specific gravity as given in the Crude Breakdown Table.

Step 3. Develop each product molecular (mol) weight similar to step 2 and again referencing the Crude Breakdown Table. There is a relationship between gravity, boiling point, and mol weight. This is given in Fig. 3.

Step 4. From the data developed in steps 2 and 3, calculate the quantity of each product in terms of BPSD, lb/h, and mol/h. The sum of each of these product quantities must equal the quantity of the crude oil feed calculated in Step 1.

This completes the description of the material balance development.

Design Characteristics of an Atmospheric Crude Distillation Fractionating Tower

In modern-day refining, the separation of the basic products from the crude feed is generally accomplished in a single atmospheric distillation tower. There are circumstances however that lead to the use of two towers to accomplish this. These circumstances usually occur where there is an abnormally high quantity of light components in the feed (such as a crude spiked with naphtha) or where the unit capacity revamp calls for such a configuration. In these circumstances, a light cut is flashed off and fractionated in a “primary” tower. The bottoms from this tower are then heated and vaporized to enter the flash zone of a “secondary” tower where it is fractionated to meet the conventional overhead and side distillate products.

This section of this chapter will deal only with the single atmospheric crude distillation process however.

The Tower Flash Zone

As described earlier the crude oil feed is heated to the required temperature for separating its distillate products from the unvaporized portion (i.e., the residue) by heat exchange with products being cooled or condensed and finally by a fired heater. This heated crude enters a section of the atmospheric fractionating tower at a point below the fractionating trays. This section of the tower is called the flash zone. The temperature and pressure conditions in this zone are such as to allow the correct amount of vapor to be flashed from the heated crude to provide the quantities of the distillate product streams and the internal reflux to control their quality.

These flash zone conditions of temperature and pressure are determined taking into consideration the shape of the crude oil’s equilibrium flash vaporization (EFV) curve, the pressure (usually the partial pressure in the case of the atmospheric tower) existing in this section of the tower, and the temperature on the EFV corresponding to the volume % cut of the total vapor to be flashed.

Setting the Flash Zone Partial Pressure

Because steam is used to strip the residue leaving the tower free of light ends, this steam enters the flash zone from the top stripping tray. The steam influences the pressure condition at which the hydrocarbon vapors separate from the residue. This pressure condition is the partial pressure exerted by the steam. It is calculated as follows:

$$\text{Partial pressure of HC vapor} = \frac{\text{moles HC vapor}}{\text{moles HC vapor} + \text{moles steam}} \times \text{Total pressure} \tag{1}$$

The total pressure of the flash zone is determined by the pressure in the tower’s overhead reflux drum plus the pressure drop over the overhead condenser(s) and the total distillate trays and internals above the flash zone. For an estimate of the flash zone partial pressure, the following rules of thumb may be considered:

Overhead reflux drum pressure	5 psig
Pressure drop over the condensers	7 psi
Pressure drop over trays or packing	10 psi (assumes 40 trays at 0.25 psi per tray)
Assume ΔP over internals are	Negligible
Then total pressure	22 psig

Assume that the steam from the residue stripper will be 1.2 lb/hot gallon of residue.

Setting the Flash Zone Temperature

Calculate the EFV of the whole crude using the method described in the "▶ Introduction to Crude Oil and Petroleum Processing" chapter of this Handbook. This EFV curve is at atmospheric pressure. The temperature of the flash at atmospheric pressure is read off as the % volume vaporized to meet the amount of distillate products *and* the overflash required by the process. This overflash is usually fixed at between 3 % and 5 % volume on crude. Its purpose in the process is to provide that extra heat in order to generate sufficient reflux downflow over the trays to satisfy the prescribed degree of separation between the products.

This atmospheric flash temperature is now adjusted to the temperature at the previously calculated partial pressure existing in the flash zone. This may be done by reading the temperature at the partial pressure using the PVT curves shown as Appendix 1 in the appendices to this chapter. This is the flash zone temperature.

Other Features of the Flash Zone Section

Most crude oils contain sulfur in some form or other and organic chlorides which are not removed in the pretreating desalter. Corrosion from these impurities is particularly virulent in mixed phases (liquid/vapor) and at the elevated temperature experienced in the unit's flash zone and made more so by the presence of steam. A cladding of 11/13 chrome is usually applied as a protective cover over the tower's carbon steel shell in this section. This cladding should be extended also to include the residue stripper and the section of the tower containing the first four to six wash trays above the flash zone. These trays and the residue stripping trays should also be of 11/13 chrome alloy.

Effective separation of the distillate vapor phase and the unvaporized residue phase is enhanced by the inclusion of a "swirl" at the inlet of the flash zone. The crude from the fired heater is routed through this "swirl" which is an inverted trough and extends around two-thirds of the tower circumference. The swirling action caused by this forced flow of the mixed phases allows the lighter vapor phase to separate to a large extent from the heavier liquid phase. The final separation occurs on the top stripping tray.

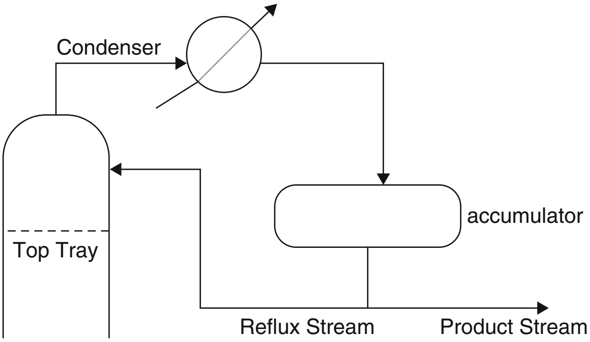
The Fractionator Overhead System

The fractionator overhead equipment has four functions. These are:

- To condense the overhead vapors including the stripping steam
- To return and control the reflux condensate to the tower
- To collect and dispatch the overhead product
- To separate and dispose of the condensed steam

These functions are accomplished in several different ways. Some of these overhead configurations are described in the following paragraphs.

Fig. 5 The most common overhead configuration



Configuration 1

This is probably the most common system and is shown in Fig. 5.

The total overhead vapor leaves the top of the tower at its dew point. It first enters a shell and tube exchanger where it is partially condensed. The cooling medium is cold crude oil feed from storage. The partially condensed overhead leaves the shell side of this crude oil exchanger to be further and totally condensed by either a trim water cooler or, more usually, an air condenser. The condensate from this final condenser enters an overhead condensate drum. This drum is designed to allow the complete separation of the condensed steam in the overhead from the hydrocarbon condensate. This condensed aqueous phase is collected in a "boot" located below the main condensate drum and is pumped under level control to the refinery's sour water disposal system. A portion of the hydrocarbon phase is pumped back to the fractionating tower to enter above the top tray. This stream is usually flow controlled which is reset by a tower top temperature control. The stream enters the tower through a spray system designed to ensure good distribution over the top tray.

The remaining hydrocarbon condensate leaves the drum under level control and is pumped to storage or a downstream process plant. The operating temperature and pressure of the condensate drum is vital to the operation of the fractionating tower. These conditions set the parameters for flash zone operation and intermediate product drawoff temperatures. These conditions are set and operated as follows:

The drum pressure. This is maintained by two pressure control valves operating on a split flow control. One of the valves is connected to the refinery flare, while the other is connected to the unit's fuel gas supply. When the pressure in the drum exceeds the pressure set point of the controller, the first valve opens to the flare thus reducing the drum pressure. When the pressure falls below the set point, then fuel gas is introduced by the second valve to correct this condition.

The drum temperature. The drum temperature is held at the bubble point of the condensate or slightly super cooled. This temperature is controlled either by fan pitch or by louvers on the final air condenser. Should the final condenser be a shell and tube water trim exchanger, then a bypass of the condensate around the exchanger activated by a temperature/flow control is installed. Such an arrangement can also be used on an air condenser.

The tower overhead temperature. The tower overhead temperature in this configuration is the dew point of the overhead product vapor at the partial pressure of the hydrocarbon.

Note: The partial pressure for this case is the total moles of hydrocarbons (includes the reflux moles) divided by the total moles of vapor (includes the steam present) times the total overhead absolute pressure.

The tower overhead pressure. The overhead tower pressure in this case is the pressure of the overhead condensate drum plus the pressure drops of the heat exchangers and the associated overhead condensate piping. This pressure drop may be taken as 7–9 psi.

Configuration 2

This second configuration is usually installed on units of high capacity at throughputs above 70,000 BPSD. Its purpose is to maintain the size of the overhead equipment to manageable dimensions. This includes drums and the heat exchangers associated with the system (Fig. 6).

In this configuration the total overhead vapors are again condensed by two exchangers as described in Configuration 1. In this second case, however, the condensate from the first condenser is collected in a drum and returned to the tower as reflux. The vapor from this first drum includes the overhead product hydrocarbon and the uncondensed steam from the fractionator. This vapor is condensed in the second overhead condenser (again usually an air condenser) to be collected in a second condensate drum as the overhead distillate product and water. Disposal of the separated aqueous and hydrocarbon streams follows the same system as in Configuration number 1. In this configuration the reflux drum acts as an additional theoretical tray because the reflux liquid is in phase equilibrium with the product vapor.

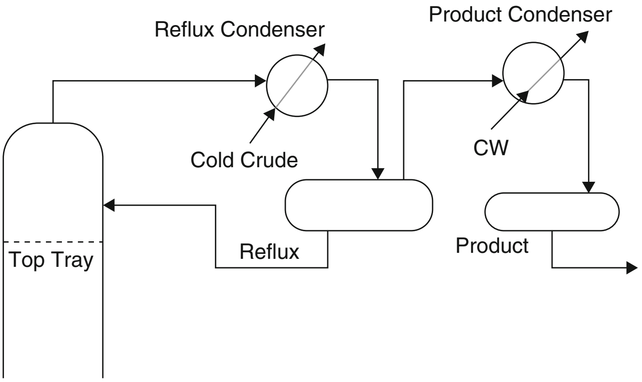


Fig. 6 The “two-drum” configuration

The product drum pressure and temperature. This again is the controlling pressure for the fractionator as a whole. It is set at the pressure which allows the vapors to be condensed at a reasonable temperature at or below its bubble point. In moderate climates with average air temperatures of 60 °F, this temperature will be around 90–100 °F with a pressure of 5 psig. Control of the drum pressure and temperature remains the same as that for Configuration 1.

The reflux drum temperature. The conditions in this drum may be considered as those for the top tray of the tower in Configuration 1. The temperature therefore is the dew point of the product distillate at the partial pressure of the hydrocarbon vapors leaving the drum. This temperature is usually controlled by a vapor bypass over the exchanger on a flow reset by temperature control valve. Alternatively, it may be controlled by the crude oil being bypassed on a similar flow/temperature reset basis. The partial pressure in this case is the moles of product vapor only divided by the total moles (including the steam) times the total absolute pressure. This total pressure is the pressure in the distillate product drum (say 5 psig) plus the pressure drop of the air condenser and piping (say about 3 psi).

The tower overhead temperature and pressure. The tower top condition in the case of this second configuration is calculated as the dew point of the reflux stream entering the tower from the reflux drum. This temperature will be at the partial pressure of the total hydrocarbons leaving the tower.

Configuration 3

In this configuration, the tower itself is used to generate the internal reflux from the overhead product (Fig. 7).

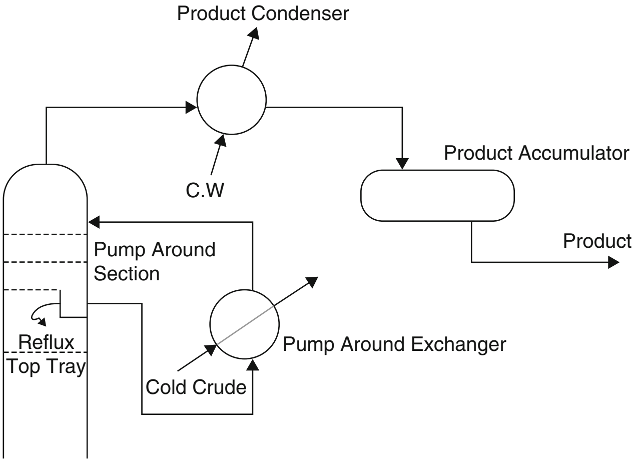


Fig. 7 The tower top pumparound configuration

The reflux is generated by a pumparound system taking the liquid from the top section of the tower and cooling it by heat exchange with cold crude oil. This cooled stream is then returned to the top tray of the tower. This is a conventional pumparound system. About three trays are used for this pumparound section in the tower. The tower top temperature remains as the dew point of the overhead product distillate at its partial pressure with steam. The temperature of the liquid leaving the tower as the pumparound will be between 5 °F and 7 °F higher than the tower top temperature. The internal pumparound section may be assumed to be equivalent to one half an actual tray for mass transfer.

Discussion

All three of these configurations have their advantages and disadvantages. These are discussed briefly in the following paragraphs:

Configuration 1. As noted earlier, this is the most common configuration. It is relatively easy to control with really only two set points that one has to be concerned with. They are the drum pressure and the tower overhead temperature. There is good heat transfer between the condensing vapors and the crude oil. The overall heat transfer coefficient is high at around 70–80 Btu/h/sqft/°F, and advantage is taken in the LMTD of the latent heat of the vapors being transferred to the low temperature of the incoming crude. The biggest disadvantage with this system is that the crude to the first condenser is of course at a much higher pressure than the vapors condensing on the shell side. The rupture of a tube in the exchanger bundle or a leak in the tube plate will cause crude to contaminate the overhead product and "dirty" the tower overhead trays. This can be quite a disaster if the downstream units (particularly the Cat Reformer) are fed directly from the condensate drum without some intermediate surge drum or tankage.

Configuration 2. This has the advantage of providing a very high LMTD in condensing with heat exchange against crude. This is due to the higher temperature now experienced in the vapors leaving the tower. As in the case of configuration 1, the overall heat transfer coefficient in this case is also high. There still remains though the problem of contamination, but in this case downstream units have a measure of protection in that only the vapors from the reflux drum are condensed to make the product. The top trays of the tower however will be contaminated as before. The two-drum system's biggest advantage however is more aligned to the installed cost of the unit. Moderately sized equipment are much cheaper than large items which may have to be field fabricated. Cost savings may in any case be achieved in the transportation costs of the drums and heat exchangers.

Configuration 3. The only major advantage in this configuration is that the liquid pumparound can be circulated at a higher pressure than the incoming crude. Thus, the problem associated with tube fracture or leakage contaminating the tower and product is eliminated. There is also an advantage in better control of the tower top temperature by the flow control of the pumparound itself. This too can be reset by temperature, but as a former plant operator, the author is not particularly in favor of temperature reset as a finite means of control. There is no other apparent advantage to this system. Indeed, the inclusion of additional trays in the tower for the pumparound is quite expensive. The trays would need to be of Monel, and some Monel lining of the shell will be required in this section as protection against chloride attack.

Some Design Considerations

Corrosion

The top section of the atmospheric distillation tower is very prone to corrosion from HCl. To combat this corrosion and to protect the carbon steel shell from damage, Monel is used in tray manufacture and as lining for the tower shell. This material is also used to line the first condenser shell interior, and the tubes may also be fabricated in Monel. Ammonia (or amine) either in its anhydrous form or as a solution is injected into the tower top and at specific intervals into the top section tray spaces. The purpose of the ammonia is to neutralize as far as possible the HCl. The injection of the ammonia is controlled by the pH reading of the condensate water leaving the boot of the product condensate drum.

Corrosion is most virulent at the liquid interface on trays. Consequently, in most modern fractionating towers, Monel lining of the shell is usually applied as strips on the top four or six trays. The strips installed at the interface of the liquid/vapor on these trays will be about 4–6 in. wide. The injection of anhydrous ammonia in the case of configuration number 2 does cause problems in the formation of ammonium chloride crystals occurring in the “dry” section of the condenser system. That is the section where the hydrocarbon is condensing, but the steam is still in its vapor phase. The injection of aqueous ammonia solution instead of the anhydrous form solves this problem.

Sulfur compounds are also a problem with respect to corrosion, particularly in the “cold” liquid phase of the distillate product drum. The drum shell in this case is gunite lined. This lining is applied to the bottom section of the main drum and extended to include the “boot” in which the condensed water is concentrated. Gunite is best described as a cement lining and is applied in the same way as refractory lining, by plastering it onto the shell. Other lining materials are also used.

The Distillate Drum

The design of the distillate drum includes space for the complete separation of the aqueous phase (condensed steam) from the hydrocarbon phase. It is important for the hydrocarbons to be as free of water as possible to protect the downstream units. The performance of these units such as hydrotreaters and, more particularly, the catalytic reformer are badly affected by the presence of water in their feed streams.

The design of the drum to allow this separation is based on one of three laws. These laws are expressed by the following equations:

$$\text{Stoke's law}: V = 8.3 \times 10^5 \times \frac{(d^2 \Delta S)}{\mu} \quad \text{(used when Re number is } <2.0) \tag{2}$$

$$\text{Intermediate law}: V = 1.04 \times 10^4 \times \frac{d^{1.14} \Delta S^{0.71}}{S^{0.29}\mathrm{c} \times \mu^{0.43}} \quad \text{(used when the Re number is } 2 - 500) \tag{3}$$

$$\text{Newton's law}: V = 2.05 \times 10^3 \times \{(d\Delta S) \div \mathrm{Sc}\}^{1/2} \quad \text{(used when the Re number is } >500) \tag{4}$$

where

$$\text{Re number} = \frac{10.7 \times dc\mathrm{Sc}}{\mu} \tag{5}$$

V = Settling rate in ins per minute.
d = Droplet diameter in inches.
S = Droplet specific gravity.
Sc = Continuous phase specific gravity.
ΔS = Specific gravity differential between the two phases.
μ = Viscosity of the continuous phase in cPs.

The following criteria may be used as a guide to estimating the droplet size:

Lighter phase	Heavy phase	Minimum droplet size
0.850 Sc and lighter	Water	0.008 in.
Heavier than 0.850	Water	0.005 in.

Piping

Vapor piping from the tower top should be sized for a minimum economic pressure drop. As a guide, vapor rundown lines should be sized to meet an average pressure drop of 0.2 psi per 100 f. and should never exceed 0.5 psi/100 ft. The vapor (and mixed phase) piping and the drums in the tower overhead system should be so arranged as to allow free drainage toward the distillate drum (or in the case of configuration 2 to each successive drum). The vapor lines should never be pocketed.

Distillate drums should be located at least 15 f. above the center line of the respective distillate/reflux and the sour water pumps (pumps are normally located at grade). For safety this measurement should be taken from the bottom tangent line of the vessel. Piping to the pump should be sized for a 0.25 psi/100 f. pressure drop, while the discharge piping from the pump may be reduced to meet a pressure drop of 2.5–4.0 psi/100 ft.

The Side Streams and Intermediate Reflux Sections

There are generally two or three side streams in the atmospheric crude distillation unit. There may be one more, but a total of three side streams is the norm. The unit that is going to be developed as an example in this work has three side streams. These are as follows:

- Kerosene
- Light gas oil
- Heavy gas oil

With three side streams there will be usually two pumparound sections. The purpose of these pumparound sections is to create the proper internal reflux to that section of the tower below the location of the respective pumparound. The pumparound takes suction from a drawoff tray in the tower. Usually this tray is also a product drawoff. The pump delivers the pumparound stream through a heat exchanger where it is cooled before returning it to a location in the tower about two to three trays above the drawoff tray. This cooling liquid flowing down the tower to the drawoff tray acts as an internal condenser. The hot vapors rising up the tower through the drawoff tray contain the side stream product, some internal overflow, and the vapor phase of all the lighter products and their overflow. This particular side stream product and overflow is selectively condensed by the cold pumparound. It enters the drawoff tray where the product quantity and pumparound leave the tower, and the remaining condensate overflows to the tray below the drawoff. This overflow material is the internal reflux stream, and its quantity determines the fractionation between this lighter side stream product and the heavier side stream product drawn from the tower at some point below.

The Side Streams

Side streams are withdrawn from selective and specially designed trays in the main tower. Each stream is usually combined with the respective pumparound as described earlier. When withdrawn from the tower, the product is in equilibrium with the total vapor rising through the drawoff tray. Consequently the product liquid will contain entrained light ends which will affect the required product properties such as flash point and its ASTM distillation. To correct this, the side stream product is steam stripped in a separate trayed stripping column. This arrangement is shown in Fig. 8.

The side stream from the main tower is routed to a distributor over the top tray of the stripping column under level control. The stripping column contains four stripping trays. Steam is introduced below the bottom tray and flows up the tower

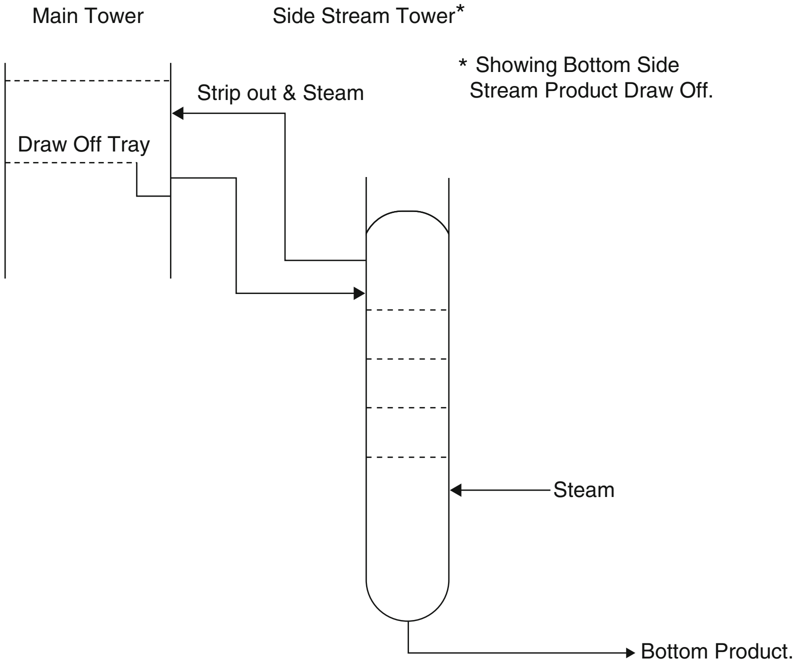


Fig. 8 A side stream stripper

countercurrent to the liquid product. The light ends contained in the stripper feed are removed by the steam, and both the stripout and steam leave the top of the stripper to enter the main tower at the vapor space directly above the drawoff tray.

The stripped product leaves the well at the bottom of the stripper to be pumped under flow control to storage or a downstream unit's surge drum. The level in the well of the stripper activates the level control valve of the incoming stripper feed.

The side stream drawoff temperature. In theory, the side stream product drawoff from the main column will be in equilibrium with the vapor rising from the tray. In other words, it will be at its bubble temperature at the partial pressure of the hydrocarbons on the tray. However, this liquid phase will contain some entrained light ends (thus the need for steam stripping) which will affect the actual temperature of the drawoff. J. W. Packie in his published work on crude oil distillation developed a curve which takes into consideration this difference between the theoretical drawoff temperature and the actual. This curve is given as Fig. 9.

In arriving at the partial pressure in this calculation, Packie assumes that all the vapor lighter than the drawoff is inert. With this as a parameter, the drawoff temperature can be calculated using the following stepwise process:

Step 1. Fix the amount of steam present in the vapor *passing through* the drawoff tray. (*Note*: This does not include the steam returning from the particular drawoff

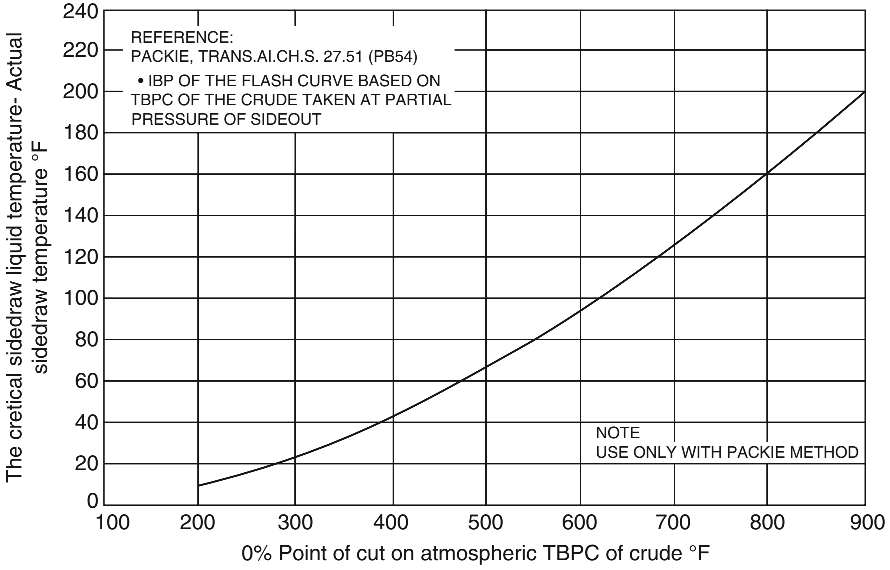


Fig. 9 The difference between theoretical and actual drawoff temperatures

stripper which enters the vapor space above the drawoff tray.) The amount of stripping steam recommended is given in Fig. 10.

Step 2. Fix the total pressure on the tray taking the estimated tower top pressure and each tray pressure drop above the drawoff tray (see the previous paragraphs on flash zone and overhead system). Estimate the position of the drawoff tray. As a guide the following rule of thumb can be used. With tray 1 as the top tray in the column:

Kero drawoff	Tray 12
Light gas oil	Tray 22
Heavy gas oil	Tray 32

There are usually 40 fractionating trays (i.e., trays above the flash zone) and four bottom stripping trays in conventional distillation towers. These amounts will be checked later using the relationship of reflux to tray ratio for fractionation criteria.

Step 3. Calculate the FRL (flash reference line) for the drawoff TBP cut. In doing this, use the TBP cut, not the TBP end points. This calculation has been described under the section on the flash zone. Establish its IBP at atmospheric pressure. This will be the 0 %vol temperature on the FRL.

Step 4. Predict the amount of overflow that will leave the drawoff tray as a liquid reflux to the tray below. Again this will be checked by the relationship of trays

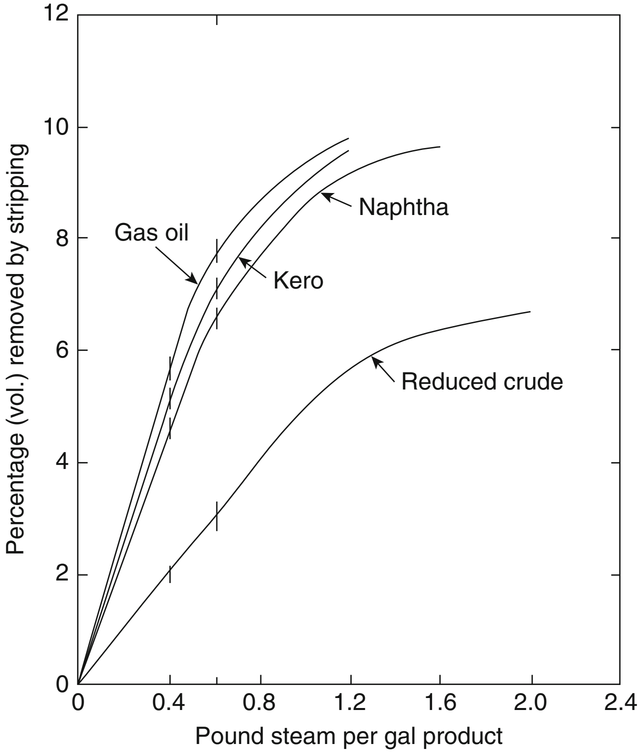


Fig. 10 The amount of stripping steam

and reflux later. For this calculation the following rules of thumb for the ratio of moles overflow to moles product may be used:

Overflow from the HGO drawoff 2.9
Overflow from the LGO drawoff 1.2
Overflow from the Kero drawoff 0.9–1.0

Step 5. Calculate the partial pressure on the drawoff tray as follows:

$$\text{Partial pressure} = \frac{(\text{total draw} - \text{off product vapor moles} + \text{total overflow moles}) \times \text{total pressure}}{(\text{total hydrocarbon vapor moles} + \text{steam passing through tray})} \tag{6}$$

Step 6. Using the vapor pressure curves (given in Appendix 1 of this chapter), relate the IBP of the cut at atmospheric pressure (step 3) to the calculated partial pressure.

Step 7. The temperature arrived at in Step 6 is the theoretical temperature of a liquid in equilibrium with its associated vapor phase. In actual practice, because a vapor phase has been continually bubbling through the liquid on the tray, that liquid will contain entrained light ends from the vapor. The actual temperature will therefore be somewhat lower than the calculated, and this difference is provided by Fig. 9. Establish the actual temperature of the side stream drawoff. Note this will also be the temperature of the pumparound liquid.

Side stream stripping. The side stream enters a steam stripper at the drawoff temperature. It is steam stripped, and the amount of stripping steam and the corresponding stripout may be read off from Fig. 10. The steam introduced below the bottom stripping tray is usually superheated at 50 psig. The temperature of the stripout and steam leaving the top of the stripper to enter the main tower can be taken as 5 °F below the temperature of the stripper feed. The mol weight of the stripout is taken as the average of the vapors lighter than the drawoff. A heat balance can now be carried out over the stripper with an unknown being the stripped product enthalpy and temperature. The product outlet temperature and enthalpy is calculated by solving the equation:

$$\text{Heat in} = \text{Heat out}$$

Side stream strippers for each product drawoff are usually stacked in one single column. It becomes an exercise in layout to locate these stripper sections. It begins with establishing the height of the bottom stripper section which will ensure sufficient head to provide available NPSH for the product rundown pump. Thereafter, each successive section is located to ensure free flow of the liquid feed into the respective stripper and to minimize the length of the vapor return line to the main tower.

The Pumparounds

The mechanism of the pumparounds and their purpose has already been described and discussed. It remains now to examine how to evaluate and detail quantitatively their size in terms of the duty they will be required to perform. This will be followed with some criteria that need to be observed in their design.

Total pumparound duties. This begins by establishing the tower bottom temperature (residue outlet temperature) and then conducting an overall tower heat balance. To calculate the tower bottom temperature, consider the diagram in Fig. 11 and the following calculation steps:

Step 1. Establish the material entering the top stripping tray. This will be the total residue product which now includes the overflash as a liquid and the stripout material (also as liquid). This is taken as being at the flash zone temperature.

Step 2. Calculate the total heat input to the bottom stripper. This will include the heat into the top stripping tray plus the heat in the stripping steam (enters below the bottom tray).

Step 3. Calculate the heat out of the stripper. This includes the bottom product at an unknown temperature and enthalpy, the stripout from the top stripping tray, and the steam from the top stripping tray. Assume the stripout and the steam will be

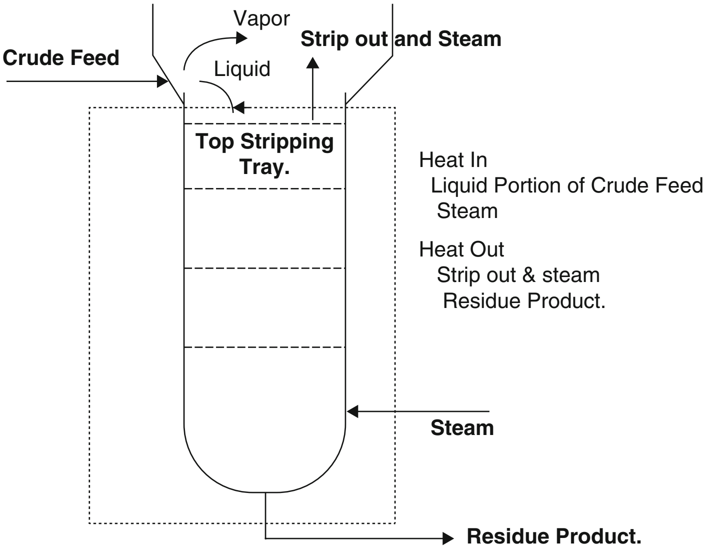


Fig. 11 Heat balance diagram for below feed tray

at 5 °F below the flash zone temperature and the steam will be at the flash zone partial pressure for the steam.

Step 4. From the equation

$$\text{Heat in} = \text{Heat out},$$

calculate the enthalpy (in Btu/lb) and thus the temperature of the residue or bottom product leaving the tower.

Note: While the author uses enthalpy data from his own files, it is recommended that engineers use their own proven data from their own files, or data contained in Maxwell's *Hydrocarbon Data*, or those given in the *GPSA Engineering Data Book*.

With all the temperature and enthalpy criteria established, an overall heat balance over the tower can proceed. In this balance the heat in with the crude will be that for the overflashed crude at the flash zone temperature. The other heat inputs are the steam streams to the various strippers. The heat out will consist of the overhead distillate product at the distillate drum temperature, the overhead condenser(s) duty, the condensed steam, all the side streams and residue as liquid and at their respective stripper bottom temperature, and finally the total of the pumparound duty.

As all the enthalpy duties are known except that for the pumparound, this can now be calculated from the expression

$$\text{Heat in} = \text{Heat out}.$$

Distributing the Total Pumparound to Meet the Required Internal Reflux

The degree of separation of one product from an adjacent one is determined by the number of fractionating trays used for the separation and the liquid overflow (reflux) entering the section used for the separation. As has been said previously, the degree of separation of products in the atmospheric crude distillation tower is measured by the difference between the 95 %vol point of the lighter fraction and the 5 %vol point of the heavier fraction as measured by their ASTM distillation curve. Packie developed a relationship between the ASTM distillation difference, the number of trays, and the amount of overflow in terms of internal reflux ratio. This relationship is given by a series of curves in the appendices to this chapter (Appendix 2). The use of these curves is illustrated by the following stepwise calculation procedure to arrive at the amount of overflow liquid.

Step 1. Establish the ASTM gap (or overlap) that is required. This is usually given in the design specification of the unit or by some constraint on one or other of the products. It is well to note here that ASTM gaps can usually be achieved between products lighter than light gas oil. Gaps can rarely be achieved within the tower for products heavier than the light gas oil cut. To trim the front or back ends of heavy products may require additional equipment such as vacuum flash equipment.

Step 2. Establish the number of trays separating the two adjacent products. This has usually been fixed by the design of the tower in operating units. For design purposes, the following fractionating number of trays can be used as a start point and guide:

	Tray number
Top tray	1
Kero drawoff	12
LGO PA return	19
LGO drawoff	22
HGO PA return	29
HGO drawoff	32

As a rule of thumb, the section of trays for the pumparound may be counted as one fractionating tray. Thus, for example, 10 + 1 trays can be counted for the separation of Kero and LGO.

Step 3. Evaluate the 50 %vol temperature difference between the TBP of the two adjacent cuts.

Step 4. Using the side stream to side stream family of curves in Appendix 2 for max steam, read out the factor corresponding to the ASTM difference required on the appropriate Δ50 % TBP temperature curve.

Step 5. The factor read is the number of trays separating the two products' drawoffs multiplied by the reflux ratio. This reflux ratio is defined as

$$\frac{\text{Hot overflow in gallons per hour leaving the lightest product draw} - \text{off tray}}{\text{Total product gallons per hour entering the lightest product draw} - \text{off tray}}. \tag{7}$$

Equate to determine the overflow quantity, in hot gallons per hour. The unit's material balance is used to resolve the flows to lbs per hour.

It now only remains to use the overflow criteria in the overall tower heat balance to arrive at a duty for the respective pumparound. If there is only one other pumparound in the tower, it can be determined by subtraction of the calculated pumparound from the total PA duty. Should there be more than two pumparounds involved, then the calculation steps given above must be repeated for the second one and the third obtained by subtraction.

On completion of setting the individual pumparound duties as described, the items determined by subtraction must be checked to ensure that they do in fact generate enough overflow to meet the fractionation criteria. If they do not fulfill this, then the overall pumparound duty must be increased. This can be achieved only by increasing overflash if the cut points are to remain the same. Should the calculations show there is somewhat more internal reflux than required, providing it is not excessive, it should remain as is. If it is excessive the overflash can be reduced accordingly.

Checking the Number of Trays Allocated to the Pumparound

With the individual pumparound duties now established, the temperatures to and from the pumparound section trays are the next items to be fixed. Use the following steps to accomplish this:

Step 1. Draw the tower temperature profile from the flash zone to the tower top tray. Use the already calculated side stream drawoff temperatures for this.

Step 2. Assume that the vapor temperature to a tray is the liquid temperature on the tray below it. This is a reasonable assumption and well within the accuracy required.

Step 3. Fix the pumparound inlet temperature. This will need to be a guess at this point and may well change on completion of the heat exchange system calculations. From the pumparound duty calculate the flow of pumparound liquid in lbs per hour.

Step 4. Carry out a heat balance over the pumparound section of the tower. This will now include the following items:

Heat in
  With the HC vapor from the tray below the section (includes the overflow)
  With steam from the tray below the section
  With steam and stripout from the product stripper (if applicable)
  With the pumparound return liquid
Heat out
  With lighter product vapors rising from the top PA tray
  Total steam from flash zone and side stream strippers below top PA tray
  Liquid pumparound leaving the tower

Liquid product drawoff plus stripout leaving to stripper (if applicable)
Liquid overflow from the PA drawoff tray
The pumparound duty in Btu/h

In these items the only unknown is the enthalpy and therefore the temperature of the vapor leaving the top pumparound tray. Equate heat in = heat out to solve the unknown.

Step 5. With the duty of the pumparound section in Btu/h and the temperatures in and out now known, the pumparound section can be treated as a heat exchanger. The area of heat transfer will be the total tray areas of the section, and the heat transfer coefficient in terms of Btu/h/sqft/°F is given in Fig. 12.

Step 6. The area is now calculated from the heat transfer equation:

$$Q = UA\,\Delta t_{\mathrm{m}} \tag{8}$$

where

Q = Heat transferred in Btu/h.
U = The overall heat transfer coefficient in Btu/h/sqft/°F.
A = Heat transfer area in sqft.
Δt_{m} = Log mean temperature difference in °F.

Step 7. The number of trays required will be determined from the tray or tower diameter calculation provided by a future calculation to determine the tower dimensions.

Calculating the Main Tower Dimensions

Having established the number of trays and the relative locations of pumparound and side stream draws, the overall dimensions of the tower can be calculated. Note: The number of trays allocated to the pumparound sections may be revised based on the tray or tower diameter calculation for those sections. This will not affect the tray loading calculations which will determine the tray diameters. The calculation to determine the tower diameter(s) is based on the vapor/liquid loading on each section of the tower. This loading is based on a series of heat balances to determine this traffic to and from the critical trays. These critical trays are:

- The top stripping tray of the residue stripping section (below the flash zone)
- The bottom side stream and pumparound drawoff tray
- The next pumparound drawoff (and the side stream if applicable) tray
- Any other lighter pumparound drawoff tray
- Any lighter side stream drawoff tray
- The top tray

The loading below the bottom pumparound and product drawoff gives the vapor loading for setting the *maximum* tower cross-sectional area and diameter. This is fixed by the crude feed cut point and the degree of overflash.

Units are in BTU/h. °F. Ft^2 Fluid being cooled	Fluid being heated	U_a
Exchangers		
Naphtha pumparound	Crude	70–80
Kero	Crude	70–75
Debutanizer bottom	Debutanizer feed	75
Gas oil (inc. BPA)	Crude	40–50
Reduced crude	Crude	20–30
Light end bottoms	Light end feed	70–75
Vacuum distillates	Crude	30–40
Bitumen	Crude	20
Cat oil slurry	FCCU feed	40
CDU overheads	Crude	80–90
Coolers		
Debutanizer bottoms	CT water	75
Light naphtha	CT water	80
Gas oils	CT water	40
DEA or MEA	CT water	110
Reduced crude	CT water	30
Vapour heat exchangers		
Reformer effluent	Naphtha feed	38
Reformer effluent	Recycle gas	38
Crude tower overheads	Crude oil feed	50
Condensers		
CDU overheads	CT water	65
Splitter overheads	CT water	85
Amine stripper overheads	CT water	100
Debutanizer overheads	CT water	90
Reformer effluent	Water	65
Air coolers		
Naphtha coolers		23
Debutanizer bottoms		30
Light end overhead		40
Reboilers (use heat flux in BTU/h/ft^2)		
	Hydrocarbon	Water
18 in. dia. bundles	20 000	30 000
30 in. bundles	17 500	26 500
> 30 in. bundles	15 000	~23 000

Fig. 12 Overall heat transfer coefficients in oil refining

Calculating the Tower Vapor and Liquid Loading

These loadings at the critical trays are calculated from a series of heat balances starting at the bottom stripping section and continuing up the tower to the top fractionation tray. Consider the loading on the bottom side stream and pumparound drawoff tray. This commences with a heat balance from below this tray and includes the streams shown in the envelope in Fig. 23.

The heat into and out of the envelope as shown is provided by the following streams:

Heat in:	The crude vapor and liquid feed at the flash zone conditions
	The steam to the residue stripper
	The overflow liquid from the drawoff tray
Heat out:	The residue product
	The vapor of the total distillate products from the tray below the drawoff
	The overflow vapor from the tray below
	The steam from the flash zone at the conditions of the tray below

The temperature and quantities of these streams are known (from the material balance), except the quantity of overflow. Their temperatures are also known from the tower temperature profile or from previous calculations. To complete the calculation, let the lbs of overflow be x, and give all the streams their enthalpy value. Then solve the equation

$$\text{Heat in} = \text{Heat out}$$

to find the value of x.

Repeat the heat balance calculation for the envelope ending below the next pumparound drawoff tray. In this case the vapor leaving the envelope will contain the overflow vapor from the pumparound tray and all the distillate products except the heavier product drawn off from the pumparound tray below. It will also contain all the steam from the flash zone *and* from the side stream stripper of the heavier product. The remaining heat out of the envelope will be the stripped heavier product and the bottom pumparound duty in Btu/h. The heat into the envelope will be as before except this time the unknown overflow quantity will be that flowing from the lighter pumparound drawoff tray. It will also include the steam from the heavier product side stream stripper.

The Tower Diameter

The tower diameter may now be calculated from the vapor flow to the tray and the total liquid load on the tray. The quantity of the vapor to the tray has already been established. The liquid load on the tray will be:

The product drawoff liquid
The pumparound liquid
The calculated over flow liquid

These quantities must be in terms of weight and volume at the tray conditions of temperature and pressure.

The calculation procedure and data described below will give a good *estimate* of the tower diameter. For design purposes however the tray fabricator or designer data and procedure should be used. Trays are usually proprietary items covered by patents, and their performance therefore is subject to guarantees.

A calculation procedure to estimate the tower diameter is as follows:

Step 1. Summarize the liquid traffic through the tray.

Step 2. Select the type of tray that is to be considered for the design (in the case of an existing unit, refer to the fabricator's drawings). Valve and sieve trays have reasonable similarity in their major characteristics. Bubble cap trays are seldom used these days. A table of the valve tray characteristics is given in Appendix 3 of this chapter.

Step 3. Compute the liquid loading on the tray being checked for size. This will include all the liquid entering the tray. For example, on a side stream drawoff tray under a pumparound section, it will include:

- The side stream feed to the stripper
- The pumparound liquid
- The liquid overflow from the tray

This loading should be in cubic feet per second (CFS).

Step 4. In the case of a new design, set the downcomer area in accordance with Appendix 4 of this chapter. For an existing tray use the fabricator's drawings. Calculate the linear velocity of the liquid in ft/s. For good design this velocity should not exceed 0.6 ft/s at the downcomer outlet. Tray spacing should be such that the liquid level in the downcomer should not exceed 50 % of the tray spacing. To meet these criteria, tray spacing on these critical liquid loading trays may be higher than the remaining tray spacing in the tower.

Step 5. Summarize the vapor traffic to the critical tray under examination. This should be in lb/h and mol/h. The vapor should be the total vapor as used to calculate the tray overflow.

Step 6. Calculate the flood vapor velocity Gf in lb/h/sqft. For good tray design (or performance of an existing tray) the actual vapor velocity should not exceed 90 % of this flood value. This vapor flood velocity is calculated using the following expression:

$$G_{\mathrm{f}} = K_{\mathrm{f}}\sqrt{\rho_{\mathrm{v}}} \times (\rho_{\mathrm{l}} - \rho_{\mathrm{v}}) \tag{9}$$

where

G_{f} = Mass velocity in lb/h/sqft of bubble area at flood.

ρ_{v} = Density of vapor at the tray conditions in lb/cuft.

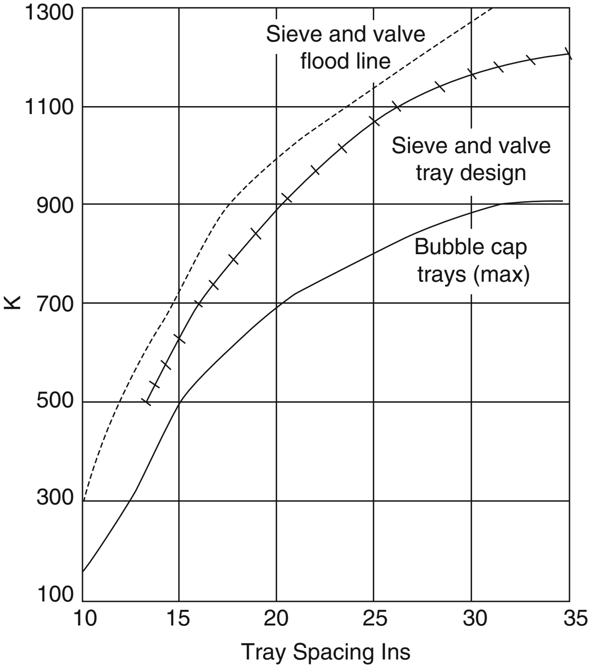
ρ_{l} = Density of liquid at the tray conditions in lb/cuft.

K_{f} = Constant based on tray spacing and given in Fig. 13.

Step 7. Using the actual vapor load per sqft of bubble area as 90 % of G_{f}, calculate the bubble area as G_{a} divided into the total vapor flow.

Step 8. Establish the following criteria using the characteristics given in Appendix 3

Fig. 13 Values for K_f



where

A_s = Total tray area in sqft.

A_{dc} = Inlet and outlet down comer areas in sqft.

A_w = Waste area (about 20 % of A_b).

A_b = Bubble area.

$A_s = A_b + A_w + A_{dc}$.

Use Appendix 4 (relationship of chord height, area, and length) as applicable.

Calculate the Overall Tower Height

Using the vapor and liquid calculations, check and fix the number of trays used to meet the tower's fractionation requirements. Then check the tray spacing. For normal fractionation a 24 in. tray spacing is acceptable. For drawoff trays with pumparound, the section should be checked for high downcomer filling (i.e., in excess of 50 %). Trays in this section often require bigger tray spacing, usually 30 in. Calculate the tower height allocated to the trays. Allow 6 f. between top tray and the top tangent line of the vessel to allow space for the reflux distributor and good liquid/vapor separation.

The space required for the flash zone (between the bottom fractionating tray and the top residue stripper tray) is usually 10–14 f. depending on throughput and the swirl size. The hot well below the bottom residue stripping tray should be sized to allow for the steam inlet distributor and a surge holdup of the residue product. This surge holdup is based on the company's operating policy, but as a guide:

- If the product is routed to storage, 5 min holdup.
- If the product is to be fed into a fired heater of a downstream unit, allow 15 min holdup.

The Stripper Column

This column is sized using the same procedure as used for the main column sizing. As mentioned earlier the strippers for the various side streams are usually stacked one above the other to form a single uniform diameter tower. The only diameter that may change is that for the holdup section in the bottom product stripper. This may be increased to adjust the height of the column to ensure the free flow of unstripped feed to each stripper from its respective drawoff tray in the main tower.

The number of trays for steam stripping is usually four. The tray spacing is also usually 24 in. For the height of the tower, begin with setting the height of the bottom stripper's bottom tangent line above grade. This should be at least 15 f. to allow a reasonable available NPSH for the product pump. From there allow a 5–15 min surge capacity at the calculated tower diameter and some 12 in. for the steam inlet distributor below its bottom stripping tray. Note the same comments apply to surge capacities in this tower as given for the residue stripper product.

The Crude Feed Preheat Exchanger System Design

All crude distillation units preheat the incoming crude oil feed by heat exchange with hot product and reflux streams. The preheated crude is then partially vaporized to satisfy the flash zone conditions by a fired heater. The degree of preheat is a question of an economic balance between the cost of the hardware and the savings in utilities due to the recovery of heat from the hot product and reflux streams. The exercise to arrive at this economic balance is a critical analysis of the respective enthalpy and the temperature levels of the various streams to be considered for heat exchange. It requires also good cost data for the heat equipment included in the system. This equipment must include the cost of the heat exchangers (usually shell and tube), cost of the final product coolers, and cost of the final crude feed fired heater.

More than one scheme can be developed and their capital costs calculated from up to date equipment vendor data, if possible. Next, the utility requirements and cost for each system are developed using the company's unit utility costs. For an examination and comparison of these systems, these cost data must be on the same basis for each of the schemes. The following procedure is one of several that can be used for this economic analysis:

Step 1. Construct the enthalpy curve for the crude feed. This stream will remain in the liquid phase through the preheat train. The enthalpy curve therefore needs only to consider sensible heat. Start at, say, 60 °F, and calculate the enthalpy by multiplying the Btu/lb (from the enthalpy curve) by the total weight in lb/h; this gives the enthalpy point on the curve in Btu/h. Proceed with a further 10–15 other temperature points to make a smooth temperature versus enthalpy curve.

Step 2. Examine the temperature and weight/h of the overhead, pumparound, and product streams. Select those that will be candidates for heat exchange against the crude feed. For example, the overhead stream from the main tower is a prime candidate for heat transfer against the cold crude because of its high heat content (latent heat) over a wide range of temperatures. The kerosene product stream on the other hand is usually a poor candidate. It contains only sensible heat over a short temperature range and is also probably the smallest product stream by weight.

Step 3. Prepare enthalpy curves for the selected candidates. In the case of pumparounds and the side stream products, only the enthalpy (in Btu/h) against, say, three or four temperatures needs to be plotted.

Step 4. The overhead vapor enthalpy curve requires a more complex calculation. Here the enthalpy curve must be based on its condensation curve. This requires a calculation of the stream's equilibrium (vapor and liquid) compositions at the condensing range of temperatures and pressures. For this purpose, assume a straight line pressure drop and temperature profiles between tower top and reflux drum. Select four to five pressures and their corresponding temperatures. For the purpose of this calculation, it is assumed that no steam condenses in this segment of the system; therefore, the equilibrium constants are taken at the partial pressure with steam. Using the overhead vapor composition (in mol/h) from the sum of overhead product plus reflux vapor, calculate its vapor/liquid composition at the selected temperatures and pressure. Apply the enthalpy values to both phases (not forgetting the steam) for the selected temperatures. Plot enthalpy in Btu/h versus the selected temperatures.

Step 5. Superimpose these product, overhead, and pumparound enthalpy curves on the crude feed enthalpy curve. Start with the overhead curve and then with each other stream in their process sequence. Draw these enthalpy curves to provide a reasonable temperature approach to the crude feed curve. Figure 14 is an example of this concept.

Reasonable temperature approaches should not be less than 20 °F for distillates and between 40 °F and 60 °F for residues and heavy distillates.

Step 6. Several different schemes can now be developed using a ruler, and set square for each of the product streams in different sequences. In the case of the exchange of heat against large volume streams such as the residue and perhaps the lower pumparound, these streams can be split. They can also be shown to flow in series against the crude or in parallel.

Step 7. Size the heat exchanger equipment required for each of the schemes developed. This includes the sizing for additional equipment for each stream to meet its required end temperature. For example, the final air coolers to meet product rundown temperature or trim coolers to meet pumparound return temperature.

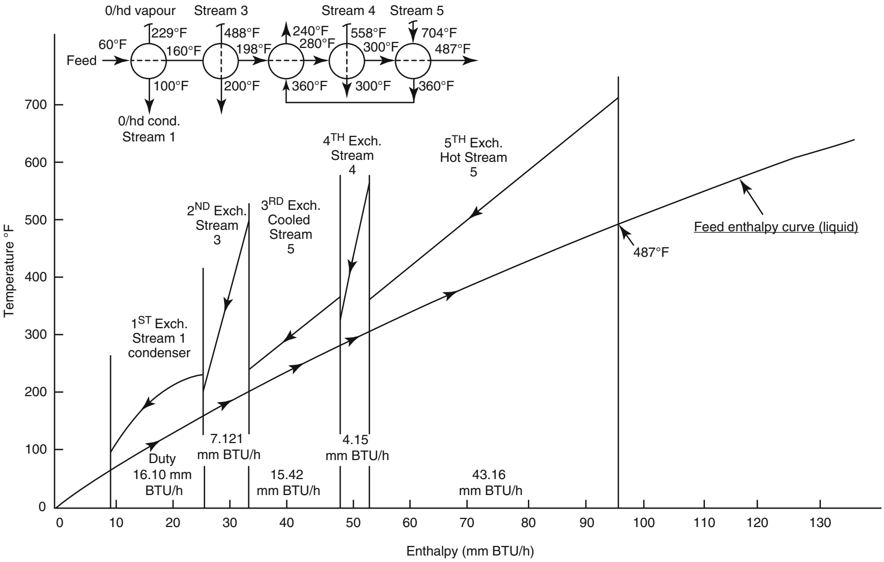


Fig. 14 Calculation of the crude preheat train

Sizing these items need not be precise as long as they are on the same basis. The simple equation for heat transfer:

$$Q = UA\,\Delta t_{\mathrm{m}} \tag{10}$$

will suffice for this purpose. The value of U may be taken from Fig. 12.

Step 8. Note the end temperature of the crude, and using this enthalpy and the total enthalpy in the crude at the flash zone of the main tower, determine the duty required by the fired heater in each case.

Step 9. Cost out the equipment required for each scheme. This includes all the heat exchangers (including trim and final coolers) and the fired heater. These can usually be obtained from equipment vendors on a unit size (e.g., $ per sqft) basis. Estimate the utility requirements for the equipment in each scheme.

Step 10. Tabulate the results starting with the highest capital cost scheme as a base case, and calculate a simple incremental return on investment based on savings for the remaining schemes. The scheme with the highest positive ROI should be the system selected.

In almost all modern crude distillation units, there are facilities to remove free salt. These desalting facilities are proprietary units which consist of freshwater injection into the crude feed and subsequent separation of the water, with the salt now in solution, from the oil. This separation takes place at a fixed temperature at the appropriate point in the crude feed preheat train. Demulsifying chemicals, or (more usually) electrostatic precipitators, or both are used to enhance this separation process. The temperature for this desalting process (usually around 220–250 °F) must be accommodated in the crude feed preheating.

An Example in the Design of an Atmospheric Crude Oil Distillation Tower

This example is confined to the design of the main fractionator and the associated stripper column. It is based on the processing of 30,000 BPSD of Kuwait crude providing the following products:

Overhead full-range naphtha	Gas to 375 °F
First side stream kerosene	375–480 °F
Second side stream light gas oil	480–610 °F
Third side stream heavy gas oil	610–680 °F

The distillation specifications shall be as follows:

- The ASTM end point of the naphtha shall not exceed 400 °F.
- The difference between the ASTM 95 % point of the naphtha and the 5 % point of the kerosene shall be at least 25 °F.
- The difference between the ASTM 95 % point of the kerosene and the 5 % point of the light gas oil shall be −10 °F (10° overlap).
- The ASTM end point of the light gas oil shall not be greater than 620 °F.
- The difference between the ASTM 95 % point of the light gas oil (LGO) and the 5 % point of the heavy gas oil (HGO) shall not exceed – 35 °F (35° overlap).
- The FBP of the TBP shall not exceed 710 °F and a Conradson carbon content of 8.0 % maximum.

Developing the Material Balance

The crude TBP and SG curves are given in Figs. 15 and 16, respectively. The TBP curve is divided into the distillate product cuts and also into narrow boiling point components.

The ASTM curves for the cuts are developed from the product cut points and probability paper. These are converted to TBP using the “Edmister” method as shown in Table 1.

These values are plotted on Fig. 17 and the narrow range components indicated for each of the product cuts. Note that the front end of the naphtha is the front end of the whole crude, so only the last segment of the cut is required in this calculation.

The cut characteristics are shown in Table 2.

Overflash	Cut range 690–725 (3 %vol on crude)
SG at 60 °F	0.891
Mol wt	295

The complete material balance can now be written as shown in Table 3.

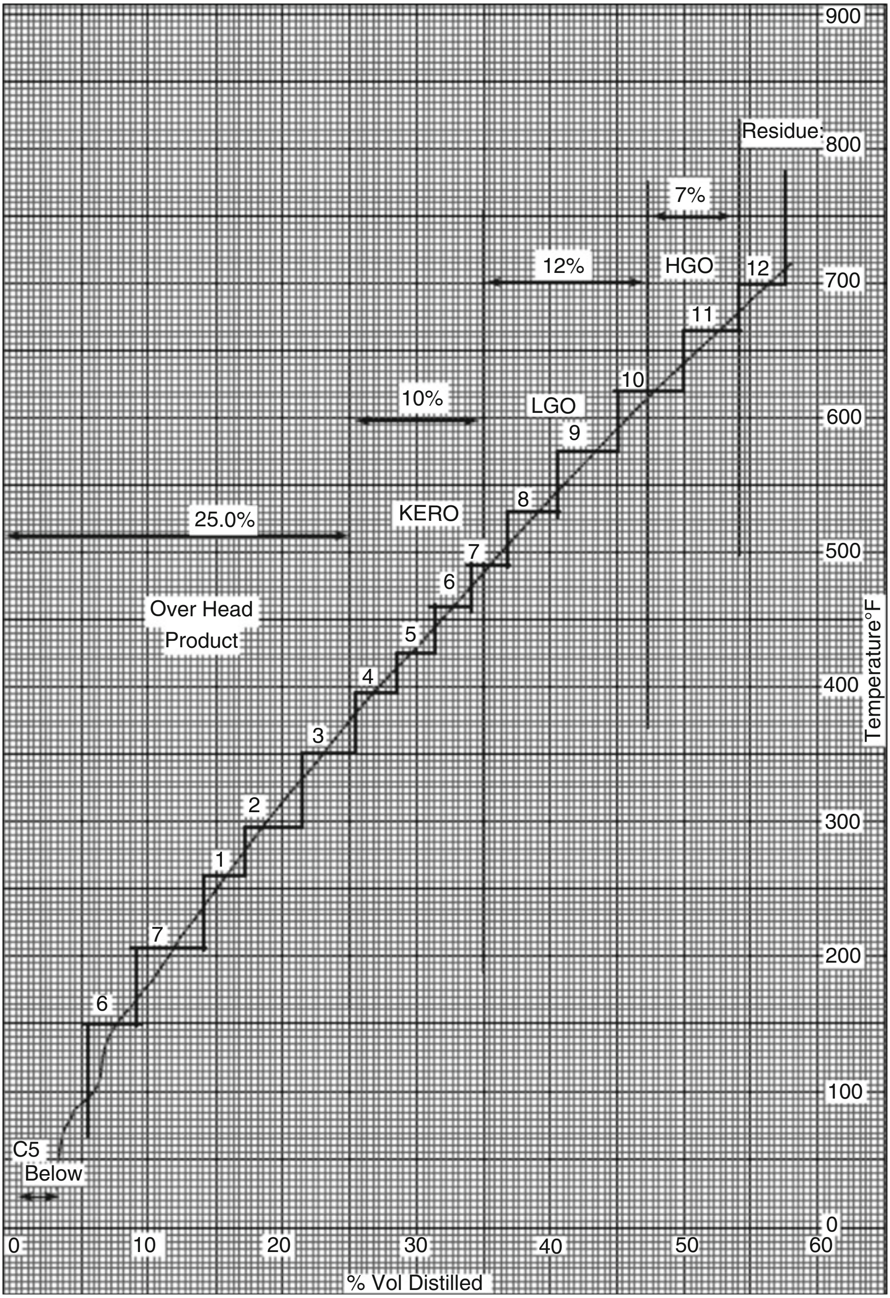


Fig. 15 The TBP curve for the example calculation

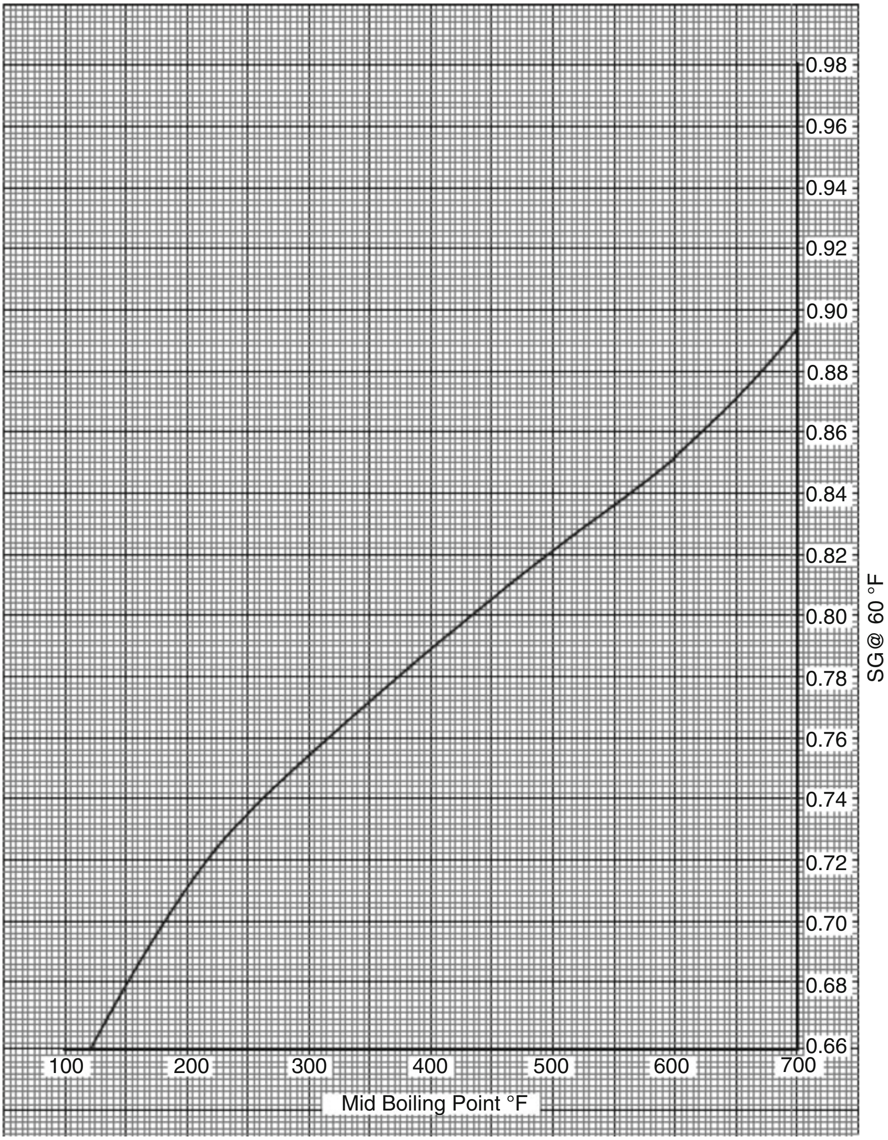


Fig. 16 The SG curve for the example calculation

Flash Zone Calculations

Total Pressure at the Flash Zone

Estimate the overhead reflux drum pressure as 5 psig (this will be checked later by a bubble point calculation at 100 °F).

Give the overhead air condenser a pressure drop of 5 psi. This is a reasonable pressure drop for this equipment and will be specified as such in the equipment data

Table 1 ASTM distillation conversion to TBP

	ASTM, °F	Δ*t* ASTM, °F	Δ*t* TBP, °F	TBP, °F
Naphtha (overhead)				
IBP		Not required		
10 %				
30 %				
50 %	300	10	14	305
70 %	310	20	27	319
90 %	330	28	32	346
FBP	358			378
Kero (first side stream)				
IBP	345	31	57	287
10 %		124	44	344
30 %	400	19	32	388
50 %	419	17	27	420
70 %	436	24	33	447
90 %	460	35	38	480
FBP	495			518
LGO (second side stream)				
IBP	495	25	48	457
10 %	520	12	25	505
30 %	532	11	20	530
50 %	543	16	26	550
70 %	559	13	19	576
90 %	572	23	27	595
FBP	595			622
HGO (third side stream)				
IBP	595	20	40	568
10 %	615	11	25	608
30 %	626	7	14	633
50 %	633	7	12	647
70 %	640	18	25	659
90 %	658	17	20	684
FBP	675			704

sheet to vendors. Give the crude to overhead vapor heat exchanger a pressure drop of 2 psi (overhead vapors flow shell side).

Neglect the pressure drop for fittings and piping – this will be quite small for a properly designed unit.

Then the total tower top pressure is 12 psig.

Assume 40 valve trays in the section of the tower between flash zone and tower top. Let the pressure drop per tray be 0.25 psi. Then pressure drop in this section of the tower is 10 psi.

Total flash zone pressure is 12 psig + 10 psi = 22 psig. Call it 25 psig (40 psia) for design purposes.

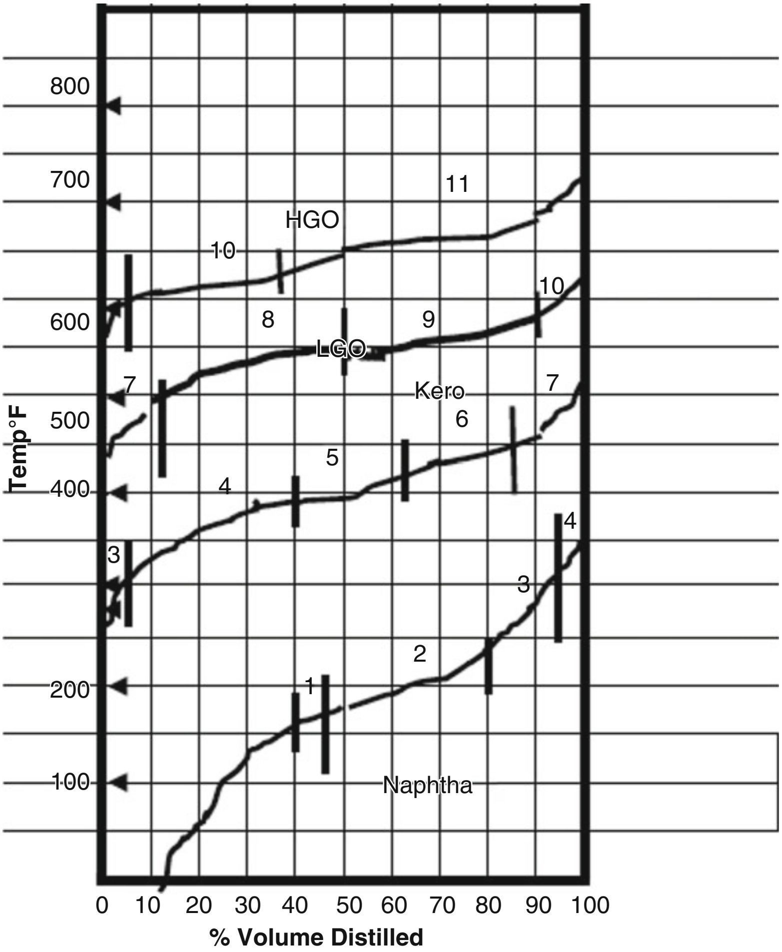


Fig. 17 Product curves and narrow range components

Calculate the Partial Pressure of the Hydrocarbon Vapor at the Flash Zone

Take the quantity of stripping steam as 1.2 lb/gal of residue (from Fig. 10).

$$\text{The lb/h of stripping steam is } 1.2 \times 24,150 \; = 28,980 \text{ lb/h.}$$
$$= 1,610 \text{ mol/h}$$

The partial pressure of the hydrocarbon vapor therefore is

$$\frac{\text{Moles HC vapor}}{\text{Total moles vapor}} \times \text{Total pressure} = \frac{1,364.4}{1,364.4 + 1,610} \times 40 \text{ psia} = 18.35 \text{ psia.}$$

Table 2 Cut characteristics

Component	%vol on crude	SG at 60 °F	Wt factor	Mol wt	Mol factor
Overheads cut from gas to 375 °F TBP cut point (25 vol% on crude)					
C2	0.11	0.374	0.411	30	0.014
C3	0.84	0.508	4.267	44	0.1
iC4	0.40	0.563	2.252	58	0.039
nC4	1.53	0.584	8.935	58	0.154
C5's	3.02	0.629	18.996	72	0.264
C6	3.60	0.675	24.300	86	0.286
C7	4.50	0.721	32.445	100	0.324
Comp 1	3.50	0.743	26.005	114	0.228
2	3.77	0.765	28.841	126	0.229
3	2.41	0.776	18.702	136	0.138
4	1.32	0.788	10.402	152	0.068
Total	25.0	0.702	175.556	95.2	1.884
Kerosene cut range 375–480 °F (10 %vol on crude)					
2	4.0	0.765	30.6	126	0.24
3	14.0	0.776	108.64	136	0.80
4	22.0	0.788	173.36	152	1.14
5	24.0	0.799	191.76	165	1.16
6	21.0	0.810	170.10	177	0.96
7	13.0	0.825	107.25	190	0.56
8	2.0	0.839	16.78	205	0.08
Total	100.0	0.798	798.49	161.6	4.94
Light gas oil cut range 480–610 °F (12 %vol on crude)					
6	2.0	0.810	16.2	177	0.09
7	9.0	0.825	74.25	190	0.39
8	38.5	0.839	323.02	205	1.58
9	40.5	0.848	343.44	238	1.51
10	10.0	0.860	86.00	250	0.34
Total	100.0	0.843	842.91	215.6	3.91
Heavy gas oil cut range 610–680 °F (7.0 %vol on crude)					
9	6.0	0.848	50.88	228	0.22
10	33.0	0.860	283.80	250	1.14
11	61.0	0.887	540.77	287	1.88
Total	100.0	0.875	875.45	270.2	3.24

Calculate the EFV Curve of Whole Crude at Atmospheric Pressure

From the crude TBP curve, the slope of the whole curve is 11.8 °F/%vol (10–70 % vol on TBP temperatures divided by 60). From the Maxwell curves the slope of the flash reference line is 8.5 °F/%vol. (See the chapter "▶ Introduction to Crude Oil and Petroleum Processing" in this Handbook.)

Table 3 The material balance

Stream	Cut range	%vol	Cum %vol	BPSD	GPH	SG	#/gal	lb/h	%wt	Mol wt	mol/h
Whole crude	–	100.0	100.0	30,000	52,500	0.8685	7.23	379,575	100.0	225.3	1,684.8
O/head	IBP	25.0	25.0	7,500	13,125	0.702	5.84	76,650	20.2	95.2	805.1
	−360										
Kero	−480	10.0	35.0	3,000	5,250	0.798	6.64	34,860	9.2	161.6	215.7
LGO	−610	12.0	47.0	3,600	6,300	0.843	7.02	44,226	11.7	215.6	205.1
HGO	−690	7.0	54.0	2,100	3,675	0.875	7.28	26,754	7.0	270.2	99.0
Resid	+690	46.0	100.0	13,800	24,150	0.957	8.16	197,085	51.9	547.6	359.9
The flash zone material balance											
O/flash	−725	3.0	57.0	900	1,575	0.891	7.4	11,655	3.0	295	39.5
Prod vapor	−690	54.0	54.0	16,200	28,350	0.773	6.43	182,490	48.1	137.7	1,324.9
Total vap	−725	57.0	57.0	17,100	29,925	0.780	6.49	194,145	51.1	142.3	1,364.4
Resid[a]	+725	43.0	43.0	12,900	22,575	0.988	8.22	185,430	48.9	578.7	320.4
Total		100.0	100.0	30,000	52,500	0.8685	7.23	379,575	100.0	225.3	1,684.8

[a] Does not include liquid overflow from bottom wash tray

Table 4 Flash curve at atmospheric pressure

	TBP		EFV				
%vol	Curve, °F	DRL	ΔT	Ratio	ΔT_1	FRL	Flash, °F
0	−127	75	−202	0.24	−48	200	152
10	190	190	0	0.4	0	285	285
30	420	430	−10	0.34	−3	450	447
50	645	667	−22	0.34	−8	627	619
70	900	900	0	0.34	0	795	795
90	1,235	1,140	95	0.34	32	915	947
100	2,192	1,250	942	0.34	320	1,040	1,360

$$\Delta \mathrm{T}_{50\%}\,(\mathrm{DRL} - \mathrm{FRL}) = 40\,^{\circ}\mathrm{F}$$

$$\mathrm{T}_{50\%}\ \mathrm{DRL} = 667\,^{\circ}\mathrm{F}$$

$$\text{Then } \mathrm{T}_{50\%}\ \mathrm{FRL} = 667 - 40 = 627\,^{\circ}\mathrm{F}$$

Table 4 defines the flash curve at atmospheric pressure.

The flash curve calculated above is that at atmospheric pressure. To plot this at any other pressure, take the 50 %vol temperature, and using the vapor pressure curves for hydrocarbons (see Appendix 1 of this chapter), read off the temperature at the desired pressure. Draw the EFV curve through this new temperature parallel to the atmospheric curve. The flash zone temperature is the temperature at the % distilled on the partial pressure curve.

$$\text{Flash zone temperature} = 720\,^{\circ}\mathrm{F}$$

The EFV curve is shown in Fig. 18.

Calculate Total Heat in the Crude at the Flash Zone Conditions

See Table 5 for the calculation of total heat in the crude at the flash zone conditions.

Please note: The enthalpy data used here are taken from the author's private files. It is recommended that the data given in Maxwell's *Hydrocarbon Data* or *The GPSA Engineering Data Book* be used for these heat balance calculations.

The Tower Heat Balances

To Calculate the Temperature of the Residue Product Leaving the Tower

Consider the heat balance over the residue stripper as shown by the envelope in Fig. 11. The product residue is 197,085 lb/h (from the material balance). The stripout vapor from the top stripping tray is 6 % (from Fig. 10) = 1,449 gal/h. Assume that the SG of the stripout is 7.5 lb/gal (about the same as the

Fig. 18 EFV curve for whole crude at flash zone conditions

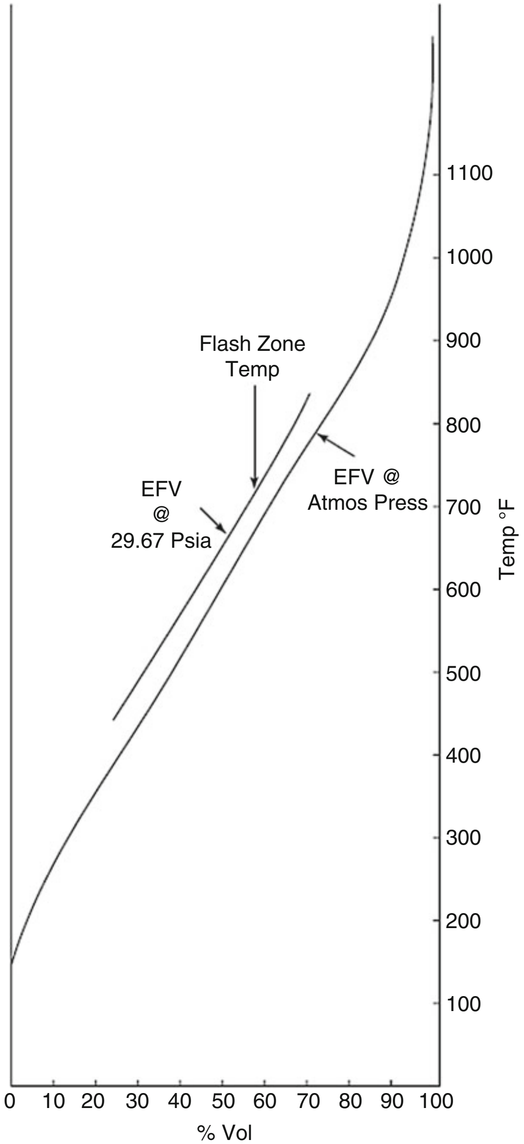


Table 5 Calculation of total heat in the crude at the flash zone conditions

Stream	V/L	°API	Wat. K	°F	Weight, lb/h	Btu/lb	MMBtu/h
Crude vapor	V	50.0	11.8	720	194,145	528	102.509
Crude liquid	L	11.5	11.5	720	185,430	396	73.43
Total					379,575		175.939

Table 6 Flash zone balance

						Enthalpy	
Stream	V/L	°API	Wat. K	Temp, °F	Weight, lb/h	Btu/lb	MMBtu/h
In							
Residue	L	13	11.5	720	197,085	396	78.046
Stripout	L	25.5	11.5	720	10,868	410	4.456
Steam	V			450	28,980	1,290	37.384
Total in					236,923		119.916
Out							
Residue	L	13	11.5	t	197,085	x	197,085x
Stripout	V	25.5	11.5	715	10,868	490	5.325
Steam	V			715	28,980	1,383[a]	40.079
Total out					236,933		45.404 + 197,085*x*

[a] At partial pressure of the flash zone = 13.53 psig

overflash) and the mol wt is 305. Then the heat balance can be written as follows (see also Table 6):

$$\text{Heat in} \quad = \text{Heat out}$$

$$197,085x + 45,404,000 = 119,916,000$$
$$x = 378 \text{ Btu/lb}$$

From enthalpy tables, this equates to 704 °F.

To Calculate the Side Stream Drawoff Temperatures

The steam rates to be used for side stream stripping will be:

All strippers will have three theoretical trays.
Each gas oil stream stripper will use 0.5 lb/gal.
The Kero stripper will use 0.65 lb/gal of steam.

Steam used is as follows:

$$\text{Heavy gas oil} = 3,675 \times 0.5 = 1,838 \text{ lb/h}$$
$$\text{Light gas oil} = 6,300 \times 0.5 = 3,150 \text{ lb/h}$$
$$\text{Kero} = 5,250 \times 0.65 = 3,413 \text{ lb/h}$$

Tower pressure profile.

There will be 40 fractionating trays in the main tower (trays above the flash zone) and four residue stripping trays (trays below the flash zone). These trays will be numbered from the bottom to the top. Thus, the bottom residue stripping tray will be tray 1. The tower top tray will be tray 45. The pressure profile is shown in Fig. 19.

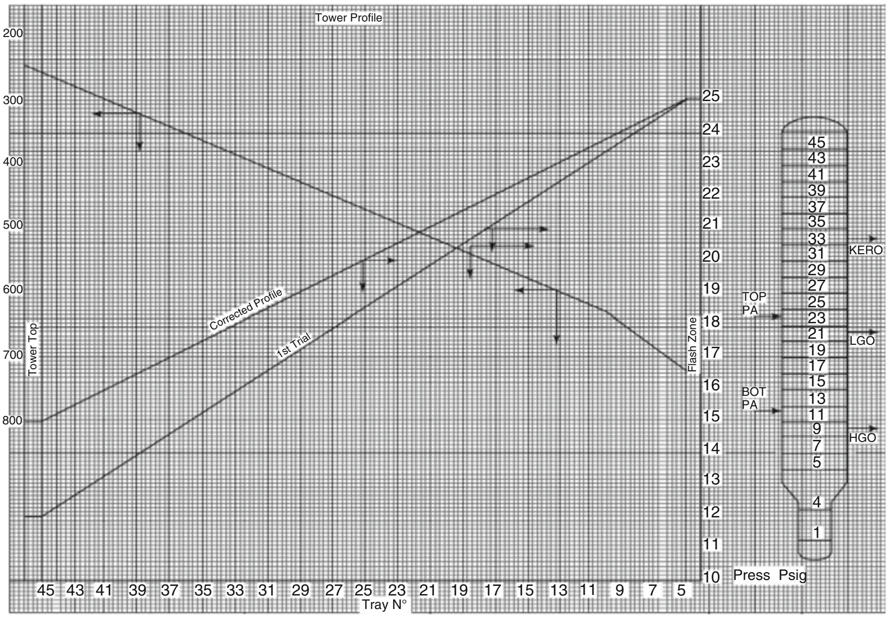


Fig. 19 Tower pressure profile

Establish drawoff tray location.

Allow six wash trays above the flash zone to the HGO drawoff. The HGO and bottom pumparound will be drawn from tray 10.

Allow two trays for the pumparound return. Thus the pumparound will return on to tray 12.

Allow ten trays from tray 12 to the LGO and the top pumparound drawoff. The drawoff tray will then be tray 22.

Again allow two trays for the pumparound return. This will be tray 24.

Allow ten trays between top pumparound return and the Kero drawoff. This locates the Kero drawoff at tray 34. It leaves 12 trays between the Kero drawoff and the top tray (includes the drawoff tray and the top tray).

Summary of tray locations and total pressure (1st trial)

	Tray no	Pressure (psig)
HGO drawoff	10	23.4
BPA return	12	22.7
LGO drawoff	22	19.5
TPA return	24	18.8
Kero drawoff	34	15.5

Calculate theoretical initial boiling points

The FRL for each cut is developed from the TBP cut. Thus,

HGO	50 % TBP is 648 °F. Slope of TBP is 0.6 °F/%vol
	Slope of FRL is 0.2 °F/%. $\Delta t50$ (DRL – FRL) is 7 °F
	50 % FRL is 641 °F. From FRL curve IBP is 626 °F
LGO	This is developed in the same manner as HGO, and the IBP of the FRL in this case is 527 °F
Kero	In the same way, the Kero FRL has an IBP of 395 °F

Now all these temperatures are at atmospheric pressure. It is now required to relate these temperatures to the partial pressure of the respective trays.

To calculate the approximate partial pressures and drawoff temperatures

Assumptions:

1. All vapor lighter than the product cut is considered inert.
2. Internal reflux is assumed as follows:
   To HGO tray 290 mol/h
   To LGO tray 250 mol/h
   To Kero tray 200 mol/h

$$\begin{aligned}\text{HGO tray partial pressure} &= \frac{\text{Moles of HGO}}{\text{Total moles HC vapor} + \text{Steam}} \times \text{ Total pressure}\\ &= \frac{1,614.9}{3,224.9} \times 38.1 = 19.6 \text{ psia}\end{aligned} \tag{11}$$

From vapor pressure curves, theoretical drawoff temperature is 720 °F.

From Fig. 9:

Theoretical temperature–Actual temperature = 93 °F.
Actual drawoff temperature is 720–93 = 627 °F.

Drawoff temperatures for the LGO and Kero are calculated in the same way and are:

LGO = 493 °F.
Kero = 364 °F.

To Calculate the Tower Top Temperature

Set the reflux drum temperature and pressure. In this case these will be set at 10 psig and 100 °F. Taking the pressure drop across the exchangers and piping the tower top pressure will be 15 psig.

Table 7 Tower overhead composition

Comp	Mol frac	First trial K	At 250 °F $X = y/K$	Mol wt	Weight factor	SG at 60	Volume factor
C2	0.008	Neg	Nil				
C3	0.054	73.77	0.001	44	0.044	0.508	0.009
iC4	0.021	35.24	0.001	58	0.058	0.563	0.010
nC4	0.084	27.05	0.003	58	0.174	0.584	0.030
C5	0.143	11.80	0.012	72	0.864	0.629	0.137
C6	0.155	4.590	0.034	85	2.89	0.675	0.428
C7	0.175	2.213	0.079	100	7.90	0.721	1.100
Comp 1	0.124	1.066	0.116	114	13.224	0.743	1.780
Comp 2	0.124	0.557	0.223	126	28.098	0.765	3.673
Comp 3	0.075	0.311	0.241	136	32.776	0.776	4.224
Comp 4	0.037	0.135	0.274	152	41.648	0.788	5.285
Total	1.000		0.984	129.7	127.676	0.766	16.675

$K2 = K1 \times Sx = 0.135 \times 0.984 = 0.133 => 246\,°\text{F}$ which will be the tower top temperature.

Fix the cold external reflux at 0.8 times the total moles overhead product.

The total number of moles of HC in the overhead vapor is 1.8 × 805.1 = 1,449.18 mol/h.

Total moles of steam in the overhead vapor is 2,076.

Partial pressure of the hydrocarbons in the overhead vapor is

$$\frac{1,449.19 \times 29.7}{3,525.18} = 12.2 \text{ psia}$$

The tower overhead temperature is the dew point of the hydrocarbons at the partial pressure and is shown in Table 7.

To Calculate Side Stream Stripper Bottom Temperatures

These are calculated by heat balances over the respective side stream strippers. The following criteria are used in these calculations:

	HGO	LGO	KERO
Total stripout % vol	5	8	8
Mol wt of stripout	230	180	120
SG of stripout	0.865	0.820	0.750

Only the heat balance calculation of the HGO stripper is given below (see also Table 8). The other two stripper calculations will be similar in form (Figs. 20, 21, and 22):

Table 8 HGO stripper balance

Stream	V/L	°API	Wat. K	°F	lb/h	Btu/lb	MMBtu/h
In							
Feed ex HGO	L	30	11.5	627	26,754	347	9.284
Steam	V	–	–	450	1,838	1,290	2.371
Stripout	L	32	11.5	627	1,390	349	0.485
Total in					29,982		12.14
Out							
HGO	L	30	11.5	t °F	26,754	x	26,754x
Steam	V			622	1,838	1,376[a]	2.529
Stripout	V	32	11.5	622	1,390	442	0.614
Total out					29,982		3.143 + 26,754x

[a] At partial pressure of 36.3 psia

$$\text{Solving for } x: 26,754\,x = 8,997,000$$
$$x = 336\ \text{Btu/lb}$$

From enthalpy tables => 615 °F.

Temperature of LGO leaving its stripper = 488 °F.

Temperature of Kero leaving its stripper = 359 °F.

Overall Tower Heat Balance

Tower Overhead Heat Balances

Balance included by envelope 1 determines the overhead condenser duty. See Tables 9 and 10.

The overhead condenser duty is 71.360 MMBtu/h; therefore, the heat removed by intermediate refluxes (pumparound) is 115.717−71.360 = 44.357 MMBtu/h.

The heat balance included in envelope 2 determines the internal reflux from the top tray.

This is as follows:

Let x be the lb/h of overflow from the top tray. Then the heat balance is as follows (see also Table 11):

$$\begin{aligned}\text{Solving for } x &= \frac{12,879,000}{121}\\ &= 106,438\ \text{lb/h}\\ &= 821\ \text{mol/h or } 16,736\ \text{GPH.}\end{aligned}$$

Check for fractionation (using this chapter's Appendix 2):

Overflow at 60 °F = 16,736 GPH.
Overflow at 255° = 19,029 GPH.
Prod vapor to top tray = 13,125 GPH.
Reflux ratio =1.45.

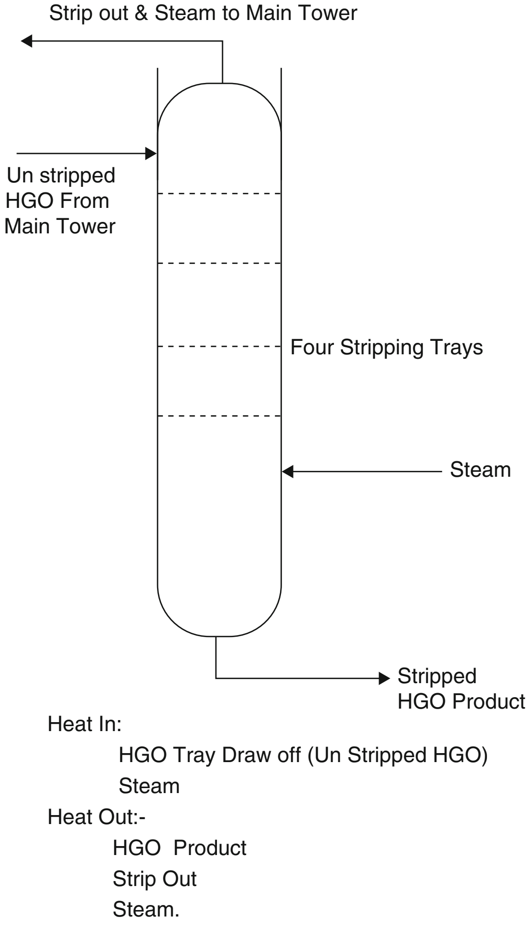


Fig. 20 Heat balance diagram over HGO stripper

Number of trays = 12.
Factor is 12 × 1.45 = 17.4.

50 % TBP difference between naphtha and Kero is 420–265 = 155 °F.
ASTM Gap is 30°F which is within Spec.

Calculating the Remaining Tower Loadings

The tower loadings at the remaining critical sections of the tower are provided by heat balances over the envelopes given in the heat balance diagram (Fig. 23). These critical sections are:

- Below bottom pumparound drawoff (envelope 1)
- Below top pumparound drawoff (envelope 2)
- Below Kero drawoff (envelope 3)

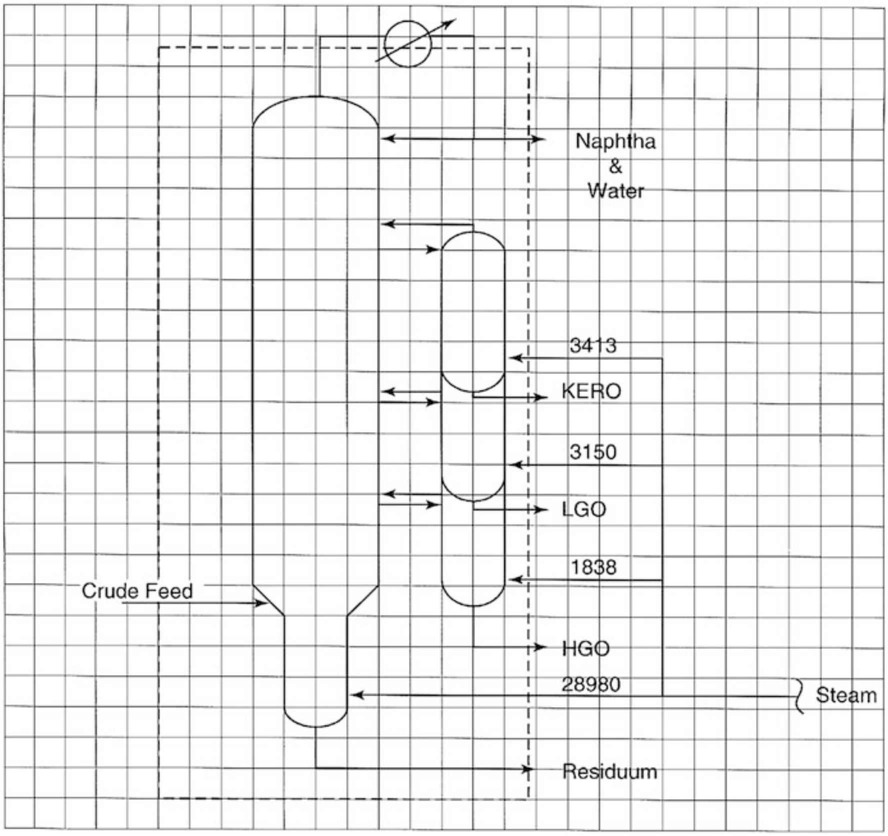


Fig. 21 Overall tower heat balance diagram

Only the heat balance over envelope 3 is given in Table 12. The others follow in a similar fashion, but the summaries of the calculated loads are given for all three sections (see Table 13):

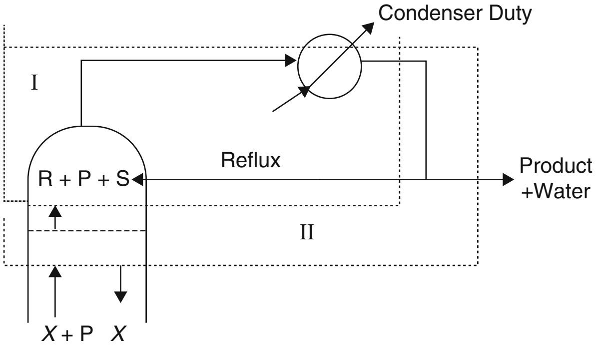
$$\text{Solving for } x_3 = \frac{2,391,000}{111} = 21,540\ \text{lb/h}.$$

Checking fractionation:

Between HGO and LGO

$$\text{Reflux ratio} = \frac{22,809}{24,675} = 0.92$$

Number of trays = 11 (2 PA trays = 1 Frac tray).
Factor = 10.2.



Envelope I:-
  Heat In
    Reflux + Product Vapor
    Steam
  Heat Out
    Reflux Liquid
    Product Liquid
    Water
    Condenser Duty
Envelope II:-
  Heat In
    Internal Reflux *X* Vapor
    Product Vapor
    Steam
  Heat Out
    Internal Reflux *X* Liquid
    Product Liqued
    Water
    Condenser Duty.

Fig. 22 Tower overhead heat balance diagram

Table 9 Tower overall heat balance

Stream	V/L	°API	Wat. K	°F	lb/h	Btu/lb	MMBtu/h
In							
Crude	V + L	–	11.7	720	379,575		175.939
Steam	V				37,381	1,290	48.221
Total in					416,956		224.160
Out							
Residue	L	13	11.5	704	197,085	378	74.498
HGO	L	30	11.5	615	26,754	336	8.989
LGO	L	36.3	11.5	488	44,226	255	11.278
Kero	L	45.5	12	359	34,860	184	6.414
Naphtha	L	70.0	12	100	37,381	100	3.738
Refluxes							115.717
Total out					416,956		224.160

Table 10 Tower overhead condenser duty

Stream	V/L	°API	Wat. K	°F	lb/h	Btu/lb	MMBtu/h
In							
Naphtha	V	70	12	246	76,650	266	20.389
Reflux	V	70	12	246	61,230	266	16.311
Steam	V			246	37,381	1,197	44.745
Total in					175,351		81.445
Out							
Naphtha	L	70	12	100	76,650	46	3.526
Reflux	L	70	12	100	61,320	46	2.821
Water	L			100	37,381	100	3.738
Cond duty							71.360
Total out					175,351		81.445

Table 11 Tower overhead heat balance

Stream	V/L	°API	Wat. K	°F	lb/h	Btu/lb	MMBtu/h
In							
Naphtha	V	70	12	262	76,650	273	20.925
O/flow	V	53	12	262	x	249	$249x$
Steam	V			262	37,381	1,199	44.82
Total in					$114, 031 + x$		$65.745 + 249x$
Out							
Naphtha	L	70	12	100	76,650	46	3.526
O/flow	L	53	12	255	x	128	$128x$
Water	L			100	37,381	100	3.738
Cond duty							71.360
Total out					$114.031 + x$		$78.624 + 128x$

Δ50 %TBP =300 °F.

ASTM gap is +31 °F which is well within the requirement for these two cuts.

Between LGO and Kero

Reflux ratio = 0.21.

Number of trays = 11 (includes credit for PA trays).

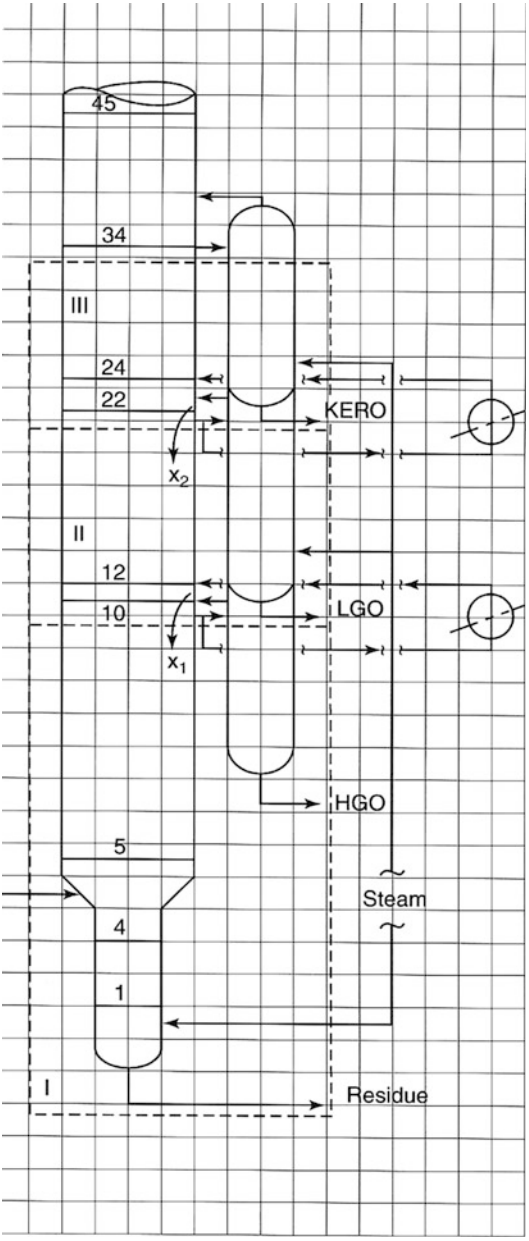
Factor = 2.3.

Δ50 %TBP = 185 °F.

ASTM gap = −10 °F.

This is poor, but as the Kero cut is to be used as a blend stock, it will be accepted. In the final design, however, provision will be made to increase the overhead reflux at the expense of the bottom pumparound to improve this separation.

Fig. 23 Remaining heat balance diagram for tower loading



Tower Diameter Calculations

The calculation for tower vapor flood capacity is given by the expression

$$G_f = K_r \sqrt{\rho_v \times (\rho_l - \rho_v)} \tag{12}$$

Table 12 Heat balance over envelope 3

Stream	V/L	°API	Wat. K	°F	lb/h	Btu/lb	MMBtu/h
ENV 3							
IN							
Heat in crude	V+L	–			379,575		175.939
Steam	V			450	33,968	1,290	43.819
Tray34 o/flow	L	46.3	12	367	$x3$	191	$191x3$
Total in					413,543 + x_3		219,758 + x_3
Out							
O/flow to tray 34	V	46.3	12	370	x_3	302	$302x_3$
Vapor to tray 34	V	62.5	12	370	111,510	320	35.683
Steam to tray 34	V			370	33,968	1,253[a]	42.562
LGO prod	L	36.3	11.5	488	44,226	255	11.278
HGO prod	L	30	11.5	615	26,754	336	8.989
Residue	L	13	11.5	704	197,085	378	74.498
Top PA							26.614
Bot PA							17.743
Total out					413,543 + x_3		217.367 + $302x_3$

[a] Steam at the partial pressure of 18.3 psia

G_f = Mass velocity of vapor at flood in lb/h·sqft of bubble area.
K_r = 1,100 for a 24″ tray spacing.

The largest diameter will always be below the bottom pumparound in terms of the vapor load. For a quick estimate let the bubble area be 80 % of the total tower diameter.

Below Bottom Pumparound Loading

Assume bottom pumparound returns to tower at 300 °F.

Total PA duty = 17,740,000 Btu/h.
Enthalpy at 627 °F = 347 Btu/lb.
Enthalpy at 300 °F = 140 Btu/lb.

$$\text{The lb/h of the PA stream is} \frac{17,740,000}{207} = 85,715\,\text{lb/h or}\,11,774\ \text{GPH}$$

GPH of unstripped HGO product = 3,668.
GPH of overflow = 23,990.

Table 13 Summary of the main tower loading

Liquid – from tray				Vapor – to tray		
Drawoff tray	lb/h	GPH	Hot GPH	lb/h	Mol wt	mol/h
Tray 10[a]		At 627 °F			At 632 °F	
Hydrocarbons	174,648	23,990	32,760	357,138	181	1,976.9
Steam	–	–	–	28,980	18	1,610.0
Total	174,648	23,990	32,760	386,118	107.6	3,586.9
Tray 22[a]		At 498 °F		At 500 °F		
Hydrocarbons	122,412	17,487	22,809	278,148	154	1,802.9
Steam	–			30,818	18	1,027.3
Total	122,412	17,487	22,809	308,966	109	2,830.2
Tray 34		At 367 °F			At 370 °F	
Hydrocarbons	21,540	3,254	3,925	133,050	115	1,157.8
Steam				33,968	18	1,887.1
Total	21,540	3,254	3,925	167,018	55	3,044.9
Tray 45		At 255 °F			At 262 °F	
Hydrocarbons	106,438	16,735	19,029	183,089	112.6	1,626.1
Steam				37,381	18	2,076.7
Total	106,438	16,735	19,029	220,469	59.5	3,702.8

[a] Does not include pumparound liquid stream

Total liquid flow on the tray = 39,632 GPH at 60 °F.

The loading data on this tray is as follows:

	Vapor	Liquid
Temperature °F	632	627
Pressure psig	23.8	–
mol/h	3,586.9	GPH hot 54,120
lb/h	386,118	lb/h 288,522
ACFS	302	2.0
ρv lb/cuft	0.355	lb/cuft 39.9

$$\begin{aligned} G_f &= 1,100\sqrt{0.355 \times (39.9 - 0.355)} \\ &= 4,121 \text{ lb/h} \cdot \text{sqft} \end{aligned}$$

$$G_a = 4,121 \times 0.8 = 3,297 \text{ lb/h sqft}$$

$$\text{Tray area required to handle vapor } = \frac{386,118}{3,297} = 117 \text{ sqft}$$

This may be considered as the bubble area.

Let the downcomer area be such that liquid flow is 0.6 ft/s. Area required is

$$\frac{2.0\text{ACFS}}{0.6} = 3\,\text{sqft}$$

$$\text{For two}(\text{inlet} + \text{outlet})A_{\text{dc}} = 6\text{sqft}$$

Waste area is taken as 20% of $A_b = 117 \times 0.20 = 23.4\,\text{sqft}$.

Then $A_s = 117 + 23.4 + 6 = 146$ sqft.
Tower diameter at this location is 13.6 f. i/d.

Other Sections of the Tower

The other sections of the tower where there may be changes in diameter are below the top pumparound drawoff and, of course, the bottom stripper top tray. The tower top tray should also be checked for loading.

The same calculation is followed for these other sections, but it is not proposed to show them here. The results of the calculations though gave the following:

Top section of the main tower above tray 24 diameter is 10 f. i/d.
Bottoms stripper section below tray 4 diameter will be 7 f. i/d.

A diagram of the main tower and the associated stripper tower is shown in Fig. 24.

The Vacuum Crude Distillation Unit

As an introduction to this part of the chapter, it will be of interest to outline briefly an important development that occurred in this process during the early 1960s. Originally vacuum units followed closely the design of the atmospheric units except, of course, they operated under a vacuum condition. The vacuum was obtained by a two- or three-stage steam ejectors, and the internals of the tower were traditional trays, mostly bubble cap type. Under these conditions the vacuum obtained in the flash zone required the injection of steam to provide the required hydrocarbon partial pressure for adequate vaporization of the fuel oil feed. With the molecular weight of steam low at 18, the tower vapor traffic was extremely high in velocity requiring a large tower diameter to accommodate it.

The breakthrough to provide vacuum towers of much lower diameters came in the 1960s with the use of high-capacity steam ejectors producing very low vacuum condition in the tower overhead. This coupled with the development of highly efficient expanded grid internals with very low pressure drop allowed the desired flash zone conditions to be met without the injection of steam. This process became known as the “Dry Vac” process and is the accepted process now for vacuum crude distillation. Such a process is described below.

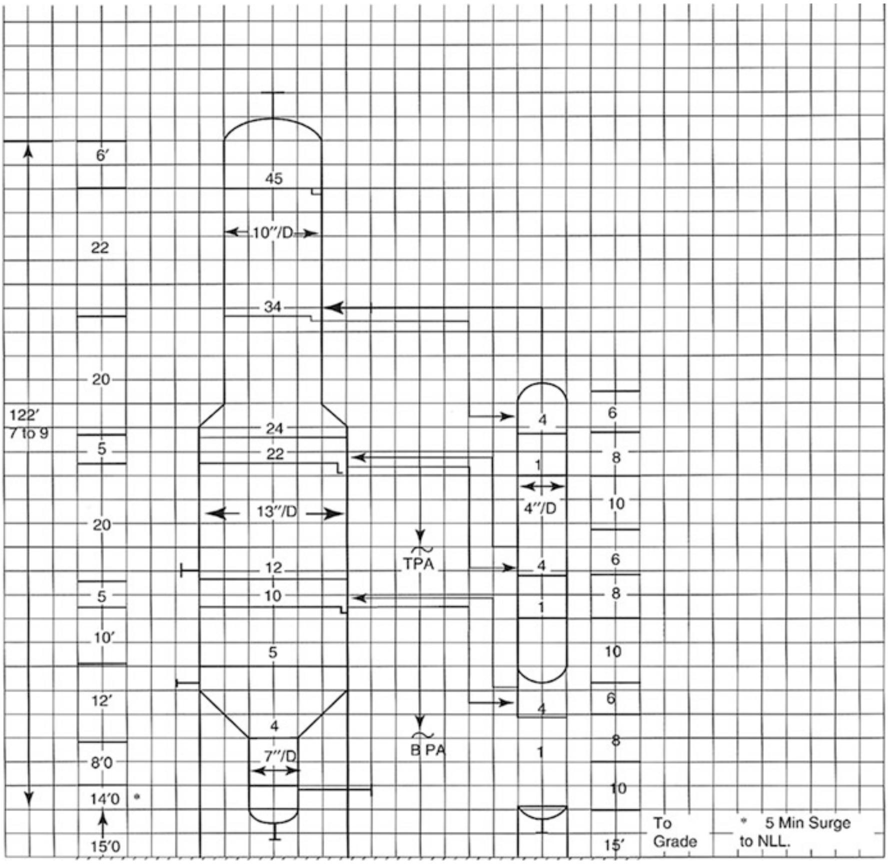


Fig. 24 Main tower and side stream tower diagram

Process Description

This process is often integrated with the atmospheric crude distillation unit as far as heat transfer is concerned. Generally the atmospheric residue from the CDU is routed hot to the fired heater of the vacuum unit (Fig. 25).

The atmospheric residue is further distilled to provide the heavy distillate streams used for producing lube oil or as feed to conversion units. This distillation however has to be conducted under subatmospheric pressure conditions. The temperature required for vaporizing the residue at atmospheric pressure would be too high and the crude would crack.

The process follows very much the same pattern as the atmospheric distillation. Should the cold feed be pumped from storage, it is heat exchanged against hot product and pumparound streams before being vaporized in the distillation unit heater. Normally, though, the feed is pumped hot directly from the CDU’s residue stripper to the vacuum unit’s heater. Thereafter the distillate vapors are condensed

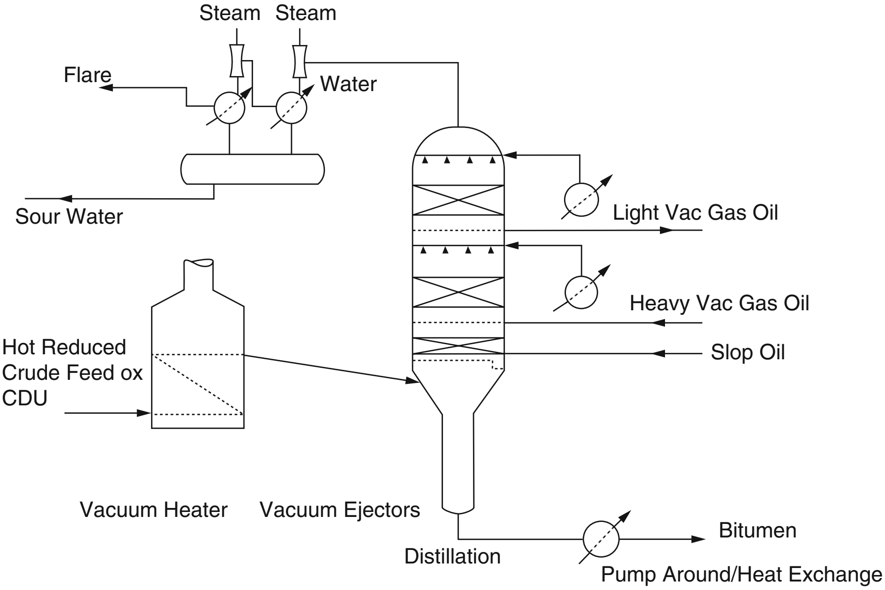


Fig. 25 Vacuum distillation unit process schematic

in the tower by heat and mass transfer with the cold reflux streams moving down the tower in the same way as the side streams in the atmospheric unit. The products are taken off at the appropriate sections and are cooled either by heat exchange with colder streams in the atmospheric unit, by air coolers, or, in some cases, as heating media for light ends reboilers. They are then pumped to storage.

Neither the vacuum residue that leaves the bottom of the tower in this process nor the side streams are steam stripped. The vacuum condition is produced by steam ejectors taking suction from the top of the tower. These ejectors remove inert and other vapors that may exist and pull a vacuum of about 5 mmHg absolute. The tower internals are usually expanded grid type which offer low pressure drop such that the flash zone pressure is about 25–30 mmHg absolute.

The Vacuum Crude Distillation Unit's Flash Zone

At atmospheric pressure the flash temperature of normal atmospheric residue to achieve any meaningful degree of vaporization would be extremely high (say in excess of 900 °F). At these temperatures the heavy residue will begin to break up or crack. This forms coke and olefinic products which may not be desirable to the refiner. Effective vaporization and fractionation can be achieved however at reduced pressures. Under this condition a reasonable flash temperature (say 650–750 °F) can be easily obtained.

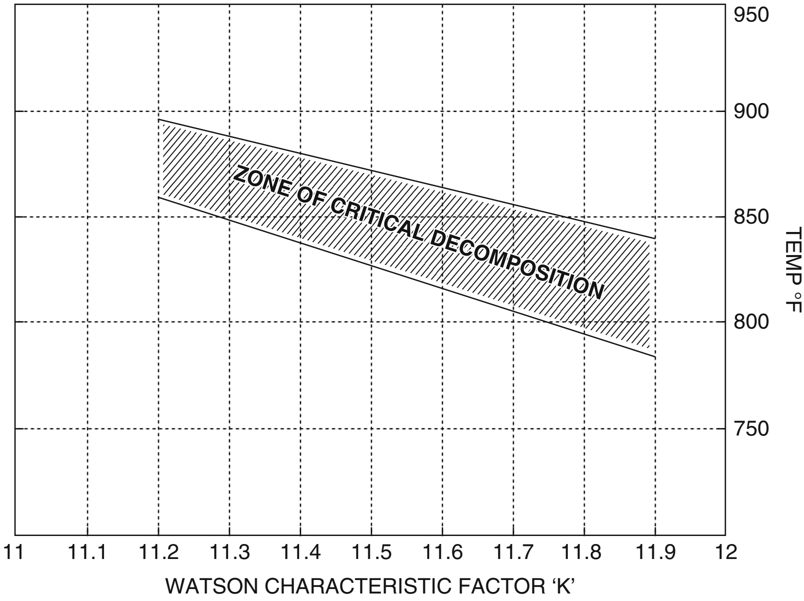


Fig. 26 Critical cracking zone

As described earlier, vacuum distillation units handling reduced crude operate at 3–5 mmHg at the top of the tower and about 25–30 mmHg in the flash zone. No steam is used for stripping. The oil can still crack of course if the cut point desired is so high that excessively high flash temperature is required to meet it even at reduced pressures. The following graph is a guide to the critical cracking temperatures (Fig. 26).

This graph shows a plot of a range of temperatures within which the oil will begin to crack. This is correlated to the Watson characterization factor "K." Most residua with a 700 °F cut point for Middle East crudes have a "K" factor of about 11.5. From the curve, therefore, it can be seen that these residua would begin to crack at temperatures between 830 °F and 855 °F. The degree of cracking at or above the "zone of critical decomposition" will be a function of temperature and the residence time of the oil at that temperature.

Significant cracking of the oil in a vacuum tower causes:

- High load to the ejectors (due to the formation of light ends)
- In lube oil production, decolorizing of the distillate streams
- When producing feed to hydrotreaters or hydrocrackers, high hydrogen consumption in these units due to the presence of unsaturates as the product of cracking

It is therefore very desirable to avoid these critical temperatures in a vacuum unit.

The Tower Overhead Ejector System

Most "Dry Vac" towers have a similar overhead ejector system, and as the design of this is critical to the unit operation, a calculation method to determine this design is described below:

The calculation procedure that is described here relates to the "dry" vacuum unit where no steam is used in the distillation process itself. This method can be used to determine the efficiency of the installed ejector set under test run conditions or indeed to specify the equipment to be purchased. The efficiency of the ejectors may be determined by the actual quantities of steam used relative to those calculated by this method.

The following data need to be obtained to use this procedure:

- Quantity of inerts – either measured at the exhaust side of the last stage or established as design criteria
- Tower top temperature and pressure required or observed
- Intermediate stage outlet temperatures and pressures of the process streams
- Total steam flow or steam flow to each stage ejector

A diagram of a typical ejector set is shown in Fig. 27.

The calculation proceeds with the following:

Step 1. Determine the quantity of inerts entering the system from the tower. If this cannot be measured, a rule of thumb is that total inerts are 0.5–1.0 % by weight on feed. This is made up of air leaking into the system and some light ends. Again by rule of thumb, light ends will be about 25 % of total inerts.

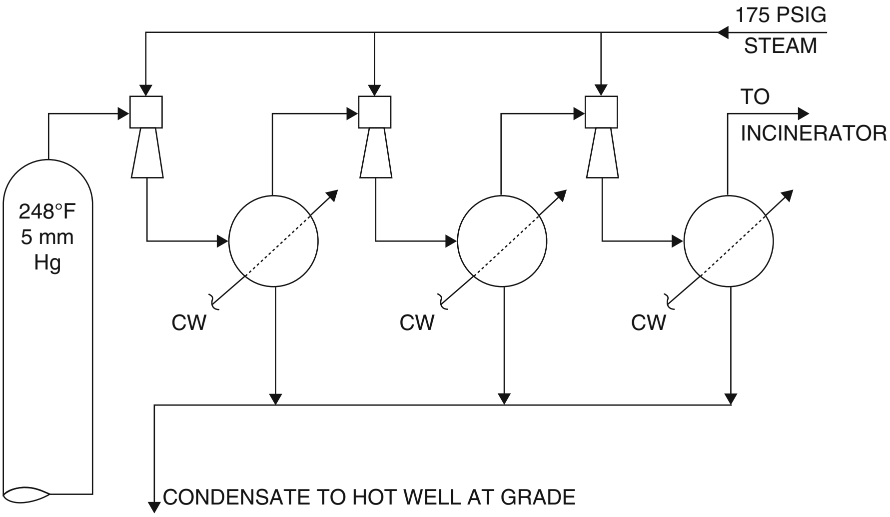


Fig. 27 Typical ejector set

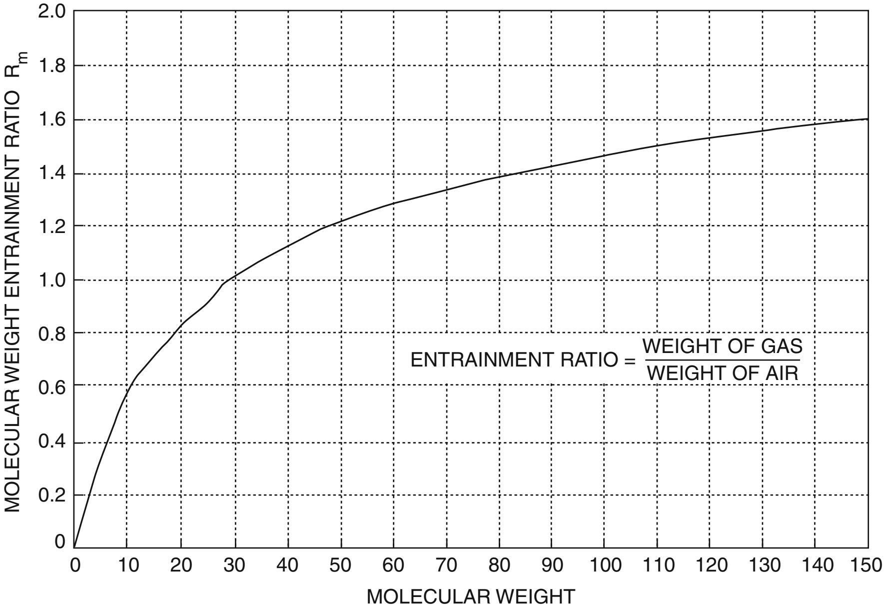


Fig. 28 Ratio factors for steam

Step 2. Calculate the "equivalent dry air load" to the first ejector stage. Using the equation

$$W_a = \frac{W_i}{Rm_i \times Rt_i} + \frac{W_s}{Rm_s \times Rt_s} \tag{13}$$

where

W_a = Equivalent air flow in lb/h.
W_i = Actual lb/h of overhead (includes air, and light ends).
Rm_i and Rt_i = Ratio factors for component i from ejector Figs. 28 and 29.
W_s = Weight flow of steam in lb/h.
Rm_s and Rt_s = Ratio factors for steam from Figs. 30 and 31.
In this case Ws will be zero, as no steam will be used in the distillation.

Step 3. Calculate the steam consumption to the first ejector using tower top pressure as the suction pressure. The consumption is calculated by

$$W_{ms} = R_a M_p W_a \tag{14}$$

where

W_{ms} = Weight flow of motive steam in lb/h.
R_a = Ratio of lb motive steam/lb air equivalent using Fig. 30.
M_r = Steam usage multiplier from Fig. 31.
W_a = Air equivalent flow in lb/h.

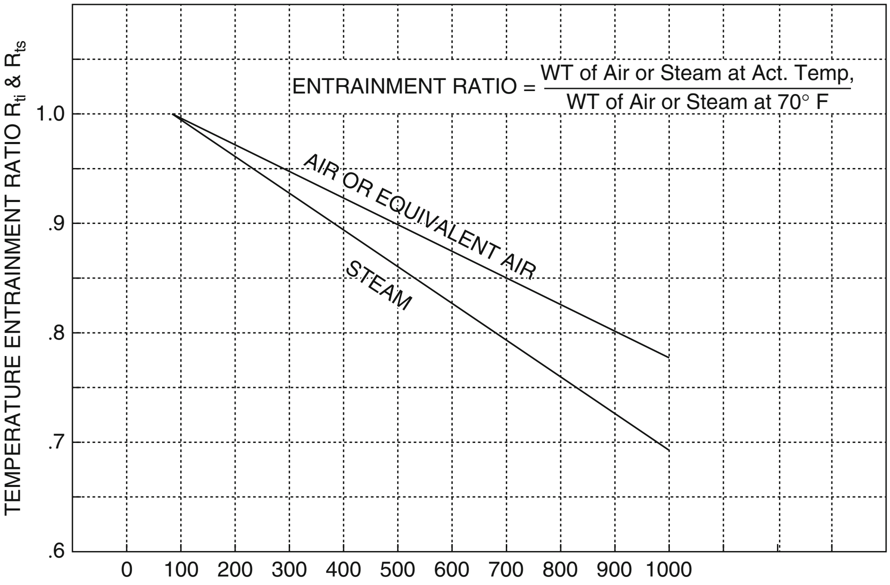


Fig. 29 Temperature entrainment ratios Rt_i, Rt_s

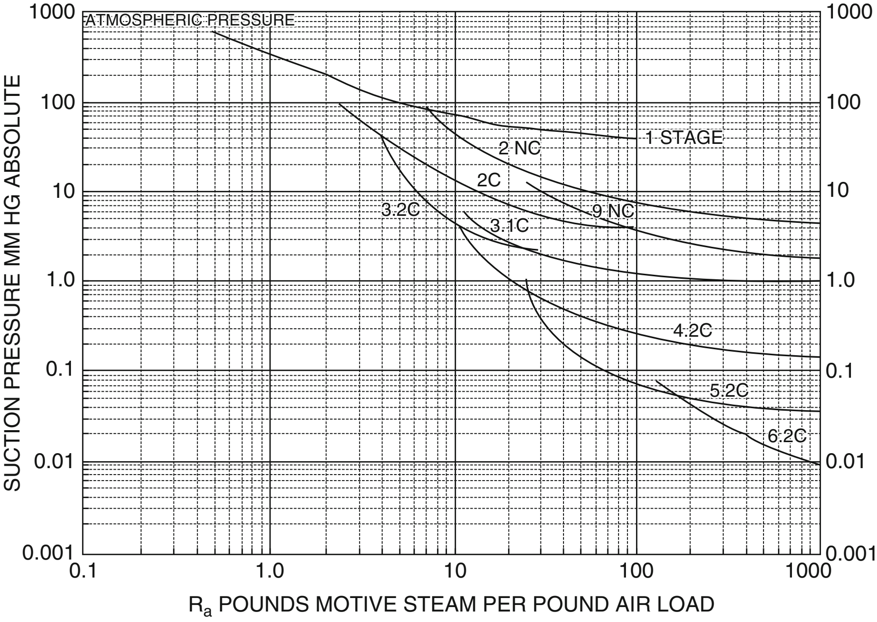


Fig. 30 Suction pressure versus weight of motive steam

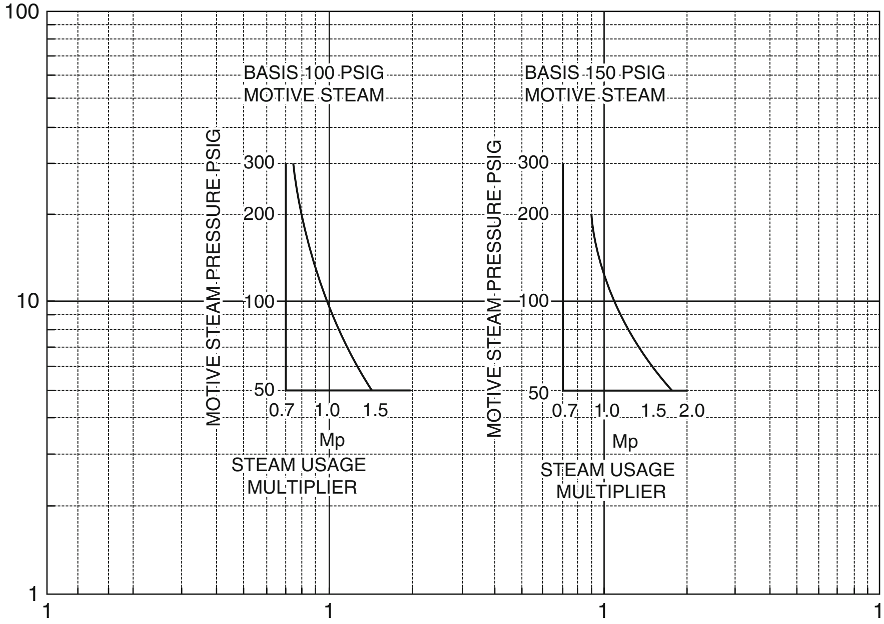


Fig. 31 Motive steam usage correction factor

Step 4. Calculate the partial pressure of steam at the condenser pressure. This pressure is the first/second stage intermediate pressure and is the suction pressure to the second ejector. It is read on the plant or it may be assumed. In the calculation it is assumed to be 50 mmHg.

Step 5. From the partial pressure of steam, the condensing temperature in the condenser is read from steam tables. Assume that 90 % steam is condensed in this first condenser.

Step 6. (Optional) Calculate heat balance across the condenser and arrive at the condenser duty.

Step 7. Repeat step 2 for “equivalent dry air load” to stage 2. Note: There will now be steam present in this calculation.

Step 8. Repeat steps 3–5 for the second stage, making an assumption for the condenser pressure or reading off the actual pressure if the unit is an installed one. Assume also the amount of steam condensed in the second condenser – this will be high around 98 %.

Step 9. Repeat steps 6 and 7 for the third stage condenser and ejector. This condenser will be about 1 or 2 psi above atmospheric pressure.

Step 10. Summarize the above results into a process specification for a required ejector set or, if already installed, compare the performance (e.g., calculated steam consumed versus actual).

Calculating Flash Zone Conditions in a Vacuum Unit

Flash zone conditions are easier to calculate for a “Dry” vacuum unit than for the atmospheric crude unit. Indeed the flash zone conditions can be measured in vacuum units with a greater degree of accuracy than in the case of the atmospheric column.

The procedure for predicting flash zone conditions in this case follows a similar route to that in the atmospheric unit case. The following steps describe this procedure.

Step 1. Develop the EFV from the TBP curve of the reduced crude. The same method that was used when discussing the flash zone of the atmospheric crude unit in this chapter will apply in this case also. Remember that the EFV calculated is for atmospheric pressure.

Step 2. Develop the material balance for the vacuum unit. As the flash zone conditions are to be used in most calculations involving the vacuum tower, it is best to develop the material balance at this stage. To do this, determine the distillate cuts required, and, by using the respective crude assays, determine the specific gravity for each cut using mid boiling points. The mid boiling point for each distillate product only should be determined in this case. Use the method described in the chapter titled “▶ Introduction to Crude Oil and Petroleum Processing” of this Handbook to determine mol weight. Some of these will need to be extrapolated.

Step 3. Set the overflash. Now in this area of the TBP and EFV curves, the slope of the curve is quite steep. That is, there is a high temperature difference for each percent of volume increase. In vacuum units, therefore, a 1–2 % overflash would be realistic to meet a realistic coil outlet temperature.

Step 4. Determine the new flash temperature to include the overflash from the EFV curve. This is the temperature at atmospheric pressure.

Step 5. Calculate the total pressure of the flash zone. Vacuum towers operate at or below 5 mmHg at the top. Pressure drop through the tower should not be more than 25 mmHg. Well-designed off-take trays and packing should be as follows:

Grid packing	6–7 mmHg per 10 f. of packed height
Drawoff (chimney trays)	2–3 mmHg/tray

Step 6. There will be no partial pressure calculation of hydrocarbon vapor (as in the case of the atmospheric unit) as there is no steam in the flash zone of a “dry” vacuum tower. The total pressure calculated in Step 5 is the actual hydrocarbon flash pressure. Using the vapor pressure curves, determine the flash zone temperature at the total flash zone pressure. This is the flash zone temperature that will now be used for all remaining heat balances.

Drawoff Temperatures

Unlike the atmospheric crude distillation unit, the temperature of the vacuum tower bottom (bitumen) will be essentially the flash zone temperature. There will be a small difference, say, 2–3 °F, below the actual flash zone temperature due to overflash returning from the wash trays. Very often the overflash amount is drawn off from below the wash section and either sent to fuel or blended into the bitumen stream external to the tower. In this case the unquenched bitumen leaving the tower will be at flash zone temperature. Again there is no steam present to influence this temperature.

Side stream drawoff temperatures are easier to calculate for a vacuum tower than was the case for the atmospheric tower. This is so because in a "dry vacuum" column, there is no steam to influence partial pressures, and of course there is no side stream stripping.

A method similar to the "Packie" method used for the atmospheric column is used for the vacuum column drawoff. In this case however, it is only necessary to determine the initial boiling point of the side stream EFV curve at the tower condition to arrive at the drawoff temperature.

Note: It is the IBP of the actual EFV curve in this case, not the IBP of the flash reference line as in the case of the atmospheric unit. Also there will be no "Packie" correction factors required in this case.

The calculation steps for this procedure are as follows:

Step 1. Draw the EFV curve from the side stream TBP curve using the method described earlier in this chapter. Only the 0, 10, 30, and 50 % vol section of the curve need to be developed.

Step 2. Set the total pressure at the drawoff tray. If this is not available as plant data, then use the criteria for pressure drop given in the item dealing with the flash zone.

Step 3. Calculate the partial pressure of the side stream product at the drawoff tray. To do this, consider all material lighter than the drawoff side stream to be inert. Include in the inert estimates of air leakage and cracked hydrocarbon vapors as described earlier in this chapter in the item dealing with tower overhead ejector system. The total hydrocarbon vapor will include the overflow from the drawoff tray. As a rule of thumb, estimate overflow as:

Top side stream	0.8 times product
Mid side stream	1.0 times product
Bottom side stream	1.5–2.0 times product

Step 4. Using the vapor pressure curves, relate the IBP temperature of the EFV to the partial pressure determined in Step 3. This is the drawoff temperature, and this will be the temperature for the respective side streams and pumparound drawoff that will be used in the tower heat balances.

Determine Pumparound and Internal Flows for Vacuum Towers

Now that the cut points and tower conditions of temperature and pressure are established, the internal flow and pumparound duties can be calculated, although generally speaking fractionation requirements are not as strict in a vacuum crude unit as in the case for the atmospheric unit. Nevertheless, proper wash streams are required in vacuum towers to protect distillates which may become feed to cracking units, from entrained undesirable components such as metals. Test runs on vacuum units therefore should include the determination of reflux streams and, in turn, tower loading.

The following steps outline a calculation procedure to determine pumparound requirements and overflow (reflux) in the wash section of the tower.

Step 1. Set the overflow requirement for the LVGO drawoff tray using the rule of thumb given in the previous item. Alternatively, if this can be measured on the plant, use that data.

Step 2. From plant data or such data as can be developed from items on ejector system and drawoff temperatures, calculate the heat balance below the LVGO drawoff tray.

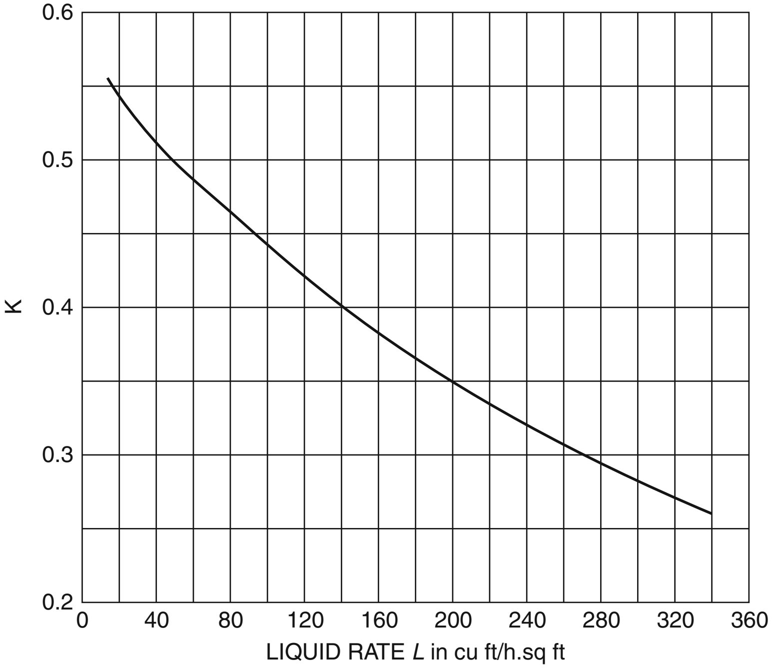


Fig. 32 Capacity factor “K” versus liquid rate

Step 3. In this heat balance the bottom pumparound duty will be the unknown. Equate heat in equals heat out to determine the duty of the pumparound required to produce the set overflow.

Step 4. This pumparound duty can be checked on the plant by multiplying the flow in the pumparound by the enthalpy difference over the exchangers.

Step 5. Carry out the overall heat balance over the tower. That is, calculate the difference between the total heat in with the feed and the total out with all the products. This difference gives the total heat to be removed by both pumparounds. Assuming there are two pumparounds (top and bottom), the duty of the bottom pumparound has already been calculated; then the top pumparound duty will be the total heat to be removed minus the duty of the bottom pumparound.

Step 6. Usually the most critical flow in a vacuum unit is the wash oil flowing over the bottom wash trays or packing. This is the area where most undesirable entrainment can occur, and this is the most vulnerable area for coking. Lack of wash oil enhances contamination of the bottom product and promotes coking in this area.

Step 7. Carry out a heat balance over the bottom wash section of the tower. The unknown in this case is the overflow liquid from the heavy vacuum gas oil. Equate the heat in with feed and overflow with the heat out from total product vapors, overflow vapor, and bitumen to solve for the unknown.

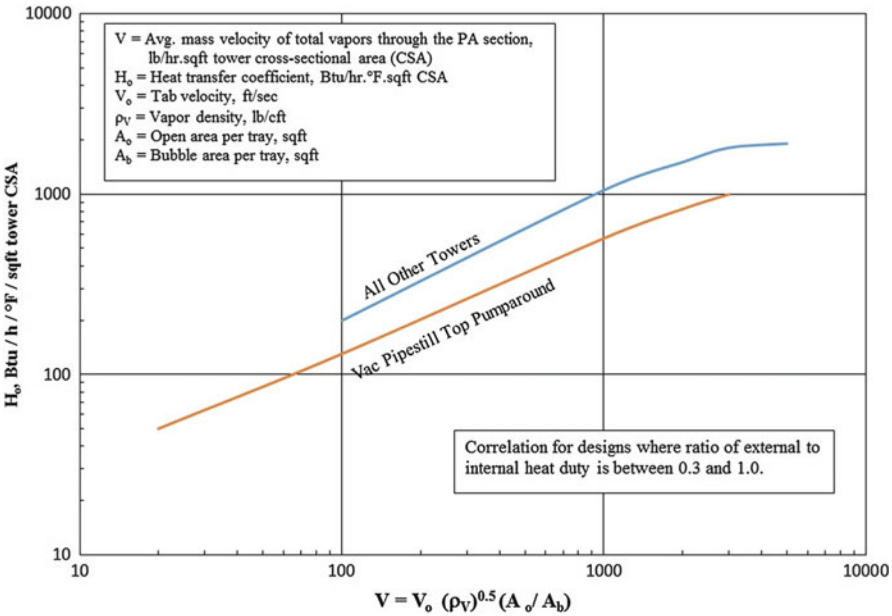
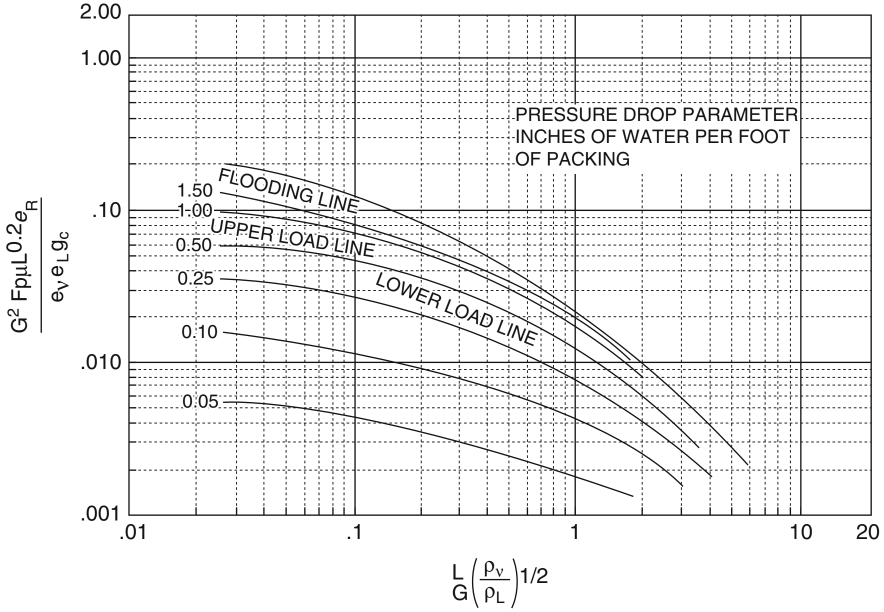


Fig. 33 Transfer coefficient H_o versus V (mass velocity factor) for pumparound zones



L = Liquid Rate, Lbs/sec., Sq.ft

e_L = Liquid Density, Lbs/cu. ft

F_P = Packing Factor ≈ a/ϵ^3

e_R = Ratio, $\frac{\text{Density of Water}}{\text{Density of Liquid}}$

G = Gas Rate, Lbs/sec., sq.ft

e_V = Gas Density, Lbs/cu. ft

μ_L = Viscosity of Liquid, Centipoise

g_e = Gravitational Conversion Factor – 32.2

Fig. 34 Pressure drop through grid in inches of hot liquid per foot height

Note: The quantity of overflow in this case is independent of pumparound duties above it. It is dependent only on the amount of overflash.

Calculate Tower Loading in the Packed Section of Vacuum Towers

As discussed earlier, most modern "dry" vacuum towers use low pressure drop grid or stacked packing. This packing enhances heat exchange in the tower and of course permits the tower to operate at very low pressures. Nevertheless, this packing can become overloaded causing high pressure drop in the tower and poor all-around performance.

The following discussion describes a general method of evaluating the grid performance in terms of its pressure drop. Please note this is a quick general method of estimating tower packing design or performance. Proprietary grid and packing manufacturers have their own correlations which they use in their design work. A more detailed examination of packed tower loading is presented in the author's

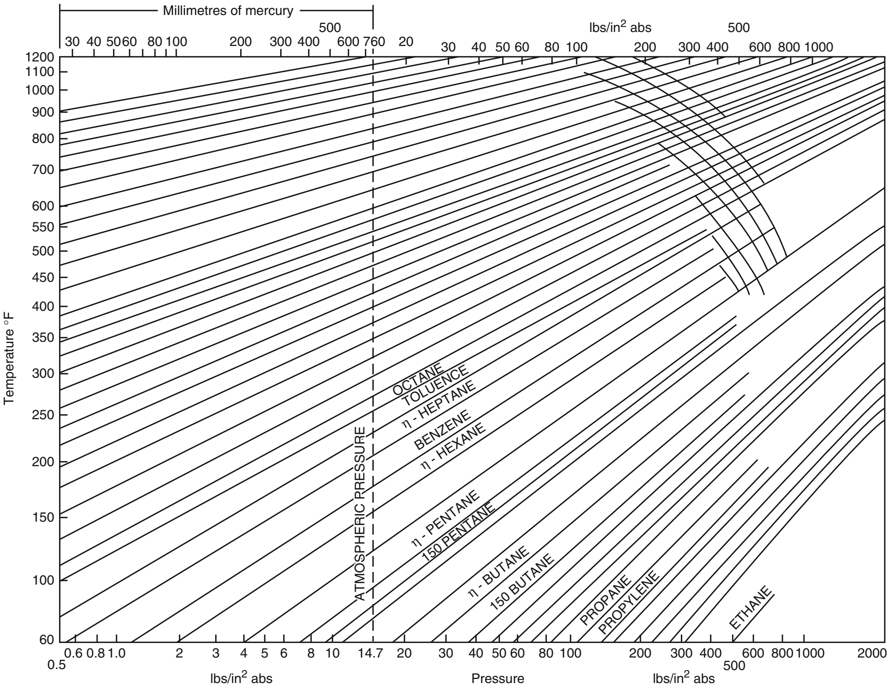


Fig. 35 Pressure-temperature curves for hydrocarbon equilibria (chart 1 of 2)

published work titled *Elements of Chemical Process Engineering*. The following are the calculation steps used for this quick general packed section evaluation:

Step 1. Determine the liquid and vapor flows across the section to be evaluated. As calculated in the previous section, "Determine Pumparound and Internal Flows for Vacuum Towers."

Step 2. If the unit is existing and this calculation is to determine tower performance, then use manufacturer's drawings for tower details such as dimensions of the packed section.

Step 3. Calculate the liquid and vapor loads in terms of actual cubic feet per second for vapor and cubic feet per hour per square foot of tower for the liquid. All these will be at tray conditions of temperature and pressure.

Step 4. Using the liquid load as calculated in step 3, read off the value for capacity factor "K" from Fig. 32.

Calculate the linear velocity of the vapor at flood from the expression

$$\mathrm{K} = V_{\mathrm{f}}\sqrt{\rho_{\mathrm{v}}/(\rho_{\mathrm{l}} - \rho_{\mathrm{v}})} \tag{15}$$

where

V_{f} = Vapor velocity at flood in ft/s.

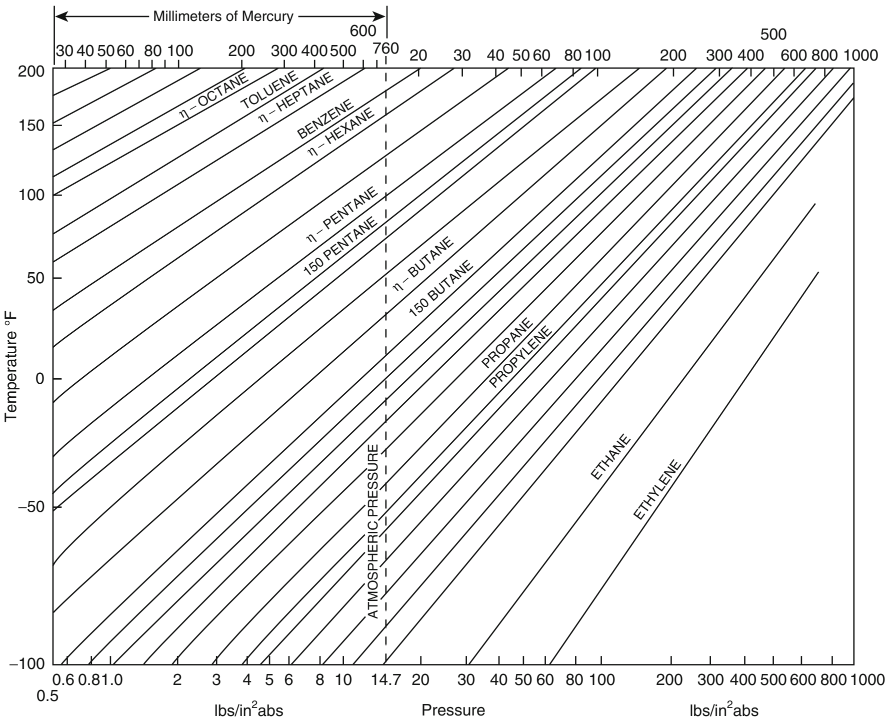


Fig. 36 Pressure-temperature curves for hydrocarbon equilibria (chart 2 of 2)

ρ_v = Density of vapor in lb/cuft at section conditions of temperature and pressure.

ρ_l = Density of liquid in lb/cuft at section conditions.

Step 5. Calculate the actual vapor velocity required by multiplying the calculated velocity at flood by percent of flood permissible if this is to be a new design. The design cross-sectional area of the tower is then the calculated vapor load in cuft/s divided by the actual vapor velocity. If the unit is existing, divide the vapor loading in cuft/s by the cross-sectional area of the tower to arrive at the actual vapor velocity in ft/s. The existing unit operation as a percent of flood will be the actual velocity divided by the calculated flood velocity times 100.

Step 6. Estimate the HETP (height equivalent to a theoretical tray) as being between 1.5 and 2.0 ft. Use the higher figure for vapor percent of flood 50–95 % or higher and the lower value for vapor flood below 50 %.

Step 7. Calculate the height of the packed section required for heat transfer using the quantity of heat to be transferred as being the pumparound duty in Btu/h. Then treat the section above the pumparound drawoff as a simple heat exchanger. Use the liquid flow to this section and the pumparound flow as calculated in the previous section (as part of the tower liquid load). The inlet temperature to the section can be taken as that for the pumparound liquid flow into the tower and the temperature out of the section as the pumparound drawoff temperature.

Step 8. Read off an overall heat transfer coefficient H_o from Fig. 33.

Calculate the LMTD over the section from the temperatures used in the previous section on pumparound. Then calculate the total area of tower required for the heat transfer from the expression

$$Q = AH_o\Delta t_m \tag{16}$$

where

Q = Heat duty in Btu/h.
A = Heat transfer area in sqft.
H_o = Overall heat transfer coefficient in Btu/sqft·h·°F.
Δt_m = Log mean temperature difference in °F.

Step 9. Calculate the theoretical number of trays required by dividing the total area calculated in step 8 by the design cross-sectional area (step 5). Multiply this number of trays by the selected HETP to give the height of packing.

Step 10. Calculate the pressure drop across the grid using the actual vapor velocity in cuft/s in the equation

$$\mathrm{K} = V_a\sqrt{\rho_v/(\rho_l - \rho_v)} \tag{17}$$

(Eq. 17) to determine the constant K. Then read off the pressure drop in inches of hot liquid per foot height from Fig. 34.

To express this pressure drop in mmHg, multiply by the SG of the hot liquid and 1.865.

Appendix 1: Pressure-Temperature Curves for Hydrocarbon Equilibria

Figs. 35 and 36.

Appendix 2: ASTM Gaps and Overlaps

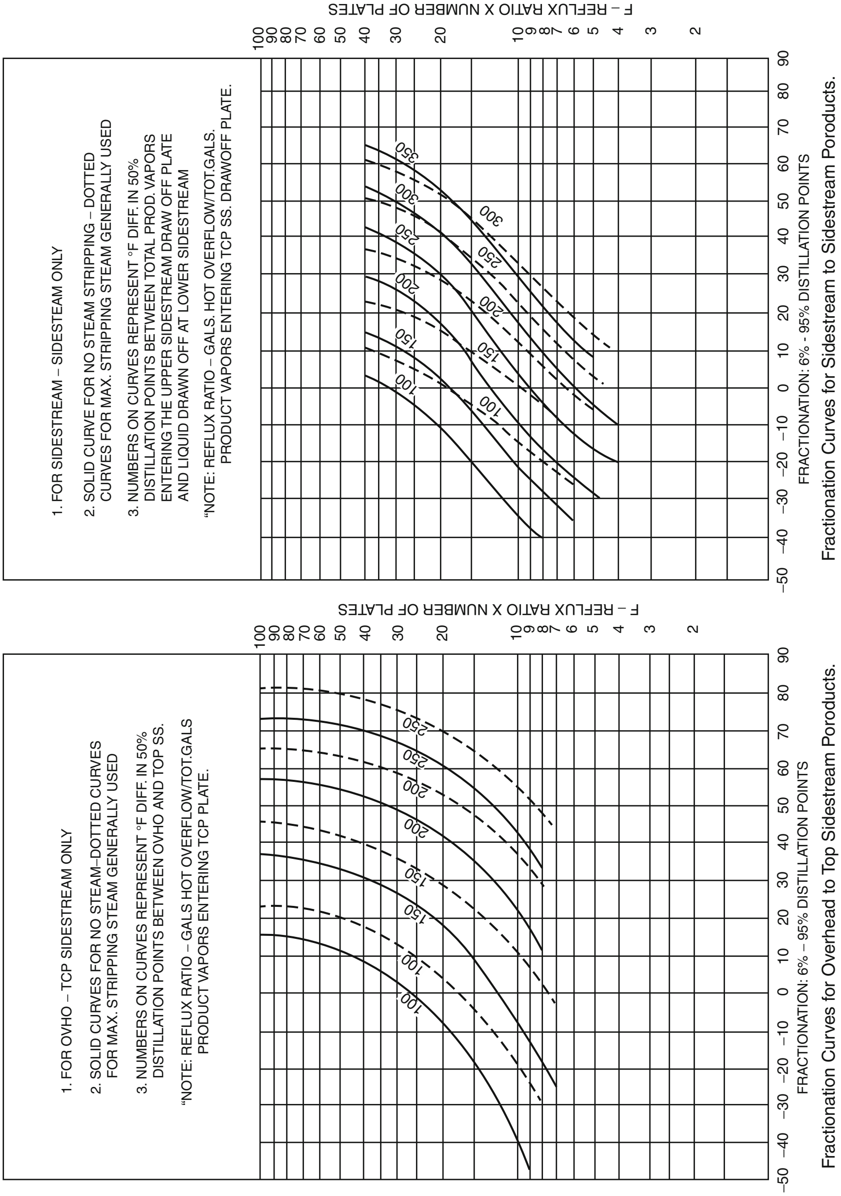
Fig. 37.

Appendix 3: Valve Tray Design Details

Table 14.

Appendix 4: Chord Height, Area, and Length

Fig. 38.



1. FOR OVHO – TCP SIDESTREAM ONLY
2. SOLID CURVES FOR NO STEAM–DOTTED CURVES FOR MAX. STRIPPING STEAM GENERALLY USED
3. NUMBERS ON CURVES REPRESENT °F DIFF. IN 50% DISTILLATION POINTS BETWEEN OVHO AND TOP SS.

"NOTE: REFLUX RATIO – GALS HOT OVERFLOW/TOT.GALS PRODUCT VAPORS ENTERING TCP PLATE.

Fractionation Curves for Overhead to Top Sidestream Poroducts.

1. FOR SIDESTREAM – SIDESTEAM ONLY
2. SOLID CURVE FOR NO STEAM STRIPPING – DOTTED CURVES FOR MAX. STRIPPING STEAM GENERALLY USED
3. NUMBERS ON CURVES REPRESENT °F DIFF. IN 50% DISTILLATION POINTS BETWEEN TOTAL PROD. VAPORS ENTERING THE UPPER SIDESTREAM DRAW OFF PLATE AND LIQUID DRAWN OFF AT LOWER SIDESTREAM

"NOTE: REFLUX RATIO – GALS. HOT OVERFLOW/TOT.GALS. PRODUCT VAPORS ENTERING TCP SS. DRAWOFF PLATE.

Fractionation Curves for Sidestream to Sidestream Poroducts.

Fig. 37 ASTM gaps and overlaps

Table 14 Valve tray design details

Valve tray design principles			
Design feature	Suggested value	Alternate values	Comment
1. Valve size and layout			
a. Value diameter	–		Valve diameter is fixed by the vendor
b. Percent hole area, A_o/A_B	12	8–15	Open area should be set by the designer. In general, the lower the open area, the higher the efficiency and flexibility, and the lower the capacity (due to increased pressure drop). At values of open area toward the upper end of the range (say 15 %), the flexibility and efficiency are approaching sieve tray values. At the lower end of the range, capacity and downcomer filling become limited
c. Valve pitch/diam. ratio	–		Value pitch is normally triangular. However, this variable is usually fixed by the vendor
d. Valve distribution		–	On trays with flow path length $\geq 5'$, and for liquid rates >5,000 GPH/ft (diameter) on trays with flow path length $<5'$, provide 10 % more valves on the inlet half of the tray than on the outlet half
e. Bubble Area, A_B	–		Bubble area should be maximized
f. Plate efficiency	–		Valve tray efficiency will be about equal to sieve tray efficiency provided there is not a blowing or flooding limitation
g. Valve blanking	–		This should not generally be necessary unless tower is being sized for future service at much higher rates. Blanking strips can then be used. Blank within bubble area, not around periphery, to maintain best efficiency
2. Tray spacing, inches	–	12–36	Generally economic to use min. Values given on p. III-E-2 which are set by maintenance requirements. Other considerations are downcomer filling and flexibility. Use of variable spacings to accommodate loading changes from section to section should be considered
3. Number of liquid passes	1	1-2	Multi-passing improves liquid handling capacity at the expense of vapor capacity for a given diameter column and tray spacing. Cost is apparently no greater – at least, for tower diameters <8 ft

(*continued*)

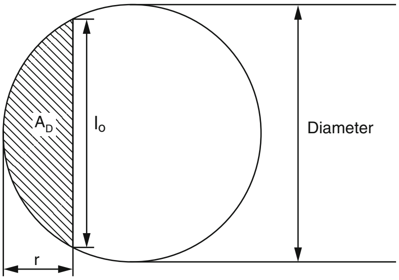
Table 14 (continued)

Valve tray design principles			
Design feature	Suggested value	Alternate values	Comment
4. Downcomers and weirs			
a. Allowable downcomer inlet velocity, ft/s of clear liq.		0.3–0.4	Lower value recommended for absorbers or other systems of known high frothiness
b. Type downcomer	Chord	Chord. arc	Min. chord length should be 65 % of tray diameter for good liquid distribution. Sloped downcomers can be used for high liquid rates – with maximum outlet velocity = 0.6 ft/s. Arc downcomers may be used alternatively to give more bubble area (and higher capacity) but are somewhat more expensive. Min. width should be 6 in. for the latter
c. Inboard downcomer width (inlet and outlet)		Min. 8 in.	Use of a 14–16″ "jump baffle" suspended lengthwise in the center of the inboard downcomer and extending the length of the downcomer is suggested to prevent possible bridging over by froth entering the downcomer from opposite sides. Elevation of base of jump baffle should be level with outlet weirs. Internal accessway must be provided to allow passage from one side to another during inspection
d. Outlet weir height	2″	1″ to 4″	Weir height can be varied with liquid rate to give a total liquid head on the tray (h_c) in the range of 2.5″–4″ whenever possible. Lower values suggested for vacuum towers, higher ones for long residence time applications
e. Clearance under downcomer, in.	1.5″	1″ min	Set clearance to give head loss of approximately 1 in. Higher values can be used if necessary to assure sealing of downcomer
f. Downcomer seal (inlet or outlet weir height minus downcomer clearance)	Use outlet weir to give min 1/2″ seal in tray liquid	Inlet weir or recessed inlet box	In most cases, plate liquid level can be made high enough to seal the downcomer though use of outlet weir only. Inlet weirs add to downcomer build up; in some cases they may be desirable for 2-pass trays to ensure equal liquid distribution. Recessed inlets are more expensive but may be necessary in cases where an operating seal would require an excessively high outlet weir
g. Downcomer filling, % of tray spacing		40–50	Use the lower value for high pressure towers, absorbers, vacuum towers, known foaming systems, and also tray spacings of 18″ or lower

WEIR LENGTH AND DOWNCOMER AREA

R*	L*	A*	R*	L*	A*	R*	L*	A*	R*	L*	A*	R*	L*	A*	R*	L*	A*
.070	.511	.0306	.120	.650	.0680	.170	.751	.113	.220	.826	.163	.280	.896	.230	.390	.977	.361
1	.514	.0315	1	.652	.0688	1	.753	.114	1	.829	.164	5	.903	.236	5	.979	.367
2	.517	.0321	2	.654	.0697	2	.755	.115	2	.831	.165						
3	.521	.0326	3	.657	.0705	3	.756	.116	3	.832	.166	.290	.906	.241	.400	.980	.374
4	.524	.0335	4	.659	.0714	4	.758	.117	4	.834	.167	5	.913	.247	5	.982	.380
5	.527	.0342	5	.661	.0722	5	.760	.117	5	.835	.169	.300	.917	.252	.410	.984	.386
6	.530	.0348	6	.663	.0731	6	.762	.118	6	.836	.170	5	.921	.258	5	.986	.392
7	.533	.0355	7	.665	.0739	7	.763	.119	7	.838	.171						
8	.536	.0362	8	.668	.0748	8	.765	.120	8	.839	.172	.310	.925	.264	.420	.987	.398
9	.539	.0368	9	.670	.0756	9	.766	.121	9	.841	.173	5	.930	.270	5	.989	.405
.080	.542	.0375	.130	.672	.0765	.180	.768	.122	.230	.842	.174	.320	.933	.276	.430	.991	.412
1	.545	.0382	1	.674	.0747	1	.770	.123	1	.843	.175	5	.937	.282	5	.993	.418
2	.548	.0389	2	.677	.0782	2	.772	.124	2	.845	.176						
3	.552	.0396	3	.679	.0791	3	.773	.125	3	.846	.177	.330	.941	.289	.440	.994	.424
4	.555	.0403	4	.682	.0799	4	.775	.126	4	.848	.178	5	.945	.294	5	.995	.430
5	.558	.0410	5	.684	.0808	5	.777	.127	5	.849	.179	.340	.948	.300	.450	.996	.437
6	.561	.0418	6	.686	.0817	6	.778	.128	6	.850	.180	5	.951	.306			
7	.564	.0425	7	.688	.0825	7	.780	.129	7	.851	.181				.460	.997	.450
8	.567	.0432	8	.691	.0834	8	.781	.130	8	.853	.182	.350	.955	.312			
9	.570	.0439	9	.693	.0842	9	.783	.131	9	.854	.183	5	.958	.318	.470	.998	.462
.090	.573	.0446	.140	.695	.0851	.190	.784	.132	.240	.855	.184	.360	.961	.324	.480	.998	.475
1	.576	.0454	1	.697	.0860	1	.785	.133	5	.860	.190	5	.964	.330			
2	.578	.0461	2	.699	.0869	2	.787	.134							.490	.999	.488
3	.581	.0469	3	.700	.0878	3	.789	.135	.250	.866	.196	.370	.967	.337			
4	.583	.0475	4	.702	.0887	4	.790	.136	5	.872	.202	5	.969	.343	.500	1.0	0.50
5	.586	.0484	5	.704	.0896	5	.792	.137	.260	.878	.207	.380	.971	.348			
6	.589	.0491	6	.706	.0905	6	.794	.138	5	.883	.213	5	.977	.354			
7	.592	.0499	7	.708	.0914	7	.795	.139									
8	.594	.0506	8	.710	.0923	8	.797	.140	.270	.888	.218						
9	.597	.0514	9	.712	.0932	9	.798	.141	5	.893	.224						
.100	.600	.0521	.150	.714	.0941	.200	.800	.142									
1	.603	.0529	1	.716	.0950	1	.802	.143									
2	.605	.0537	2	.718	.0959	2	.803	.144									
3	.608	.0545	3	.720	.0969	3	.805	.145									
4	.610	.0553	4	.722	.0978	4	.806	.146									
5	.613	.0561	5	.724	.0987	5	.808	.148									
6	.615	.0569	6	.726	.0996	6	.809	.149									
7	.618	.0576	7	.728	.1005	7	.810	.150									
8	.620	.0584	8	.729	.1015	8	.812	.151									
9	.623	.0592	9	.731	.102	9	.813	.152									
.110	.625	.0600	.160	.733	.103	.210	.814	.153									
1	.628	.0608	1	.735	.104	1	.816	.154									
2	.630	.0618	2	.737	.105	2	.817	.155									
3	.633	.0624	3	.738	.106	3	.819	.156									
4	.635	.0632	4	.740	.107	4	.820	.157									
5	.638	.0640	5	.742	.108	5	.822	.158									
6	.640	.0648	6	.744	.109	6	.823	.159									
7	.643	.0656	7	.746	.110	7	.824	.160									
8	.645	.0664	8	.747	.111	8	.826	.161									
9	.648	.0672	9	.749	.112	9	.827	.162									

* THIS TABLE RELATES THE DOWNCOMER AREA THE WEIR LENGTH, AND THE HEIGHT OF THE CIRCULAR SEGMENT FORMED BY THE WEIR.



$R = \frac{\text{* Downcomer Rise}}{\text{Diameter}} = \frac{r}{\text{Dia.}}$

$L = \frac{\text{* Weir Length}}{\text{Diameter}} = \frac{l_o}{\text{Dia.}}$

$A = \frac{\text{* Downcomer Area}}{\text{Tower Area}} = \frac{A_D}{A_S}$

Fig. 38 Chord height, area, and lengths

Distillation of the “Light Ends” from Crude Oil in Petroleum Processing

David S. J. Jones

Contents

David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_26

Abstract

The “light ends” unit is the only process in a refinery configuration that is designed to separate “almost” pure components from the crude oil. Its growth initially resulted from the need of those components such as butanes and propanes to satisfy a market of portable cooking fuel and industrial fuels. The need for modern gasolines has added to the demand for light ends to make high-octane blending components. This chapter describes the process and design of units to separate the light ends into useful products or into cuts for further processing in the refinery. An example design is provided.

Keywords

Light ends • Butane • Propane • LPG • Refinery

Introduction

The “light ends” unit is the only process in a refinery configuration that is designed to separate “almost” pure components from the crude oil. Its particular growth has resulted from the need for those components such as butanes and propanes to satisfy a market of portable cooking fuel and industrial fuels. That these products can be suitably compressed and stored in small, easily handled containers at ambient temperatures provided the market popularity for these products, suitably titled butane LPG and propane LPG. The term LPG refers to liquefied petroleum gas.

The introduction of “no lead” gasoline in the late 1960s established the need of octane sources additional to the aromatics provided by high severity catalytic reforming. A source of such high-octane additives is found in some isomers of butane and pentane. This added to the need for light ends processes which in many cases included the separation of isobutanes from the butane stream and also isopentanes from the light naphtha stream.

A Process Description of a “Light End” Unit

The “light ends” of crude oil are considered to be those fractions in the crude that have a boiling point below cyclohexane. The “light ends” distillation units however include the light naphtha cut separation, which is predominately pentanes and cyclopentanes, from heavy naphtha which contains the hexanes and heavier hydrocarbons necessary for the catalytic reformer feed. The feed to the “light ends” distillation process is usually the full range naphtha distillate from the atmospheric crude distillation unit overhead condensate drum. In many cases the distillates from stabilizing cracker and reformer products are added to the crude unit overhead distillate to be included in the “light ends” unit feed.

A typical process configuration for this unit is given in the flow diagram (Fig. 1).

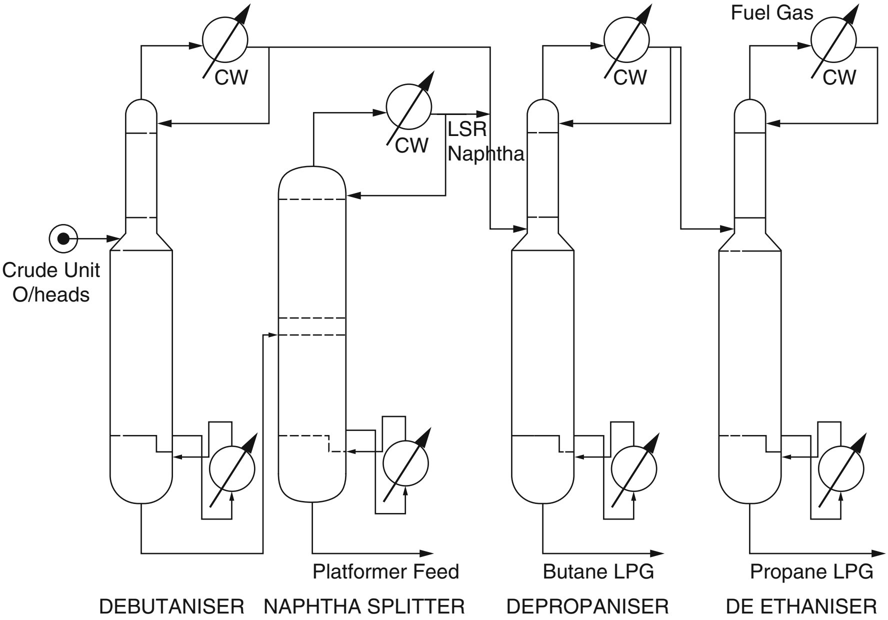


Fig. 1 A typical light ends unit configuration

In this configuration the total feed to the unit is debutanized in the first tower. The butanes and lighter hydrocarbons are totally condensed and collected in the column's overhead drum. Part of this condensate is returned to the tower top tray as reflux. The remainder is routed to a depropanizer column. The bottom product from the debutanizer is the full range naphtha product. This enters a naphtha splitter column where it is fractionated to give an overhead distillate of light naphtha and a bottom product of heavy naphtha.

The depropanizer separates the debutanizer overhead distillate to give a propane fraction as an overhead distillate stream and the butane fraction (butane LPG) as the bottom product. The overhead distillate is fractionated in a deethanizer column to produce a rich propane stream (propane LPG) as the bottom product. The overhead from this column is predominately hydrocarbons lighter than propane. This stream is only partially condensed to provide reflux for the tower. The uncondensed vapor is normally routed to the refinery's fuel gas system.

The products from the "light ends" unit are as follows:

Naphtha splitter – light naphtha (overhead distillate)
Heavy naphtha (bottom product-reformer feed)
Depropanizer – butane LPG (bottom product)
Deethanizer – propane LPG (bottom product)
Fuel gas (overhead vapor)

Developing the Material Balances for Light Ends Units

In light ends towers, the material balance is developed on a molal balance. This type of balance is determined by the degree of separation of the feed molal components that enter the distillate fraction and those that leave with the bottom product.

Effective separation by fractionation in light ends towers obeys the same laws as those in the crude distillation units, that is: the degree of separation is the result of the number of trays (or stages) and the reflux (or overflow) in the column.

In the crude unit, this separation was measured by the difference between the ASTM 95 % point of the lighter fraction and the 5 % ASTM point of the heavier fraction. This is the ASTM gap or overlap.

In light ends towers the degree of separation is a little more precise. This is determined by the distribution of key components in the two fractions to be separated. Key components may be real components (such as C_4s or C_5s) or pseudo-components defined by their mid-boiling points. Normally key components are adjacent components by boiling point in the feed composition. Any two key components may be selected – a light key and a heavy key. By definition, the light key has the lower boiling point. Both key components must, however, be present in the distillate and bottom products of the column. If a side stream exists, then these keys must also be present in the side stream product.

There are several correlations that describe the behavior of these key components in their distribution and relationship to one another. By far, the more common of these correlations is the Fenske equation which relates the distribution of key components at minimum trays with infinite reflux. The equation is relatively simple and does not require iterative calculation techniques to solve it. The Fenske equation is:

$$N_{\mathrm{m}+1} = \frac{\mathrm{Log}\left[\left((\mathrm{LT\ key}/\mathrm{HY\ key})_D \times (\mathrm{HY\ key}/\mathrm{LT\ key})_W\right)\right]}{\mathrm{Log}\dfrac{K_{LT\ \mathrm{key}}}{K_{\mathrm{HY\ key}}}} \tag{1}$$

where:

N_{m} = minimum number of theoretical trays at total reflux. The +1 is the reboiler which is counted as a theoretical tray.

LT key = is the mole fraction of the selected light key.

HY key = is the mole fraction of the selected heavy key.

D = fractions in the distillate product.

W = fractions in the bottom product.

$K_{\mathrm{LT\ key}}$ = the equilibrium constant of the light key at mean system condition of temperature and pressure.

$K_{\mathrm{HY\ key}}$ = the equilibrium constant of the heavy key again at mean system conditions.

The ratio of the equilibrium constants is called the "relative volatility" of the keys. Setting fractionation requirements for light ends towers is usually done to meet a product specification. More often than not, this specification is the vapor pressure of the heavier fraction or the tolerable amount of a heavy key allowed in the lighter fraction.

Sometimes, however, a specification for the separation may not be given. Under this circumstance, some judgment must be made in determining the most reasonable separation that can be achieved with the equipment. This item of the handbook addresses calculation techniques that satisfy either premise.

It is common to use process simulation software (HYSYS, Pro/II, and others) to perform the design calculations for light ends units. This allows case studies to optimize the process design. The details of the computer simulations are beyond the scope of this handbook. The manual procedure for the calculations is described here. It is helpful to understand the manual approach to establish the background and limitations behind the computerized calculations.

Light Ends Specifications Cases

Case 1: *Setting separation requirements to meet a specification*

In this case it is required to determine the amount of butanes that can be retained by a light naphtha cut to meet a RVP specification. The steps are as follows:

Step 1. Calculate the properties of the C_5 + naphtha from a component breakdown. These properties should give weight and mole rates per hour.

Step 2. Carry out a bubble point calculation of the C_5 + fraction and inserting butane as the unknown quantity x.

Step 3. The equilibrium constant used (K) in the calculation will be at the temperature and pressure conditions of the RVP (i.e., normally at 100 °F which is the test temperature).

Step 4. Either the equilibrium constants given in the charts in Appendix 3 of the chapter entitled "Process equipment for petroleum processing" in this handbook or the relationship of vapor pressure divided by the total system pressure may be used.

Step 5. By definition, the total moles of liquid given is equal to the total moles of vapor (calculated) in equilibrium at the bubble point. Thus equate and solve for x as the quantity of butanes tolerable to meet RVP.

Case 2: *Setting fractionation where no specification is given*

Step 1. Determine the composition of the feed in terms of real components, pseudo-components, or both. Calculate this in moles/h and mole fractions.

Step 2. Select the key components, and decide the minimum distribution of one or other key. For example, in a debutanizer C_5s allowed into LPG must not be more than 2 % of the total C_4s and lighter. This is to protect the Butane LPG "Weathering" Test Specification.

Table 1 Rules of thumb for number of light ends column trays

Tower	Number of actual trays
Debutanizer	30–35
Depropanizer	35–40
Deethanizer	38–42
Naphtha Splitter	25–35

Step 3. Give values to the fraction of LT and HY keys in the distillate and bottoms. Use *x* as the unknown where appropriate.

Step 4. The Fenske equation will be used to calculate the distribution of keys. Determine the value of N_m by taking the actual number of trays and using an efficiency of 70–75 % to arrive at total theoretical trays. Divide this figure by 1.5 to arrive at the minimum theoretical trays N_m. Do not forget to add 1 for the reboiler to use in the equation.

Step 5. Estimate the mean tower conditions. This can be achieved by examining past plant logs and other sources. Determine *K* values for the keys at this mean tower condition. Use published data for real components and the ratio of vapor pressure divided by total systems pressure for pseudo-components.

Step 6. Solve for *x* in the Fenske correlation. This will be the split of the key components and the basis for the material balance.

Very often when setting up a design for a light ends tower, the actual number of trays is not known at the time when calculation number two is required. The rules of thumb in Table 1 may be used as a guide.

Example Case

An example for illustrating Case 1 above is given in the chapter entitled "▶ Introduction to Crude Oil and Petroleum Processing" of this handbook where the amount of butane LPG allowed to meet gasoline RVP is calculated. An example of Case 2 is given as follows:

The overhead distillate from an atmospheric crude distillation unit operating at 50,000 BPSD of Murban crude has the composition noted in Table 2.

The key components for the debutanizer will be nC_4 and iC_5 as LT and HY keys, respectively. In the Fenske equation let *x* be the moles/h of nC_4 in the distillate. To satisfy the weathering test for butane LPG, the maximum amount of C_5s allowed in the debutanizer distillate is 2.0 mol% of the total C_4s and lighter. A reasonable number of actual trays in a debutanizer is 30. Allowing an efficiency of 70 %, the number of theoretical trays will be 21. It is reasonable to predict that the minimum theoretical trays will be the actual theoretical number divided by 1.5. Then N_m will be $21/1.5 = 14$ adding one for the reboiler giving $N_{m+1} = 15$.

From past data, average operating conditions of temperature and pressure for a debutanizer are 210 °F and 110 psig. At these conditions, the equilibrium constants for both keys are read from curves given in the GPSA Engineering Data as:

Table 2 Full range naphtha composition

Comp	BPSD	lb/gal	Gals/h	lb/h	MW	Moles/h
C2	20	3.42	35	120	30	4
C3	240	4.23	420	1,777	44	40.38
iC4	275	4.70	481	2,262	58	39.0
NC4	735	4.87	1,286	6,264	58	108.0
iC5	915	5.21	1,601	8,343	72	115.87
nC5	1,216	5.26	2,126	11,184	72	155.33
C6	2,170	5.56	3,798	21,114	84	251.36
C7	2,930	5.71	5,128	29,278	100	292.78
Mbpt 224	1,075	6.12	1,881	11,513	106	108.62
239	1,525	6.15	2,669	16,413	109	150.58
260	1,345	6.22	2,354	14,640	115	127.31
276	895	6.26	1,566	9,805	120	81.71
304	895	6.35	1,566	9,946	130	76.51
Total	14,235	5.73	24,911	142,659		1,551.45

$$nC_4 = 1.48$$
$$iC_5 = 0.94$$

Then the relative volatility $\phi = 1.48/0.94 = 1.57$.

Using the Fenske equation:

$$N_{m+1} = \frac{\text{Log}\left((\text{LT key}/\text{HY key})_D \times (\text{HY Key}/\text{ LT key})_W\right)}{\text{Log}\phi}$$
$$15 = \frac{\text{Log}((x/3.8 \times 112.1/108 - x))}{\text{Log } 1.57}$$
$$15 \times 0.196 = \text{Log}((112.1x)/(410.4 - 3.8x))$$
$$871 = 112.1x/(410.4 - 3.8x)$$
$$x = 104.48\,\text{moles/h}.$$

Associated with nC_4 in the bottom product will be an equilibrium amount of iC_4. Although small, this will have an effect on the bottom product bubble point and therefore the tower bottom temperature. The amount of this iC_4 in the bottom product can be calculated using a similar method as that for the split between nC_4 and iC_5; thus the keys for this calculation will be iC_4 and nC_4. Let x be the moles/h of iC_4 in the bottom product. Then:

	Feed	Dist	Bottoms
iC4	39	x	39 – x
nC4	108	104.48	3.52

Using the Fenske equation again:

$$\begin{aligned}15 &= \frac{\log((x/104.48)\times(3.52/39-x))}{\log(K\mathrm{iC}_4/K\mathrm{nC}_4)}\\ &= \frac{\log((x/104.48)\times(3.52/39-x))}{\log 1.3}\\ 1.709 &= \log((x/104.48)\times(3.52/39-x))\end{aligned}$$

Then:

$x = 38.99$ mol/h. This gives zero iC4 in the bottom cut.

The material balance for the debutanizer can now be written and is given in Table 3.

The material balances over the naphtha splitter, depropanizer, and the deethanizer follow the same technique in identifying key components and utilizing the Fenske equation.

Calculating the Operating Conditions in Light Ends Towers

Light ends units follow two calculation procedures for setting the conditions of temperature and pressure in the fractionating towers. The first procedure relates to towers in which the overhead product and reflux are totally condensed. The second procedure relates to those towers where the overhead product is not totally condensed.

Calculating the Tower Top Pressure and Temperature for Totally Condensed Distillate Product

This procedure commences with setting a realistic reflux drum temperature. This is fixed by the cooling medium temperature, such as ambient air temperature (for air coolers) or cooling water. As total condensation is required, then the pressure of the reflux drum must be the bubble point of the distillate product (and reflux) at the selected drum temperature. Once the drum pressure has been calculated, the tower top pressure can be determined by taking into account estimated or manufacturer's specified pressure drops for equipment and piping between the drum and the tower top. As a rough estimate, condensers and/or heat exchangers in the system have between 3 and 5 psi pressure drop. Allow also about a 2 psi pressure drop for piping.

The tower top temperature is calculated as the dew point of the distillate product at the total overhead pressure. There are usually no steam or inert gases present in the light ends tower overheads, so total pressure may be used. The following example uses the debutanizer overhead from the material balance given in section "Developing the Material Balance for Light Ends Units" above.

Table 3 Debutanizer material balance

	Feed			Dist			Bottoms		
Comp	BPSD	lb/h	mol/h	BPSD	lb/h	mol/h	BPSD	lb/h	mol/h
C2	20	120	4	20	120	4.00			
C3	240	1,777	40.38	240	1,777	40.38			
iC4	275	2,262	39.00	275	2,262	39.00			
nC4	735	6,264	108.00	711	6,061	104.48	24	203	3.52
iC5	915	8,343	115.87	30	274	3.80	885	8,069	112.07
nC5	1,216	11,184	155.33				1,216	11,184	155.33
C6	2,170	21,114	251.36				2,170	21,114	251.36
C7	2,930	29,278	292.78				2,930	29,278	292.78
MBPt224	1,075	11,513	108.62				1,075	11,513	108.62
239	1,525	16,413	150.58				1,525	16,413	150.58
260	1,345	14,640	127.31				1,345	14,640	127.31
276	895	9,805	81.71				895	9,805	81.71
304	895	9,946	76.51				895	9,805	76.51
Total	14,236	142,659	1,551.45	1,276	10,494	191.66	12,960	132,165	1,359.79

Table 4 Debutanizer reflux drum pressure. Distillate bubble point calculation at 100 °F (Trial 1)

Comp	Mol frac *x*	*K* at 125 psia	$Y = X \bullet K$
C2	0.0209	4.8	0.3906
C3	0.2107	1.48	0.4054
iC4	0.2035	0.68	0.0830
nC4	0.5451	0.5	0.1254
iC5	0.0198	0.23	0.0009
Total	1.0000		1.0053

Reflux drum pressure = 125 psia and 100 °F

Table 5 Tower top temperature

Comp	Mole fract (*y*)	*K* at 152 °F	Mole fract (*x*)
C2	0.021	6.2	0.003
C3	0.211	2.1	0.100
iC4	0.203	1.1	0.185
nC4	0.545	0.83	0.657
iC5	0.02	0.41	0.048
Total	1.000		0.993

The ambient air temperature for the site is 60 °F, and the operating temperature for the reflux drum will be set at 100 °F. The bubble pressure at this temperature is calculated and given in Table 4.

Allowing 3 psi pressure drop over the overhead condenser and 2 psi for the associated overhead piping, the tower top pressure becomes 130 psia (115 psig). The temperature of the tower top is the dew point of the distillate product at the top pressure. This is given in Table 5.

There is reasonable agreement that total y = total x; therefore the dew point and the tower top temperature at 115 psig is 152 °F.

Calculating the Overhead Conditions for Partially Condensed Distillate and Product

There are two circumstances where the overhead stream from a light ends tower may not be totally condensed. The most common of these is in the case of the deethanizer. Here, usually, only sufficient overhead stream is condensed to provide the overhead reflux stream. The reason for this is that at a normal condensing temperature, the pressure required at the reflux drum would be unacceptably high. It would be so high that the tower bottom pressure required would be higher than the bottom product's critical pressure, and thus fractionation would not be possible. In this case the tower pressure is set again by the reflux drum pressure. Unlike the case of total condensation, the reflux drum pressure for this partial condensation is found as the dew point at the condensing temperature of the distillate product. In fact the reflux drum becomes a theoretical fractionation stage. In certain cases refrigeration is used to totally condense the overhead stream at an acceptable pressure, but this selection would be as a result of a study of the operation's economics.

In certain processes where a high tower pressure (and consequently high temperature) may cause deterioration of one or more of the products from the tower, the tower pressure is reduced by condensing only a fraction of the overhead distillate product. For this purpose, a vaporization curve for the distillate product is constructed at a selected reflux drum temperature. This curve is developed by calculating a series of equilibrium compositions of the distillate product at the reflux drum temperature but over a pressure range. A reflux drum pressure can then be selected from the curve that satisfies an acceptable tower pressure profile. A final equilibrium calculation is then made at this pressure to provide the component and quantity composition of the liquid and vapor streams leaving the reflux drum.

An example of deethanizer overhead operating conditions is given below:

Assume that the overhead vapor from the reflux drum, which is the product in this case, has the following molar composition:

Mole	Fraction
C_1	0.063
C_2	0.443
C_3	0.494

A reasonable temperature for operating the reflux drum is 100 °F (based on local ambient conditions). The reflux drum pressure is calculated from the dew point of the vapor at the reflux drum pressure, thus:

	Vapor mole fract y	K at 100 °F and 350 psia	Liquid mole fract x
C_1	0.063	7.0	0.009
C_2	0.443	2.0	0.222
C_3	0.494	0.64	0.772
Total	1.000		1.003

This was the second trial starting with the pressure at 450 psia. The total x value is close enough to y to allow the pressure to be 350 psia.

Now the tower top conditions will be at the dew point of the reflux plus the product leaving the tower. The pressure will be the reflux drum pressure plus, say, 7 psi for the condenser and piping pressure drop. In this case this pressure will be 357 psia. Set the reflux ratio (moles reflux/mol product) to be 2.0:1 where the moles/h rate of the product is 7.9. The composition of the reflux stream is the x value of the product vapor. The dew point calculation to establish the tower top temperature therefore will be as shown in Table 6.

Note this dew point calculation may change if subsequent calculations show that the reflux ratio required will be significantly different to the one assumed here.

It is not proposed to show the case of the partially condensed product here. This calculation would be similar to the deethanizer and in this case the reflux composition will be the liquid phase from the equilibrium flash of the product.

Table 6 Calculating the tower top temperature for a deethanizer

Component	Mole/h prod	Mole/h reflux	Total moles/h	Mole fraction *y*	*K* at 357 psia and 133 °F	Mole fract liquid *x*
C1	0.5	0.14	0.64	0.027	0.42	0.064
C2	3.5	3.49	6.99	0.295	2.00	0.148
C3	3.9	12.17	16.07	0.678	0.86	0.788
Total	7.9	15.80	23.70	1.000		1.000

Table 7 Debutanizer bottom temperature (bubble point)

Components	Moles/h	Mol fract *x*	*K* at 138 psia and 358 °F	$Y = x/K$
nC4	3.5	0.003	3.7	0.010
iC5	112.1	0.082	2.4	0.198
nC5	155.33	0.114	2.0	0.228
C6	251.35	0.185	1.4	0.259
C7	292.78	0.215	0.77	0.166
Mpt 224 ° F	108.62	0.080	0.58	0.046
239 °F	150.58	0.111	0.49	0.054
260 °F	127.31	0.094	0.38	0.036
276 °F	81.71	0.060	0.29	0.017
304 °F	76.51	0.056	0.21	0.012
Total	1,359.79	1.000		1.026

The tower bottom condition is therefore 138 psia and 358 °F

Calculating the Tower Bottom Conditions for Light Ends Towers

The calculation to establish the tower bottom conditions for all light ends towers is the same. Only the values for pressure and composition change. The temperature of the product leaving the bottom of the tower will be at its bubble point at the tower bottom pressure. Consider the debutanizer column whose material balance was given in Table 2.

The number of actual trays (estimated) to accomplish the separation between the C_4s and the C_5s is 30. The pressure drop for fully loaded trays can be taken as being between 0.15 and 0.2 psi. Assume then a pressure drop of 0.17 psi per tray. The tower top pressure calculated earlier is 125 psia, and then the bottom pressure is $125 + (0.17 \times 30) = 130$ psia (Table 7).

Calculating the Number of Trays in Light Ends Towers

For definitive design work, one of the many excellent simulation packages should be used. However most simulation packages require good quality input data. This often means a fairly accurate estimate of the number of theoretical trays and the liquid/vapor traffic in the tower. An acceptably accurate “short-cut” method to arrive at the number of theoretical trays is given here. The estimate of the liquid/ vapor traffic is discussed later in this chapter.

The Short-Cut Method for Predicting Number of Theoretical Trays

Three calculations or relationships are used to determine the number of theoretical trays in this method. These are:

The Fenske calculation to determine the minimum number of trays at total reflux
The Underwood calculation to determine the minimum reflux at infinite number of trays
The Gilliland correlation which uses the result of the two calculations to give the theoretical number of trays

The Fenske Equation This has been discussed earlier under the section dealing with the “Material Balance for Light Ends Towers.” The equation is as follows:

$$N_{\mathrm{m}+1} = \mathrm{Log}\left[(\mathrm{LT\,key}/\mathrm{HY\,key})_D(\mathrm{HY\,key}/\mathrm{LT\,key})_W\right] \div \mathrm{Log}\left(K_{\mathrm{LT\ key}}/K_{\mathrm{HY\ key}}\right) \tag{2}$$

where:

N_{m} = minimum number of theoretical trays at total reflux. The +1 is the reboiler which is counted as a theoretical tray.

LT key = is the mole fraction of the selected light key.

HY key = is the mole fraction of the selected heavy key.

D = fractions in the distillate product.

W = fractions in the bottom product.

$K_{LT\ \mathrm{key}}$ = the equilibrium constant of the light key at mean system conditions of temperature and pressure.

$\mathrm{K}_{\mathrm{HY\ key}}$ = the equilibrium constant of the heavy key again at mean system conditions.

The Underwood Equation and Calculation The Underwood equation is more complex than the Fenske and requires a trial and error calculation to solve it. The equation itself is in two parts: the first looks at the vapor volatilities (ratio of the Ks) of each component to one of the keys and then by trial and error arriving at an expression for a factor B that forces the equation to zero. This first equation is written as follows:

$$\sum((\phi i)\cdot(xiF)\div(xiF)-B))=0 \tag{3}$$

where:

ϕi = the relative volatility of component i
xiF = the mole fraction of component i in the feed
B = the factor that forces the expression to zero

The second part of the equation is expressed as follows:

$$R_{(\mathrm{m}+1)} = \sum ((\phi i) \cdot (xiD)) \div ((xiD) - B) \tag{4}$$

where:

R_{m} = minimum reflux at infinite number of trays
xiD = the mole fraction of i in the distillate

The relationship between the Fenske equation and the Underwood is given by the Gilliland correlation shown in Fig. 2.

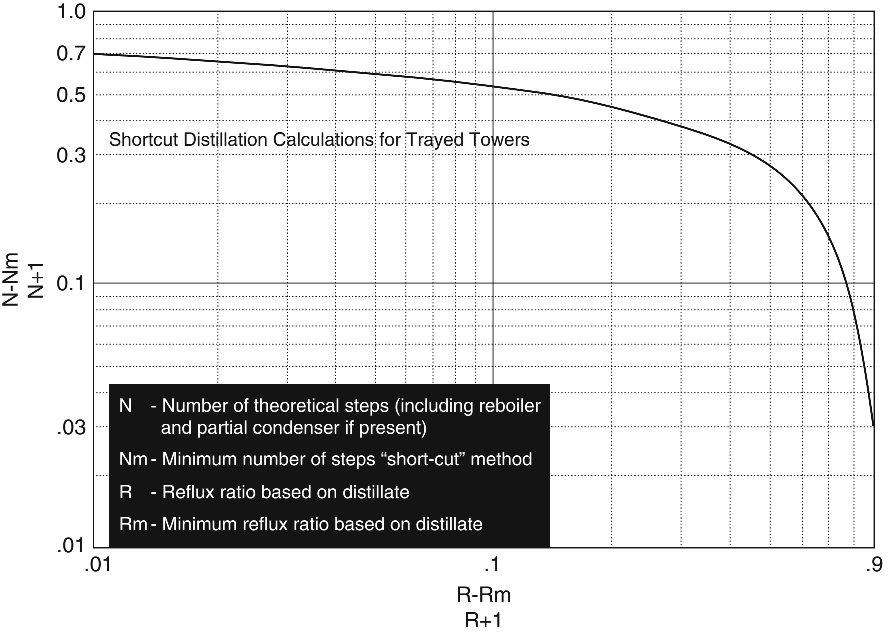


Fig. 2 The Gilliland correlation for calculating theoretical trays

Table 8 Underwood equation, Part 1, calculation example

Comp	Mol fract x_f	K at Ave[a] cond	Rel vol Φ	$x_f \times \Phi$	Trial 3(1) $B = 0.815$
C2	0.003	9.0	4.5	0.0135	0.0037
C3	0.026	4.2	2.1	0.0545	0.0424
iC4	0.025	2.4	1.2	0.0300	0.0776
nC4 (Key)	0.070	2.0	1.00	0.0700	0.3753
iC5	0.075	1.2	0.62	0.0450	−0.2108
nC5	0.100	1.0	0.52	0.0500	−0.1595
C6	0.162	0.49	0.245	0.0397	−0.0698
C7	0.188	0.25	0.125	0.0235	−0.0341
M Bpt 224 °F	0.070	0.16	0.08	0.0056	−0.0076
239 °F	0.097	0.13	0.065	0.0040	−0.0084
260 °F	0.082	0.097	0.0485	0.0039	−0.0052
276 °F	0.053	0.069	0.0345	0.0018	−0.0023
304 °F	0.049	0.042	0.021	0.0010	−0.0013
Total	1.000				0

[a] Ave conditions are 134 psia and 255 °F

$\Sigma((\phi i) \cdot (xiF) \div (xiF) - B)) = 0(1)$

Table 9 Underwood equation, Part 2, calculation example

Comp	Mole fract x_D	Rel vol Φ	$(x_D)(\Phi)$	$(x_D)(\Phi)/(\Phi - B)$
C2	0.022	4.5	0.0945	0.0257
C3	0.217	2.1	0.4431	0.3444
iC4	0.207	1.2	0.2436	0.6303
nC4 (Key)	0.544	1.00	0.5450	2.9223
iC5	0.010	0.60	0.012	−0.0562
Total	1.000			3.8665

$R_{m+1} = 3.8665$ $R_m = 2.87$ and $R = 2.87 \times 1.5 = 4.3$

An Example of the Underwood Equation Calculation

Consider the material balance of a debutanizer developed in Table 2.

Part 1 of the Underwood equation is calculated as shown in Table 8.

Part 2 of the Underwood equation is calculated as shown in Table 9.

Using the Gilliland Curve: $\frac{(R - R_m)}{R + 1} = 0.27$

And from the curve: $\left(\frac{N - N_m}{N + 1}\right) = 0.4$.

Then number of theoretical trays N will be $N - N_m = 0.4\ N + 0.4$.

N_m calculated from the Fenske equation (see section on “Developing the Material Balance for Light Ends Units”) is 14.

Then $N = 24$.

Assume an average tray efficiency of 70 % then total actual trays = 34.

Condenser and Reboiler Duties

Both the condenser and reboiler duties are the result of the light ends tower heat balance that meets the degree of separation required in the products. It may be said that the condenser duty and operation determine the amount of wash liquid flow in the tower to meet the degree of rectification required for the lighter product. The reboiler in turn generates the vapor flow in the tower to satisfy the degree of stripping required for the particular separation and the quality of the heavy product. At a constant feed temperature and pressure, changes to either the condenser duty or the reboiler duty will affect the duty of the other. In other words the tower must always be in heat balance.

Calculating the Condenser Duty

The duty of the overhead condenser is determined by a heat balance over the tower top (above the top tray) and reflux drum, with the condenser duty being the unknown quantity. Using the data already determined for the debutanizer in the previous sections, the following is a calculation to determine the condenser duty for this unit.

Consider the following heat balance sketch (Fig. 3).

In the following heat balance, the liquid overflow from the top tray is based on the internal reflux ratio obtained from the Fenske, Underwood equations, and the Gilliland correlation. This ratio is in moles and its molecular weight is derived from the molal composition of the dew point calculation to establish the tower top temperature. It is the mole weight of the liquid in equilibrium with the overhead distillate vapor. Thus the total moles of the overflow liquid are 4.3 × 191.66 = 824.14 mol/h. Its mole weight is 56.79. Therefore overflow liquid is 46,803 lb/h. The heat balance now follows (Table 10).

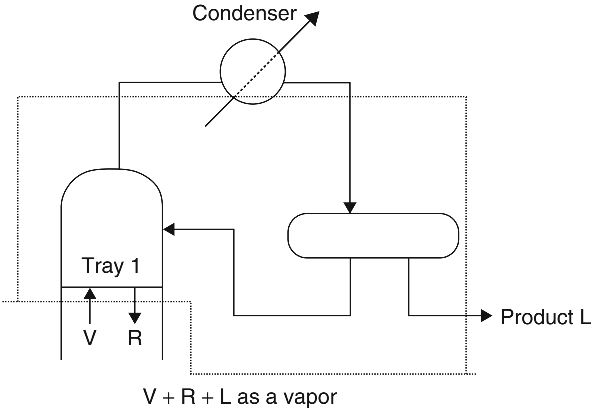


Fig. 3 The overhead heat balance figure

Table 10 Tower top heat balance example

Stream	L/V	Mole wt	°F	lb/h	Btu/lb	MMBtu/h
In						
Ref o/flow	V	56.8	160	46,803	305	14.275
Distillate	V	55	160	10,494	306	3.211
Total in				57,297		17.486
Out						
Dist Prod	L	55	100	10,494	150	1.574
Ref Liquid	L	56.8	155	46,803	190	8.893
Condenser				By difference		7.019
Total out				57.297		17.486

The top tray temperature is taken as 3° F above the tower top temperature. The vapor to the top tray is taken to be about 5° F above the top tray.

Condenser duty is 7,020,000 Btu/h.

Calculating the Reboiler Duty

It is important that the reboiler duty achieve a balance between generating an effective rate of vapor for stripping the bottom product while maintaining an economic vapor load on the stripping trays. As a rule of thumb, this can be achieved with a stripping rate as a percent of bottom product of between 70 and 90 mol %. The tower bottom temperature has already been calculated as 358 °F at 138 psia. The composition of the vapor in equilibrium at these conditions has also been calculated. Thus the moles/h of bottom product are 1,359.79; then the moles of strip-out required will be $1{,}359.79 \times 0.9 = 1{,}223.8$ mol/h. The molecular weight of the strip-out is 88 (from the equilibrium composition). The heat balance to determine the reboiler duty now follows. In this calculation the draw-off tray to the reboiler is about 10° F lower than the tower bottom temperature, that is, 348 °F (Table 11).

Calculating the Overall Tower Heat Balance

Knowing the reboiler and condenser duties, an overall heat balance over the tower can be calculated and will provide the preheat required in the feed and consequently its temperature. A calculation to determine the bubble point of the feed at 134 psia (mean inlet pressure) was made. This temperature was 305 °F. Should the calculated temperature be above this, then an enthalpy curve would need to be developed for the feed to determine its actual enthalpy and temperature. The overall heat balance now follows (Table 12).

Enthalpy of the feed is $\frac{21,713,000}{142,659} = 152.2\,\mathrm{Btu/lb}$; from the enthalpy tables, the temperature is found to be 276 °F. The feed tray is based on a preliminary tower

Table 11 Bottom tray heat balance

Stream	L or V	Temp °F	lb/h	Btu/lb	MMBtu/h
In					
Liquid ex tray 34	L	348	239,860	198	47.492
Reboiler			By difference		13.403
Total in					
Out					
Bot product	L	358	132,165	200	26.433
Strip out	V	358	107,695	320	34.462
Total out			239,860		60.895

Reboiler duty is 13,403,000 Btu/h

Table 12 Overall tower heat balance

Stream	V or L	Temp °F	lb/h	Btu/lb	MMBtu/h
In					
Feed	L	T	142,659	By diff	21.713
Reboiler					13.403
Total in					35.116
Out					
Distillate	L	100	10,494	150	1.574
Bot prod	L	358	132,165	200	26.433
Condenser					7.109
Total out			142,659		35.116

temperature profile with a 75 % efficiency for rectifying trays and a 65 % efficiency for the stripping trays (see Fig. 4). Both the temperature profile and the tray efficiencies will be finalized by a suitable computer simulation package or a rigorous tray-to-tray calculation. Note: The calculation techniques and examples given here are good input to computer simulation packages; wherever possible, these packages should be used for final process design.

Tower Loading and Sizing

Light ends towers all follow the following principles of cross-sectional area sizing and tower height. These dimensions are interrelated by the height required between trays to ensure proper separation of clear liquid from the frothy mixture of the tray inlet fluid. There are many procedures and correlations to determine these dimensions. The following method is just one which will provide a good estimate for tower design. For definitive design, however it is essential that tray manufacturers be consulted and their methodology be used. After all they, the manufacturers, will be required to guarantee the performance of the unit in terms of flooding capacity and tray efficiency. In all cases this has to be a significant consideration, but in case

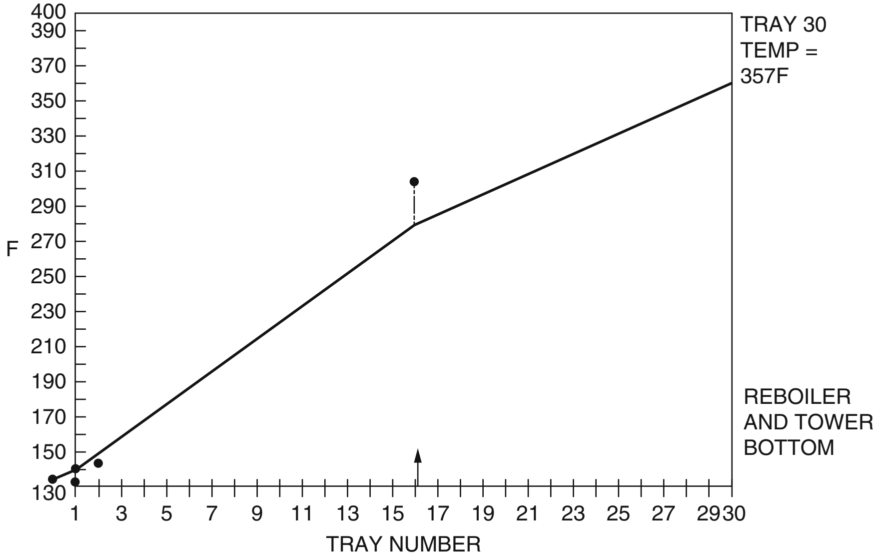


Fig. 4 Tower temperature profile

of super fractionating units with over a hundred trays in many cases, this has to be a primary consideration.

There are many light ends tower computer simulation packages in the market, and most of these calculate vapor and liquid traffic in the tower on a tray-to-tray basis. The input for these programs however does require a fairly accurate estimate of these values for easy convergence and subsequent use of the program. The following procedure with the equations used can provide details of tower loading and tray criteria at critical trays in the tower. A linear correlation between these points will then provide a reasonable loading profile over the tower sufficient for good computer input.

Tower Loading and Overall Tower Diameter

The diameter of a fractionating tower is usually based on the vapor loading on two critical trays. These are the tower top tray which will set the diameter for the rectifying section (i.e., the trays above the feed tray) and the tower bottom tray. This lower tray sets the tower diameter for the stripping section of the tower (i.e., the feed tray and the trays below the feed tray). These two sections may have different diameters.

The vapor loading is based on the rate of vapor passing through the tray and the density of the vapor and the liquid on the tray through which the vapor bubbles. This relationship is given by the Brown and Souders equation. There are several forms of this equation which can be used with the appropriate physical tray constants. One of the forms used here is as follows:

$$G_f = K\sqrt{}(\rho_v \times (\rho_1 - \rho_v)) \tag{5}$$

where:

G_f = mass of vapor per sq foot of tray at flood (lb/h · ft^2)
K = a constant based on tray spacing at flood (see chapter "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries")
ρ_v = density of vapor at tray conditions of temperature and pressure in lb/cuft
ρ_l = density of liquid at tray conditions in lb/cuft

The area thus determined is the "bubble" area of the tray. Normally trays are designed at 85–90 % of flood. Therefore for good design, the G_f is divided by this percentage to give the actual or design area of the tray. The whole tray is made up of two other areas: that for the downcomers and a waste area which is allocated to calming the liquid leaving the bubble area before entering the downcomer. The relationship of these areas to one another is given in Table 13.

Using the criteria in Table 13 and the value of the bubble area based on the vapor loading, the total tray area and therefore the tower diameter can be determined. This relationship is summed up by the following expression:

$$A_s = A_B + A_{dc} + A_w \tag{6}$$

where:

A_s = total tray area
A_B = bubble area
A_{dc} = downcomer area (inlet + outlet)
A_w = waste or calming zone area (usually 15 % of A_s)

Tray Spacing

The tray spacing used in the initial determination of flood loading needs to be checked. If necessary, the spacing and the calculation will be revised to meet the correct spacing criteria. Usually this first guess at tray spacing is taken as 24″. The following equations are then applied to determine whether this spacing is satisfactory. These equations calculate the pressure drop across the tray in terms of the clear liquid holdup (or height) in the downcomer. This height of liquid must be less than 50 % of the tray spacing for most applications. In the case of a high foaming process, this height must be less than 40 % of the tray spacing. These pressure drop criteria concerning the tray hydraulics and their associated equations now follow:

Table 13 Valve and sieve tray characterization

Design feature	Suggested value	Alternate values	Comment
1. Valve size and layout			
(a) Valve diameter	–	–	Valve diameter is fixed by the vendor
(b) Percent hole area A_o/A_b	12	8–15	Open area should be set by the designer. In general, the lower the open area, the higher the efficiency and flexibility, and the lower the capacity (due to increased pressure drop). At values of open area toward the upper end of the range (say 15 %), the flexibility and efficiency are approaching sieve tray values. At the lower end of the range, capacity and downcomer filling become limiting
(c) Valve pitch diam ratio	–	–	Valve pitch is normally triangular. However, this variable is usually fixed by the vendor
(d) Valve distribution	–	–	On trays with flow path length $\geq 5'$, and for liquid rates $>5{,}000$ GPH/ft. (diameter) on trays with flow path length $<5'$, provide 10 % more valves on the inlet half of the tray than on the outlet half
(e) Bubble area, A_b or A_B	–	–	Bubble area should be maximized
(f) Tray efficiency	–	–	Valve tray efficiency will be about equal to sieve tray efficiency provided there is not a blowing or flooding limitation
(g) Valve blanking	–	–	This should not generally be necessary unless tower is being sized for future service at much higher rates. Blanking strips can then be used. Blank within bubble area, not around periphery to maintain best efficiency
2. Tray spacing	–	12–36	Generally economic to use min. values which are which are usually set by maintenance requirements. Other considerations are downcomer filling and flexibility. The use of variable spacing to accommodate loading changes from section to section should be considered

(*continued*)

Table 13 (continued)

Design feature	Suggested value	Alternate values	Comment
3. Number of liquid passes	1	1–2	Multi-passing improves liquid handling capacity at the expense of vapor capacity for a given diameter column and tray spacing. Cost is apparently no greater – at least, for tower diameters <8 ft.
4. Downcomers and weirs			
(a) Allowable downcomer inlet vel ft/s of clear liq		0.3–0.4	Lower value recommended for absorbers or other systems of known high frothiness
(b) Type of downcomer	Chord	Chord, arc	Min. chord length should be 65 % of tray diameter for good liquid distribution. Sloped downcomers can be used for high liquid rates – with maximum outlet velocity = 0.6 ft/s. Arc downcomers may be used alternatively to give more bubble area (and higher capacity) but are somewhat more expensive. Min. width should be 6 in. for the latter
(c) Inboard DC width (inlet and outlet)		Min. 8 in.	Use of a 14–16″ "jump baffle" suspended lengthwise in the center of the inboard downcomer and extending the length of the downcomer is suggested to prevent possible bridging over by froth entering the downcomer from opposite sides. Elevation of base of jump baffle should be level with outlet weirs. Internal access way must be provided to allow passage from one side to another during inspection
(d) Outlet weir height	2″	1–4″	Weir height can be varied with liquid rate to give a total liquid head on the tray (hc) in the range of 2.5–4″ whenever possible. Lower values suggested for vacuum towers, higher ones for long residence time applications
(e) Clearance under DC	1.5″	1″ min	Set clearance to give head loss of approximately 1 in. Higher values can be used if necessary to assure sealing of downcomer

(*continued*)

Table 13 (continued)

Design feature	Suggested value	Alternate values	Comment
(f) DC seal (inlet or outlet weir height minus DC clearance)	Use outlet weir to give min. ½″ seal in tray liquid	Inlet weir or recessed inlet box	In most cases tray liquid level can be made high enough to seal the downcomer through use of outlet weir only. Inlet weirs add to downcomer buildup; in some cases they may be desirable for 2-pass trays to ensure equal liquid distribution. Recessed inlets are more expensive but may be necessary in cases where an operating seal would require an excessively high outlet weir
(g) DC filling (% of tray spacing)		40–50	Use the lower value for high pressure towers, absorbers, vacuum towers, known foaming systems, and also for tray spacing of 18″ or lower

Clear Liquid Height, h_{cl}

$$h_{\mathrm{cl}} = 0.5 \times \left[V_L \div \left(N_p \times l_o\right)\right]^{2/3} \tag{7}$$

where:

h_{cl} = height of clear liquid on tray in inches of hot liquid
V_{L} = liquid loading in gallons per minute of hot liquid
N_{p} = number of passes on tray
l_{o} = length of outlet weir in inches

Effective Dry Tray Pressure Drop, h_{ed} The effective dry tray ΔP shall be the greater of the following two expressions:

(a)

$$\Delta P_{\mathrm{po}} = 1.35\, t_{\mathrm{m}}.\rho_{\mathrm{m}}/\rho_1 + \mathrm{K}.\left(V_{\mathrm{o}}^2\right).\rho_{\mathrm{v}}/\rho_{\mathrm{l}} \tag{8}$$

(b)

$$\Delta P_{\mathrm{fo}} = K_2\left(V_{\mathrm{o}}^2\right)\rho_{\mathrm{v}}/\rho_{\mathrm{l}} \tag{9}$$

where:

ΔP_{po} = dry tray ΔP, valve partially open. In inches of hot liquid
ΔP_{fo} = dry tray ΔP, valve fully open. In inches of hot liquid
t_{m} = valve thickness in inches (see Table 14)
ρ_{m} = valve metal density in lb/cuft (see Table 15)
V_{o} = vapor velocity through valves in ft/s (= cuft/s/A_{o})

Table 14 Valve thickness in inches

Gage	t_m
20	0.037
18	0.050
16	0.060
14	0.074
12	0.104
10	0.134
8	0.250

Table 15 Valve metal densities (in lb/cuft)

Metal	Density, ρ_m
C.S.	480
S.S.	510
Nickel	553
Monel	550
Titanium	283
Hastelloy	560
Aluminum	168
Copper	560
Lead	708

Table 16 Values of K_1 and K_2

Type of unit	K_1	K_2			
Deck thickness ins		0.074	0.104	0.134	0.25
Normal valves	0.2	1.05	0.92	0.82	0.58
Vacuum valves	0.1	0.50	0.39	0.38	–

Constants K_1 and K_2 are given in Table 16.
In calculating V_o, assume ratio hole to bubble area (A_o/A_B) is 12 %.

Total Tray, ΔP · ht

$$\text{Total tray } \Delta P = h_{\text{cl}} + h_{\text{ed}} \tag{10}$$

where:

h_{cl} = height of clear liquid on tray in inches of hot liquid
h_{ed} = effective dry pressure drop in inches of hot liquid

Head Loss Under Downcomer, h_{ud}

$$h_{ud} = 0.06\left[\text{GPM} \div \left(cL_i - N_p\right)\right]^2 \tag{11}$$

where:

h_{ud} = head loss under downcomer in inches of hot liquid
c = constant = 1.5
L_i = length of inlet weir in inches

Inlet Head in Inches of Hot Liquid, h_i When there is an inlet weir, use:

$$h_i = 0.06\left[GPM \div \left(N_p \cdot L_i\right)\right]^{2/3} + h_{wi} \tag{12}$$

where:

h_i = tray inlet head in inches of hot liquid
L_i = length of inlet weir in inches
h_{wi} = height of inlet weir in inches

Where there is no inlet weir, then $h_i = h_{cl}$.

Downcomer Filling in Inches of Hot Liquid

$$L_d = h_i + (h_t + h_{ud}) \cdot [\rho_1 \div (\rho_1 - \rho_V)] + 1.0 \tag{13}$$

where:
L_d = downcomer filling in inches of hot liquid

Example Tower Sizing Calculations

The following is an example of tower sizing and hydraulic analysis. Tray loading data that is used for this example are those calculated for the debutanizer column earlier in this chapter. Thus, all data are at tray conditions of temperature and pressure (Table 17):

Bubble area on top tray at flood:

$$G_f = K\sqrt{(\rho_v \times (\rho_1 - \rho_v))} \tag{14}$$

where:

G_f = load at Flood in lb/h ft^2
K = 1,110

Table 17 Example tower sizing basis

Vapor	Top tray	Liquid	Top tray
Moles/h	1,012	lb/h	46,803
lb/h	57,297	GPM	187
ACFS	14.3	CFS	0.147
ρ_v lb/cuft	1.11	ρ_l lb/cuft	31.18
Vapor	Bottom tray	Liquid	Bottom tray
Moles/h	1,223.9	lb/h	239,860
lb/h	107,695	GPM	768.4
ACFS	8.7	CFS	1.715
ρ_v lb/cuft	3.44	ρ_l lb/cuft	38.9

$\rho_v = 1.11$
$\rho_l = 33.37$
$G_f = 6{,}415.8$ lb/h ft^2

Tower diameter will be designed to 80 % of flood. Then $G_A = 5{,}132.6$ lb/h ft^2
Bubble section A_B of tray at 80 % flood will be $\frac{57,297}{5,132.6} = 11.16$ ft^2.
Downcomer area (inlet and outlet) A_{dc}:
Downcomer velocity will be 0.4 ft/s (see Table 13).
Then area of one downcomer will be $0.417 \div 0.4 = 1.04$ ft^2.
Total downcomer area $A_{dc} = 2.08$ ft^2.
Waste area of tray A_w will be 15 % (see Table 13).
Total tray area $A_s = A_B + A_{dc} + A_w$.
Then for the top section of the tower, the diameter will be:

$A_s - 0.15A_s = 2.08 + 11.6$ ft^2
$A_s = 15.58$ ft^2 diameter = 4.45 f. say 4.5 ft

Similarly for the stripping side of the tower:

$$\begin{aligned} G_f &= 1,110\surd 3.44 \times (38.9 - 3.44) \\ &= 12,259 \text{ lb/h ft}^2 \text{ and at 80 \% flood } G_a = 9,807 \text{ lb/h ft}^2 \end{aligned}$$

Downcomer area = 1.715/0.4 = 4.29 ft^2 and $A_{dc} = 8.58$ ft^2.
$A_s = 24$ ft^2 and diam is 5.53 ft, say 6 ft.

Tower Hydraulics and Downcomer Filling

Using the pressure drop equations defined earlier, the percentage of downcomer filled by liquid is calculated. This calculation is based on the stripping section of the tower only. A similar one will be completed for the rectifying section. Thus:

Clear Liquid Height, h_{cl}

$$h_{cl} = 0.5 \times \left[V_L \div \left(N_p \times L_o\right)\right]^{2/3} \tag{7}$$

$V_L = 768.4$ GPM.
$N_p = 2$ (liquid loading is relatively high so the option of a two pass tray is used).
$L_o = 58.8$ in. Use the correlation given in Appendix 1 of the chapter entitled "▶ Process Equipment for Petroleum Processing" in this handbook.
Then $h_{cl} = 1.74$ in. of hot liquid.

Effective Dry Tray, ΔP

(a)

$$\Delta P_{po} = 1.35 t_m . \rho_m / \rho_l + K_1 . \left(V_o{}^2\right) . \rho_v / \rho_l \tag{8}$$

(b)

$$\Delta P_{\mathrm{fo}} = K_2(V_{\mathrm{o}})\rho_{\mathrm{v}}/\rho_{\mathrm{l}} \tag{9}$$

Use $A_o/A_B = 12\ \%$ giving A_o as 1.32 ft^2.
Valve thickness is 0.05 in., and metal density is 480 lb/cuft.

$K_1 = 0.2, K_2 = 0.92$
$V_o = 6.6$ ft/s
$\Delta P_{po} = 1.603$ in. of hot liquid
$\Delta P_{fo} = 3.54$ in. of hot liquid

Total Tray, ΔP · h_t $h_t = 1.74 + 3.54 = 5.28$ in. of hot liquid

Head Loss Under Downcomer, h_{ud}

h_ud = 0.06[GPM ÷ ($cL_i \cdot N_p$)]2
$c = 3.2$ (estimated)
$L_i = 58.8$ in.
$h_{ud} = 0.96$ in. of hot liquid

Inlet Weir Head, h_i There is no inlet weir therefore $h_i = h_{cl}$.

Total downcomer filling, L_D

$$\begin{aligned} L_D &= 1.74 + (5.28\ + 0.96)(38.9/35.46) + 1 \\ &= 9.54\ \text{ inches of hot liquid.} \\ &= 40\,\%\ \text{ of tray spacing, which is satisfactory.} \end{aligned}$$

Checks for Light Ends Tower Operation and Performance

Most light ends towers are very stable in their operation. That is, once they are lined out for an operating requirement under normal unit control, they maintain their stability. When performance falls off, it can be attributed to one of a few reasons. This section looks at some of these reasons and how they can be evaluated and checked. Performance in this case is meant the ability of the unit to make product quality at the prescribed throughput.

Cold Feed

The condition of the feed entering the tower is very important to the tower operation. Ideally the feed should enter the tower at as close to a calculated feed tray temperature as possible. If the feed is well below its bubble point on entering the tower, several trays below the feed tray are taken up for heat transfer before effective mass transfer can begin. This could prevent the specified product separation occurring and tray efficiency in this section of the tower falls off dramatically. Feed condition can be checked by bubble point calculation and a flash calculation.

Hot Feed

This situation is probably the more serious regarding feed condition. If the feed enters at a temperature far above its bubble point, its resulting enthalpy will be such as to reduce the reboiler duty. This will occur automatically as the tower must always be in heat balance. The tower controls will maintain the product quantity and split. However, if the reboiler duty is drastically reduced, insufficient stripper vapors will be available for the stripping function. Poor separation will result.

As a rule of thumb, the stripping vapor to the bottom tray must be at least 70 % mole of the bottom product made. In super fractionation, such as a deisopentanizer, this figure would be at least 80–100 % of bottoms made.

Heat balances as shown will quickly determine the stripping vapor status.

Ideal Feed Condition

Ideally the feed should enter the tower close to the feed tray temperature. Usually then at the inlet pressure, the feed will be in a mixed phase with the vapor portion very close in quantity to the distillate product. As the feed to these units is generally heated by the bottom product heat exchange, the approach temperatures are always a consideration. To maintain good feed conditions, however it is often beneficial to include a separate steam (or hot oil) feed preheater.

Entrainment

A common cause of poor plant performance at high throughout or high reflux rates is liquid entrainment or carryover from tray to tray. Very often in a high load and entrainment situation, the problem is further aggravated by increasing reflux to attempt separation improvement.

A well-designed light ends tower can operate up to about 120 % of allowable flood before substantial carryover occurs. Loading above this figure would result in some degree of entrainment.

Downcomer Backup and Flooding

If tower loadings are increased well above allowable flood point, there is a real danger that downcomers become unable to cope with the liquid load. They would fill, and the tower would be in a state of flood. This will be very apparent with very high, abnormal pressure drops occurring across the tower. Separation by fractionation is not possible under these conditions. Heat input (and feed rate) to the tower must be reduced to bring the unit back to a normal pressure drop.

Low Tower Loading

Most towers have been designed with at least a 50 % turndown ratio for the trays. This means that the trays should operate satisfactorily at 50 % of their loading. Nevertheless tray performance does fall off at these low loadings. Below this turndown ratio, performance, particularly in sieve trays, is drastically reduced. This is almost certain to be due to "weeping" where liquid falls from tray to tray. If the low loads are to be for only a short time due to temporary reduced throughput, tray loading can be increased by increasing reflux. If the low throughput is to continue for an extended period of time, a tray blanking schedule should be considered to reduce the active tray area.

Operating Close to Critical Conditions

Deethanizers in particular operate close to critical pressure at the bottom of the tower. Careful attention should be paid to avoid any pressure surges in this unit. Feed to the unit and reflux streams should be on flow control.

No separation by fractionation can occur at pressures in excess of critical. Very often chilled water is used for overhead condensing to reduce reflux drum pressure but maintaining minimum C_3 loss in the case of deethanizers.

Catalytic Reforming in Petroleum Processing

Mark P. Lapinski, Stephen Metro, Peter R. Pujadó, and Mark Moser

Contents

Peter R. Pujadó has retired.

M.P. Lapinski (✉) • S. Metro • M. Moser
UOP LLC, A Honeywell Company, Des Plaines, IL, USA
e-mail: mark.lapinski@honeywell.com; steve.metro@honeywell.com;
mark.moser@honeywell.com

P.R. Pujadó
UOP LLC, A Honeywell Company, Kildeer, IL, USA
e-mail: prpujado@gmail.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_1

Abstract

Catalytic naphtha reforming is a major process in the petroleum refinery that converts low value naphthas into high-octane reformate product for gasoline blending and into high-value aromatics for petrochemical processing. Catalytic reforming also provides valuable hydrogen for hydroprocessing units to produce clean fuels. In the reforming process, naphthas rich in paraffins and naphthenes are converted mainly to aromatic hydrocarbons by contacting with a platinum-containing acidic catalyst at elevated temperatures and pressures. This chapter will briefly review the history of catalytic reforming and then describe the naphtha feed properties, market trends, reforming reactions, catalysts, deactivation mechanisms, catalyst regeneration, unit diagrams, process conditions and economics.

Keywords

Catalytic reforming • Platforming • Semiregenerative • Continuous • Cyclic • Platinum • Chlorided alumina • Fixed-bed • Naphtha • Octane • Aromatics • Paraffins • Naphthenes • Motor fuels • Reformate • CCR • Redispersion • Deactivation • BTX • Rhenium • Pt-Re • Pt-Sn • Hydrotreating

Introduction

Catalytic reforming is a process in which petroleum naphthas, rich in paraffins and naphthenes, are contacted with a platinum-containing acidic catalyst at elevated temperatures and pressures for converting to a product that is rich in aromatic hydrocarbons. When the objective is to create motor fuels, low octane naphtha feed is converted, or “reformed,” to a high-octane liquid gasoline blending component called reformate. When the objective is to create aromatics as a feedstock for the petrochemical industry (Huebner 1999), more severe conditions are employed to increase the conversion of the naphtha feed to maximize the production of aromatics. In both cases, hydrogen and other light hydrocarbons are produced in the reactions as by-products. In some applications, hydrogen has a high value and is a desired product from the process.

History

The need to upgrade naphthas for transportation fuels was recognized early in the twentieth century. Thermal processes were initially used, but catalytic processes introduced in the 1940s offered better yields and higher octanes. The first catalysts were based on supported molybdenum oxide, but were soon replaced by platinum-containing catalysts. The first platinum-based reforming process, UOP's Platforming™ process, came on-stream in 1949 at Old Dutch Refining in Muskegon, Michigan, USA. Since the first Platforming unit was commercialized, innovations and advances have been made continuously, including process flow schemes and parameter optimization, catalyst formulations, equipment design, and maximization of reformate and hydrogen yields. The need to increase yields and octane led to lower pressure, higher severity operations. Higher severity generally refers to conditions such as higher temperature that lead to higher naphtha conversion. This also results in increased catalyst coking, faster deactivation rates, decreasing yields, and shorter catalyst lives.

The first catalytic reforming units were designed as semiregenerative (SR) or fixed-bed units with three to four reactors in series, using Pt/alumina catalysts. SR reforming units are periodically shut down for catalyst regeneration. A cycle may run from 6 to 36 months, typically about 1 year. Regeneration involves burning off coke and reconditioning the catalyst's active metals. To minimize catalyst coking and deactivation, these older units were operated at high pressures in the range of 2,760–3,450 kPa (400–500 psig).

Catalytic reforming processes were improved by the introduction of bimetallic catalysts. These catalysts allowed lower pressure, high severity operations at about 1,380–2,070 kPa (200–300 psig) and could achieve a 95–98 research octane number (RON) with typical cycle lengths of 1 year between catalyst regenerations.

The cyclic reforming process was developed in the 1960s by several major oil companies such as Esso (Powerforming™), Standard Oil (Ultraforming™), and Shell. These processes allow operation at increased severity by significantly decreasing the time between regenerations. Cyclic reformers typically employ five fixed-bed reactors in which each can be isolated from the main process flow, regenerated, and put back into service without shutting down the unit and losing production. Each reactor is regenerated every 3–30 days depending on severity, feed type, and reactor position. The average reactor pressures are approximately 1,380 kPa (200 psig) producing reformates with research octane numbers near 100.

A significant innovation addressing catalyst deactivation and on-stream efficiency was the commercialization of the Platforming™ process with continuous

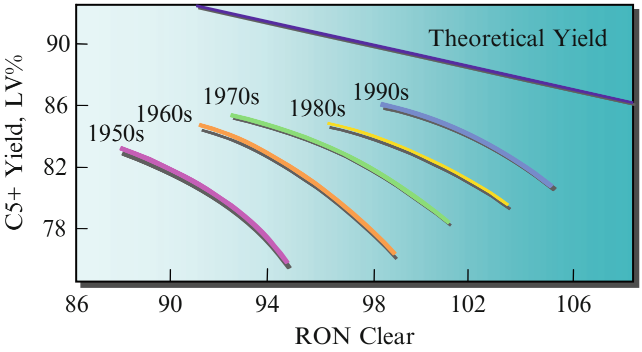


Fig. 1 Increases in catalytic reforming yields and octanes with catalyst and process innovations (Reprinted with permission from UOP LLC)

catalyst regeneration, or the CCR Platforming process, by UOP in 1971. The Institut Français du Pétrole commercialized a continuous regeneration reforming process (Octanizing and Aromizing process versions) a few years later. With continuous catalyst regeneration, small amounts of catalyst are continuously removed from the last reactor where the coke level is highest, regenerated in a controlled environment in a separate regeneration vessel that is in series with the process, and transferred back to the first reactor. The catalyst travels around a closed loop between the reactors and regenerator. The CCR Platforming process has enabled the use of significantly lower pressures of 345 kPa (50 psig) and significantly higher product octanes, as high as 108 RON, compared to both cyclic and SR reforming processes. More than 95 % of all new catalytic reformers today are designed with continuous regeneration. In addition, many units that were originally built as SR reforming units have been revamped to continuously regenerable reforming units.

Figure 1 is a representation of the evolution of catalytic reforming showing the increases in C_5+ reformate yield and research octane number (RON) from the 1950s to the 1990s, stemming from the introduction of new processes, equipment, and new catalysts in this period.

Feedstocks

Naphtha feedstocks to reformers contain paraffins, naphthenes, aromatics, and in some cases very small amount of olefins. For the production of motor fuels, the feeds are typically "full range" naphthas consisting of hydrocarbons with 6–11 carbon atoms. For geographical regions with regulations on the benzene content of gasoline, the initial boiling point of the feed may be increased by fractionation to reduce the amount of benzene precursors such as cyclohexane and methylcyclopentane. Reforming units with the objective of producing benzene, toluene, and xylenes are commonly referred as BTX or aromatic reformers, and naphthas

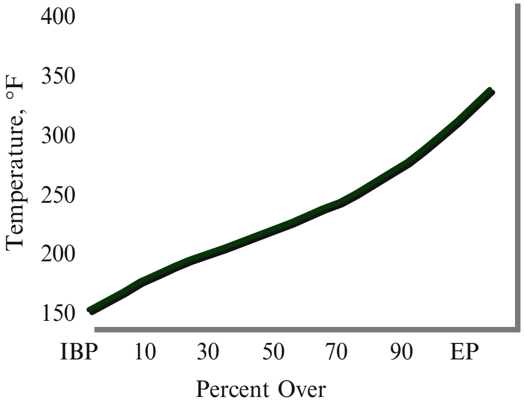


Fig. 2 ASTM D-86 distillation curve for naphtha (Huebner et al. 1999)

for these units ideally contain naphthenes, aromatics, and paraffins in predominantly the six to eight carbon atom range.

The most common type of naphtha is derived directly from crude distillation and is called straight run naphtha. In addition to straight run, naphthas can be derived from other processes that catalytically or thermally crack heavier hydrocarbons to naphtha range hydrocarbons. For example, cracked feedstocks may be derived from fluid catalytic cracking (FCC) units, hydrocracking units, cokers, and visbreaking units. Naphthas can also be synthetically derived from a Fischer-Tropsch process.

Characterization

Naphthas are characterized by their boiling point curves and component compositions. Distillation values for the initial boiling point (IBP), the mid-boiling point, and the endpoint (EP) as shown in Fig. 2 are often used to classify the naphtha as light or heavy. Straight run naphtha from crude distillation with a boiling range of 150–400 °F (65–200 °C) would be classified as heavy naphtha.

Table 1 shows the composition for typical naphtha that contains 55.4 wt.% total paraffins, 30.7 wt.% total naphthenes, 0.1 wt.% total olefins, and 13.9 wt.% total aromatics. Naphthas are classified as lean or rich based on their compositions. A lean feed has a high concentration of paraffins and relatively low concentrations of naphthenes and aromatics, whereas a rich feed has a low paraffin concentration and relatively high concentrations of naphthenes plus aromatics.

The heaviness (distillation endpoint) and type (lean or rich) are indicators of the difficulty in reforming the naphtha. For example, light-lean naphtha with an endpoint of 320 °F (160 °C) and 65 wt.% paraffins is more difficult to reform than a heavy-rich naphtha with an endpoint of 370 °F (188 °C) and 60 wt.% naphthenes plus aromatics.

Table 1 Composition of a typical naphtha

Component	Concentration, wt%
Aromatics	
Benzene	1.45
Toluene	4.06
Ethylbenzene	0.52
p-Xylene	0.92
m-Xylene	2.75
o-Xylene	0.87
C9+ aromatics	3.31
Total aromatics	13.88
Paraffins and naphthenes	
Propane	0.79
Isobutane	1.28
n-Butane	3.43
Isopentane	5.62
n-Pentane	6.19
Cyclopentane	1.40
C6 isoparaffins	6.00
n-Hexane	5.30
Methylcyclopentane	2.58
Cyclohexane	3.26
C7 isoparaffins	4.55
n-Heptane	4.65
C7 cyclopentanes	2.77
Methylcyclohexane	7.57
C8 isoparaffins	4.24
n-Octane	3.43
C8 cyclopentanes	1.52
C8 cyclohexanes	5.23
C9 naphthenes	3.63
C9 paraffins	5.93
C10 naphthenes	1.66
C10 paraffins	3.41
C11 naphthenes	1.04
C11 paraffins	0.53
Total paraffins	55.35
Total olefins	0.11
Total naphthenes	30.66

Naphtha Feed Pretreatment

In order to prevent contamination and deactivation of a reforming catalyst, most naphtha feeds must be hydrotreated to remove several types of contaminants. Common poisons for reforming catalysts include sulfur (Fig. 3), nitrogen, and

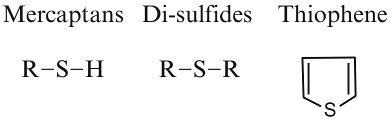


Fig. 3 Sulfur types found in naphthas

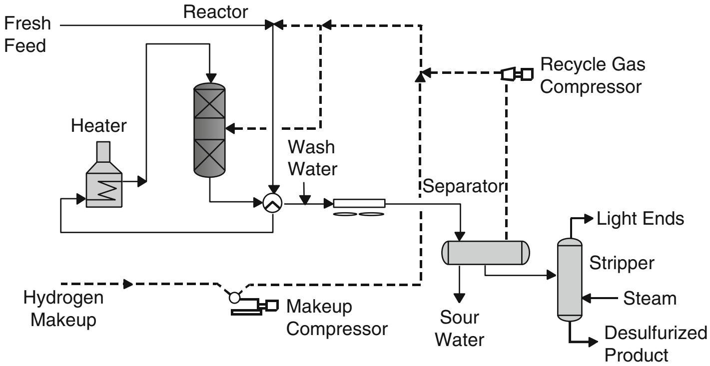


Fig. 4 Naphtha hydrotreater flow scheme

oxygen compounds. Removing these requires breaking of a carbon-sulfur, a carbon-nitrogen, or a carbon-oxygen bond and formation of hydrogen sulfide, ammonia, or water, respectively. Figure 4 shows a naphtha hydrotreater that is used to reduce the contaminant levels in naphthas to acceptable levels. Hydrotreaters will also saturate olefins and remove metal contaminants such as Si, As, and Pb by adsorption on the naphtha hydrotreating catalyst support.

Some naphtha hydrotreaters are two-stage units. The first stage operates at low temperature for the hydrogenation of diolefins and acetylenes that could polymerize and plug the second, higher severity stage. The effluent from the first stage is cooled and fed to the second stage for the hydrogenation of olefins and the removal of sulfur and nitrogen compounds.

Reformate Properties

The reformate product from a catalytic reforming unit is used either as a high-octane gasoline blending component or as a source of aromatics such as benzene, toluene, and xylenes (BTX), and C_9+ aromatics. Table 2 shows an example of reformate composition.

Octane Number

For motor fuel applications, the octane number is the dominant parameter of product quality. Octane number is a measure of a fuel's resistance to burn. A higher

Table 2 Reformate composition

Component	Mass%	Liq-vol%
Aromatics		
Benzene	3.72	3.39
Toluene	13.97	12.93
Ethylbenzene	3.13	2.90
p-Xylene	3.39	3.14
m-Xylene	7.47	6.91
o-Xylene	4.83	4.47
C9+ aromatics	36.05	33.30
Total aromatics	72.56	67.04
Paraffins and naphthenes		
Propane	0.00	0.00
Isobutane	0.14	0.20
n-Butane	0.94	1.32
Isopentane	2.52	3.29
n-Pentane	1.74	2.29
Cyclopentane	0.10	0.10
C6 isoparaffins	3.91	4.77
n-Hexane	1.74	2.12
Methylcyclopentane	0.28	0.30
Cyclohexane	0.03	0.03
C7 isoparaffins	7.70	9.02
n-Heptane	2.22	2.60
C7 cyclopentanes	0.33	0.35
Methylcyclohexane	0.04	0.04
C8 isoparaffins	2.86	3.24
n-Octane	0.62	0.70
C8 cyclopentanes	0.14	0.14
C8 cyclohexanes	0.06	0.06
C9 naphthenes	0.04	0.04
C9 paraffins	0.90	0.99
C10 naphthenes	0.04	0.04
C10 paraffins	0.24	0.26
C11 naphthenes	0.00	0.00
C11 paraffins	0.03	0.04
Total paraffins	25.56	30.84
Total olefins	0.82	1.02
Total naphthenes	1.06	1.10

octane number reflects a lower tendency of the hydrocarbon to undergo a rapid, inefficient detonation in an internal combustion engine. This rapid detonation can be heard as an audible knocking or pinging sound in the engine, so octane is often referred to as the antiknock quality of a gasoline. Motor fuel octanes are measured at low engine speeds (research octane number, or RON, as measured by ASTM

Table 3 Examples of research and motor octanes of pure hydrocarbons

Component	RON	MON
Paraffins		
n-Heptane	0.0	0.0
2-Methylhexane	42.4	46.3
3-Ethylpentane	65.0	69.3
2,4-Dimethylpentane	83.1	83.8
2,2,4-Trimethylpentane	100.0	100.0
Aromatics		
Toluene	120.1	103.2
Ethylbenzene	107.4	97.9
Isopropylbenzene	113.0	99.3
1-Methyl-3-ethylbenzene	112.1	100.0
1,3,5-Trimethylbenzene	>120	>120

Table 4 Octane and blending octane numbers by the research method

Component	RON	Blending octane
2,2-Dimethyl butane	92.8	89
2-Methyl-1-butene	102	146
Cyclopentane	101	141
1,4-Dimethylbenzene	117	146

D2699) or at high engine speeds (motor octane number, or MON, as measured by ASTM D2700). In the USA, the octane values posted on gasoline pumps are the arithmetic average of the MON and the RON. The acronym RONC, research octane number clear, is used to denote that there are no additives, such as tetra-ethyl lead (TEL) or methyl-tertiary-butyl-ether (MTBE), included to increase the octane number. Table 3 provides a listing of the various octane numbers of pure hydrocarbons according to the American Petroleum Institute, API (American Petroleum Institute Research Project 45 1954).

Octane numbers of a hydrocarbon or hydrocarbon mixture are determined by comparing its antiknock qualities with various blends of *n*-heptane (defined as zero octane) and 2,2,4-trimethylpentane or iso-octane (defined as 100 octane). Hydrocarbons may appear to have different octane numbers when blended with other hydrocarbons of a different composition; these are denoted as “blending octanes” and may be significantly different from the actual octane numbers of the individual hydrocarbon components. Table 4 shows that the differences between the RON and the blending octane can be significant for some compounds (Marshall and Owen 1995).

Other Properties

Another important property specification of reformate is its volatility or vapor pressure, often given in terms of the Reid vapor pressure or RVP. Sufficient RVP is needed in order to facilitate starting of an internal combustion engine, particularly in cold climates. However, too high of an RVP results in undesirable hydrocarbon emissions into the atmosphere. Other properties are endpoint and color (Marshall and Owen 1995). High-endpoint reformates, for example, may not combust well in an internal combustion engine and lead to formation of carbonaceous or gummy hydrocarbon deposits.

Market Segmentation

The reforming market can be separated into two distinct segments: motor fuels and aromatics. Some reformers operate in both motor fuels and aromatic modes, largely achieved by changing the operating temperature. The mode of operation is dependent upon the processor's downstream configuration and product demand.

Motor Fuels

The gasolines available to the consumer consist of a mixture of gasoline fractions from many refinery sources, including: straight run naphtha, isomerate, alkylate, reformate, polymer, and FCC fractions. Gasoline also contains additives such as ethanol, used to lower emissions via oxygenate addition, boost octane, and consume a biofuel source, typically from corn and sugar cane.

As shown in Fig. 5, gasoline demand has risen from slightly less than 20 million B/D in 2000 to about 23 million B/D in 2013. Gasoline demand is expected to rise to 28 million B/D over the next decade. About half of the demand has been in developed regions such as North America, Europe, and Japan. Growth has been categorized as flat to declining in these regions due to increased use of ethanol,

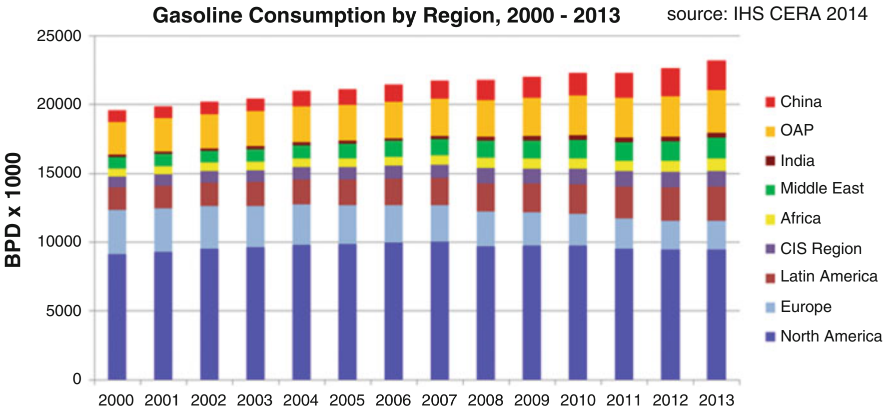


Fig. 5 Overall gasoline demand by region

increased use of diesel fuel, and improved automobile fuel efficiencies. The strongest growth over the past decade has occurred in emerging regions such as Asia, Russia, Middle East, and Latin America, which currently make up roughly 50 % of demand and is expected to rise to 58 % by 2025 (IHS CERA Annual Long-Term Strategic Workbook and Product Markets 2014). The drivers for growth include large, growing populations and economies, increased wealth, and export of goods and services.

Gasoline is subject to many local, national, and international regulations. New regulations affecting gasoline composition have been enacted in most regions of the world, driving the increase in demand for clean fuels. These regulations include many clean fuel initiatives, including lead phase down; minimization of RVP, sulfur, benzene, aromatics, and olefin content; and addition of oxygenates. For example, Euro 5 motor fuel specifications, last updated in 2009, limit aromatics to 35 vol.%, olefins to 18 vol.%, and benzene to 1 vol.% maximum. Currently many non-EU countries are still in the planning phases of implementing either Euro 4 or Euro 5 specifications. Table 5 shows the Euro 1–5 gasoline specifications (Euro Fuel Specifications).

In the USA, the Environmental Protection Agency (EPA) sets the standards. There are some variations from state to state, with California generally being the most stringent. Gasoline specifications set by the California Air Resources Board (CARB) have the following limits: 35 vol.% aromatic maximum, 1.1 vol.% benzene maximum, 10 vol.% olefins maximum, 10 vol.% ethanol minimum, RVP 6.4–7.2 psi, and sulfur less than 20 wppm. It should be noted that the US EPA's Tier 3 sulfur limits have been set for 10 wppm maximum by 2017.

As indicated above, benzene content in gasoline is one component broadly regulated. For instance, in the USA, the EPA has implemented a Mobile Source Air Toxics (MSAT) rule to reduce hazardous air pollutants (US EPA MSAT program regulations 2014). As of 2011, the EPA requires that refiners must meet a maximum annual *average* gasoline benzene content of 0.62 vol.%. The maximum permissible level is 1.3 vol.% as of July 2012. These are applied to US refiners as well as gasoline imported into the USA.

Many of the items regulated for motor fuels are key components produced by reforming naphtha. However, the catalytic reformer is typically part of a naphtha complex, where the naphtha feed is divided into lighter and heavier fractions using a naphtha splitter distillation column. The heavier fraction, typically C_7+ hydrocarbons, is sent to the reformer, whereas the lighter fraction, typically a C_5/C_6 fraction, is sent to an isomerization unit, the subject of another chapter in this handbook. The isomerization unit, such as the UOP Penex^{TM} process, for example, saturates benzene to cyclohexane and converts the C_5 and C_6 paraffins and naphthenes to high-octane, highly branched paraffins.

One of the by-products from reforming, whether motor fuels or aromatics, is hydrogen. Many reformers are critical for production of hydrogen in a refinery, used for hydrotreating and hydrocracking processes. Some reformer units are operated for hydrogen production at the expense of making reformate at a higher octane than required.

Table 5 Euro fuel specifications

		Directive	EN 228	DIR 98/70	DIR 98/70	DIR 98/70	DIR 98/70
		Year	1993	1996	2000	2005	2009
Euro fuel specifications		Class	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5
Aromatics	Vol %	Max	No limit	No limit	42	35	35
Olefins	Vol %	Max	No limit	No limit	18	18	18
Benzene	Vol %	Max	5	5	1	1	1
Oxygen	Wt %	Max	2.5	2.5	2.7	2.7	3.7
Sulfur	ppm	Max	1,000	500	150	50	10
RON		Min	91	92	93	94	95
RVP	kPa		35–100	35–100	60–70	60–70	60–70
Lead	g/l	Max	0.013	0.013	None	None	None

Aromatics

Approximately one-third of reforming capacity is used for the production of aromatics. Many reformers are an integral part of an aromatic complex, producing an aromatic-rich feed to other process units to make benzene, toluene, and xylenes, particularly para-xylene.

Benzene is primarily used in the production of ethylbenzene, cumene, and cyclohexane. Plastics and polymers are produced from styrene, which is made from ethylbenzene. Resins and adhesives are produced from phenol, which is made from cumene. Nylon is produced from cyclohexane. The majority of reformers produce mixed aromatics which are subsequently converted and/or purified to benzene. There are a few catalytic reforming units such as UOP RZ Platforming process that are dedicated to on-purpose benzene production with very high selectivity to benzene. Toluene is a common solvent used in paints, lacquers, rubber, ink, adhesives, silicone sealants, polyurethane foam, and TNT.

Para-xylene is the primary C_8 aromatic of interest, since it is used to make polyesters. The polyester chain generally begins with *p*-xylene and ends with a form of polyethylene terephthalate or more commonly PET. *p*-Xylene is converted to purified terephthalic acid (PTA), and a melt polymerization process is used to make polyester. Approximately two-thirds of PET is used for production of polyester fibers in filament and staple forms, with the former used to make textiles and apparels. One-third is used for production of resins used for PET bottles, packaging, and film. *p*-Xylene demand (Fig. 6) has had a steady growth trend along with world population growth. *p*-Xylene capacity grew fourfold from 10,000 kMTA in 1990 to

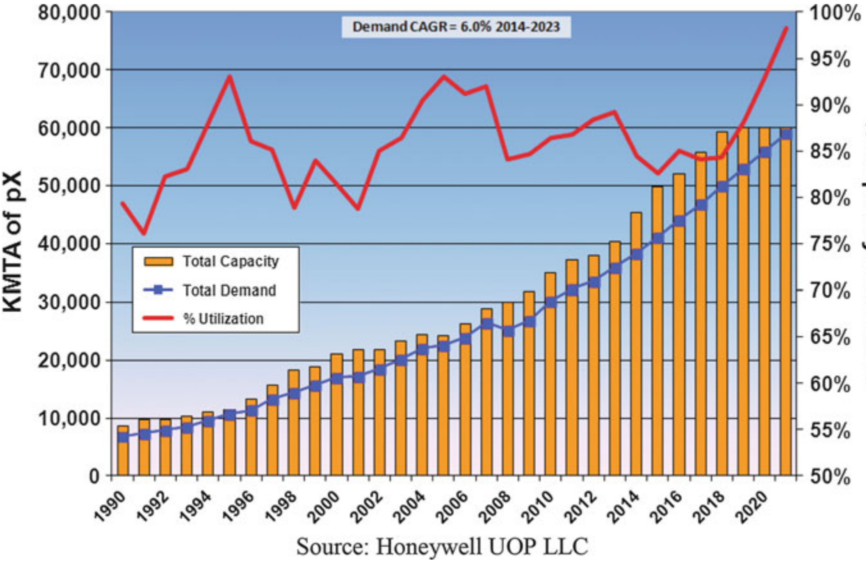


Fig. 6 Para-xylene supply and demand (Source: Honeywell UOP LLC)

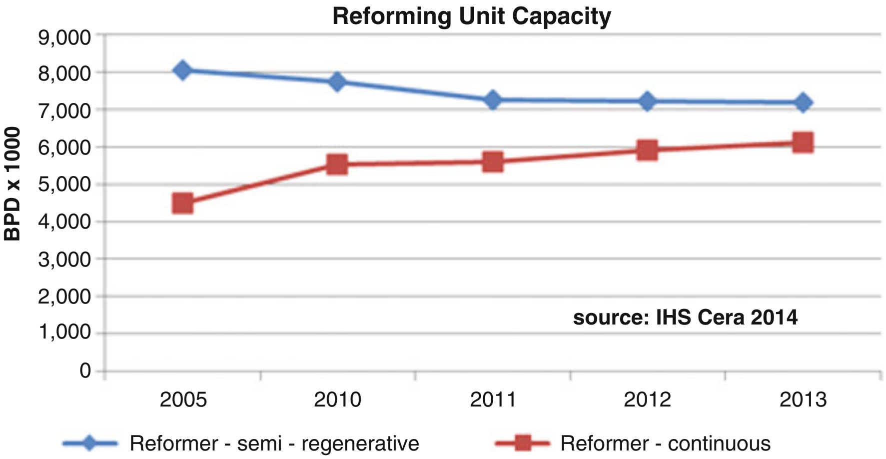


Fig. 7 Reforming capacity

40,000 kMTA in 2015. The growth rate is expected to be approximately 6 % over the next decade. Capacity utilizations range from 75 % to 95 % and, when high, tend to drive investment for new capacity. The market is fairly cyclic for addition of new capacity.

Trends and Regulations

As previously mentioned, the first SR type reforming unit was introduced in 1949 by UOP. At its peak, over 700 fixed-bed reforming units were in operation. The first continuous regeneration type reforming unit was introduced in 1971 by UOP. In 2014, approximately 300 continuous type units were in operation, 250 designed and licensed by UOP, and the balance from Axens IFP Group. IHS Cera data (Fig. 7) indicate that the total global reforming capacity for refining was about 13.3 million B/D in 2013, 7.2 from SR type units, and 6.1 from continuous type units.

Due to the improved efficiency of CCR type units, the majority of new units licensed today are the continuous type. While most are new units, some are conversions from existing SR units. It is estimated that the number of SR units today is less than 400 in part due to conversion to CCR or even isomerization but also due to shutdown because of age or lack of demand for gasoline. Cyclic fixed-bed reforming units total less than 30 as of 2014, and the expectation is for continued retirement due to maintenance costs and efficiency issues. Shutdown of fixed-bed reformers is most prevalent in developed regions such as the USA, Europe, and Japan. This can be observed in the capacity trends: in 1990, SR reformate capacity was 8.8 million B/D (85 %) and CCR was 1.6 million B/D. It is projected that in 2020, three decades later, SR reformate capacity will be 7.2 million B/D (49 %) and CCR will be 7.6 million B/D.

Another important trend is that unit capacity continues to increase which provides higher efficiency via economy of scale. CCR reforming unit capacities range from 5,000 to 100,000 B/D, with unit capacity trending higher beginning after the year 2000. The average unit capacity as of 2014 is approximately 23,000 B/D.

Reforming Reactions

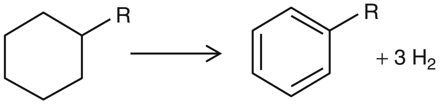
In BTX production, the objective is to transform paraffins and naphthenes into benzene, toluene, and xylenes with minimal cracking to light gases. The yield of desired product is the percentage of feed converted to aromatics. In motor fuel applications, the objective is to greatly increase the octane value which is accomplished via aromatization of paraffins and naphthenes, isomerization of the paraffins into higher octane branched species, and the removal of low octane paraffins by cracking to gaseous products. The yield is defined as liquid product with five or more carbons (C_5+ reformate). This section will describe the main reactions in reforming.

Reaction Sites

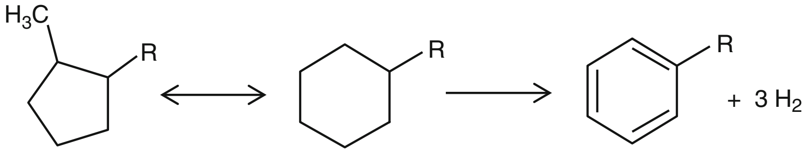
Typical reforming catalysts consist of platinum with additional metals as modifiers or attenuators supported on chlorided alumina. In these bifunctional catalysts, separate and distinct reactions occur on the platinum sites and on the acidic chlorided alumina sites. The platinum sites primarily perform dehydrogenation and hydrogenolysis (C-C scission), while the acidic alumina sites mainly perform isomerization, cyclization, and hydrocracking.

Naphthene Reactions

The conversion of naphthenes to aromatics is one of the key reactions on reforming catalysts. Naphtha feeds contain both five-member and six-member naphthene rings such as cyclopentanes, substituted cyclopentanes, cyclohexanes, and substituted cyclohexanes. The six carbon ring cyclohexanes, for example, can be directly dehydrogenated to produce aromatics and hydrogen on platinum sites. This is a very fast reaction which produces significant endotherms in the lead reactors due to the large amount of naphthenes typically in the naphtha feed.



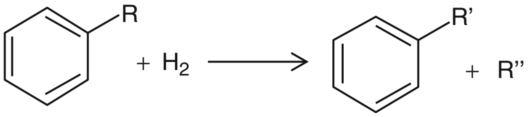
However, the five-member ring cyclopentanes must be hydroisomerized to give a cyclohexane intermediate prior to dehydrogenation to aromatics.



Acid-catalyzed reactions together with the Pt-catalyzed dehydrogenation function are largely responsible for hydroisomerization reactions that lead to the formation of aromatics.

Aromatic Reactions

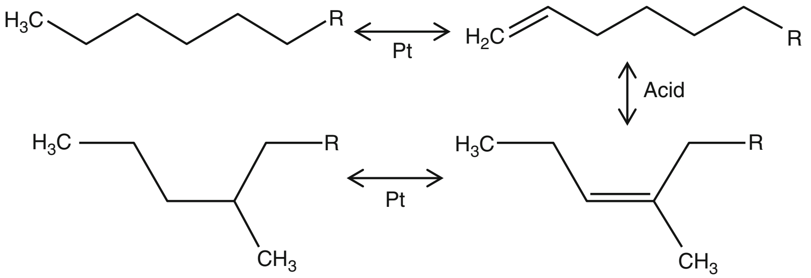
Aromatics are stable species and relatively inert, but the side groups can react under reforming conditions. Reactions of substituted aromatics include isomerization, dealkylation, disproportionation, and transalkylation. Dealkylation can include making the alkyl side chain smaller or completely removing the side chain. Dealkylation is favored by high temperatures and high pressures.



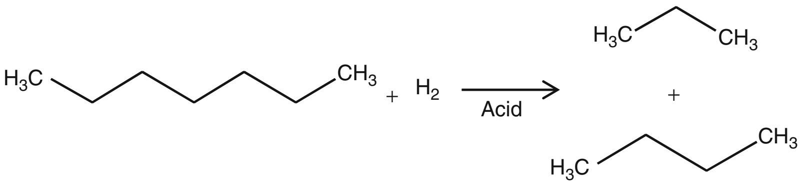
Paraffin Reactions

Paraffin conversion is the most difficult step in reforming. For that reason, the ability to convert paraffins selectively is of paramount importance. The most desired pathway for paraffins is to cyclize to form aromatics. It is also desirable for paraffins to dehydrogenate to olefins and to isomerize to branched paraffins. The least desirable reaction is paraffin hydrocracking which produces lower value light hydrocarbons and consumes valuable hydrogen. While hydrocracking of paraffins does lead to the removal of lower value octane components in the reformate for gasoline blending, it is more valuable to convert the paraffins to aromatics or multibranched paraffins and maintain high reformate yields. For BTX operations, it is critical to maximize the selectivity of paraffin cyclization over paraffin hydrocracking in order to maximize the production of aromatics and hydrogen. Each of the paraffin reactions is discussed below.

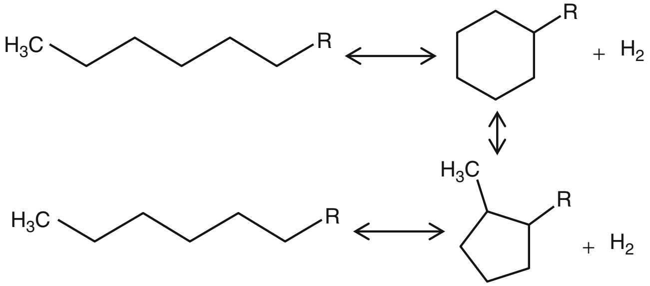
Paraffins are dehydrogenated on the platinum sites (Mills et al. 1953) to form olefins which can then isomerize over the acid function of the catalyst to provide higher octane branched paraffins.



Acid-catalyzed hydrocracking reactions convert paraffins to mostly C_3 and C_4 products. Longer chain paraffins can also produce C_5 and C_6 cracked products. All of these paraffin reactions are thought to proceed through olefin intermediates as demonstrated above (bifunctional mechanism). Additional paraffin cracking (hydrogenolysis or metal-catalyzed cracking) reactions occur on the metal sites resulting in predominantly C_1 and C_2 products.



The most desired reaction for paraffins is to cyclize to form cyclohexanes and cyclopentanes as shown below (dehydrocyclization). These reactions are also believed to proceed through olefin intermediates. The cyclization of the olefin may be catalyzed by the acidic alumina support. As already shown, after cyclization, cyclohexane rings undergo rapid dehydrogenation to aromatics.



Rates and Equilibrium

The dehydrogenation of naphthenes and paraffins is rapid, and equilibrium concentrations are established in the initial portions of a catalyst bed. Isomerization

Table 6 Thermodynamic data for reforming compounds at 800 K, ideal gas in kcal/mol

	ΔH_f^o	ΔG_f^o
Typical C_6's		
n-Hexane	−48.26	73.08
2-Methylpentane	−49.68	72.74
3-Methylpentane	−49.32	73.67
Cyclohexane	−37.19	75.94
Methylcyclopentane	−33.73	71.92
Benzene	15.51	52.84
Typical C_7's		
n-Heptane	−54.20	87.43
2-Methylhexane	−55.91	87.23
3-Methylhexane	−55.28	87.07
Methylcyclohexane	−45.10	86.15
Toluene	6.65	61.98

reactions are sufficiently fast that actual concentrations are near equilibrium. The observed reaction rate for dehydrocyclization is reduced by the low concentrations of the olefin intermediates that exist at equilibrium. Hydrogen partial pressure significantly affects olefin equilibrium concentrations and has a significant impact on aromatization and dehydrocyclization of paraffins. Lowering hydrogen partial pressures results in an increase in the rate of aromatization, a decrease in the rate of hydrocracking, and an increase in the rate of coke formation.

Table 6 provides thermodynamic data for typical compounds in reforming reactions at a reference temperature of 800 K. Thermodynamic data can be obtained from standard sources (American Petroleum Institute Research Project 45; Stull et al. 1969). Production of aromatics is favored by reforming conditions, specifically high temperatures and low pressures. Current reforming unit designs at low hydrogen partial pressures ensure full conversion to the equilibrium limits.

Reforming Catalysts

As mentioned above, reforming catalysts consist of platinum with additional metals as modifiers or attenuators supported on a chlorided alumina support. The specific composition of the catalyst depends on the type of reforming process: fixed-bed which includes semiregenerative and cyclic reforming and continuous which includes the UOP CCR Platforming process and the Axens IFP Octanizing process for gasoline and the Aromizing process for BTX aromatics. This section describes the metal and support and then describes the specific catalyst formulations for each type of reforming process.

Metal

The concentration of Pt on reforming catalysts is generally in the range of 0.2–0.6 wt.%. The platinum must be dispersed over the alumina surface such that

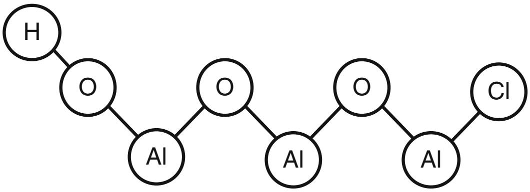


Fig. 8 Alumina schematic

the maximum number of active sites for dehydrogenation is available. Platinum cluster size dimensions are on the order of angstroms or 10^{-10} m. The interaction of the platinum with the alumina surface is such that the platinum clusters are relatively immobile and do not agglomerate during reforming reactions. However, there is Pt agglomeration during regeneration and the Pt must be redispersed.

The cost of the Pt to a refiner can be significant, with Pt prices increasing fourfold from about US$400 per troy ounce in the 1990s to US$1,600 per troy ounce (US$ 51,440/kg) in the 2010s. At 2014 market prices for Pt and catalyst, the value of the Pt content is approximately four times as much as the base catalyst cost to a refiner.

Sulfidation of the platinum is sometimes used to partially poison the platinum or reduce its activity; this has the beneficial effect of reducing a major portion of the hydrogenolysis or metal-catalyzed cracking reactions. Liquid product yields are improved, and the light gas production, particularly methane, is reduced.

Alumina Support

The alumina support can be in the eta (η) or gamma (γ) phase, but gamma is most often utilized in reforming catalysts. Chloride is added during the catalyst finishing step to promote acidity. It is also added to the process during regeneration to maintain the level, typically with a compound such as perchloroethylene (PERC). A simplified schematic diagram of the alumina functionality is shown in Fig. 8. There are two main shapes of the catalyst supports, cylindrical and spherical. The cylindrical catalysts are usually extruded alumina. The spherical catalysts may be formed through a dropping method or by rolling wet, soft alumina dough. In some instances, factors such as the resistance to flow or flow distribution concerns may cause one form to be chosen over the other. The density of the support may vary from approximately 0.5–0.8 g/cm^3. The variability in density allows more pounds of catalyst to be loaded in the reactors which can provide additional catalyst activity or stability.

Catalysts for Semiregenerative Units

Catalysts that are used in SR units must have long catalyst life cycles since the catalyst is only regenerated typically once every 6–24 months or longer. Modifiers are crucial to reduce the effect of coke buildup and to lengthen the catalyst cycle length. SR reformers make use of catalysts that contain platinum modified by rhenium or, to a lesser extent, iridium. These modifiers act by either hydrogenating the coke to a less graphitic species (Augustine et al. 1989) or by cracking the coke precursors (Sorrentino et al. 1984). Rhenium or iridium significantly enhances the life of the catalyst over older catalysts that only contained Pt. Pt-Re catalysts have been improved by increasing the ratio of Re to Pt which provides additional catalyst stability. All SR catalysts are sulfided to minimize metal-catalyzed hydrogenolysis reactions that produce light gases and reduce gasoline yield.

The support is most often gamma alumina, although there have been some uses of eta alumina (Mills et al. 1953). The supports are typically extrudates in cylindrical form with diameters that range from 1.6 mm (1/16 in.) to 2.1 mm (1/12 in.).

Since the reactors are fixed in an SR unit, different catalysts can be loaded in different positions. The use of two catalysts in an SR unit – one catalyst in the front reactors and another catalyst in the back reactors to provide maximum yield, activity, and stability – was commercialized in 1994 (Weiszmann 1986). New-generation SR catalysts are further improving C_5+ reformate yields by the addition of promoters to attenuate metal cracking, by modification of the support density, by optimization of the Pt/Re ratio, and by improvement of manufacturing procedures (Moser et al. 1996; Lapinski et al. 2006).

Catalysts for Cyclic Units

Cyclic reforming units have fixed beds, but there is an additional swing reactor that is substituted in any reactor position to allow regeneration of each reactor on an ongoing basis. The catalysts types that have been used in cyclic reforming include Pt, Pt-Re, Pt-Ir, and Pt-Sn on chlorided alumina. Because the reactors can be regenerated one after another, lower stability Pt-only catalysts are still being used by some refiners in their cyclic units.

Catalysts for CCR Process Units

In moving bed continuous regeneration units (Weiszmann 1986), the catalyst flows through the reactors and is regenerated continually in a separate regeneration vessel that is part of the reactor-regenerator loop. Process conditions are much more severe, thus shortening catalyst life and requiring regeneration cycles of only a few days. The catalysts types found best for this service are Pt-Sn on chlorided alumina. These catalysts increase the liquid, aromatic, and hydrogen yields by reducing the activity of the platinum for hydrogenolysis or metal-catalyzed cracking reactions. These components also provide some stabilization of the catalyst relative to Pt alone.

New proprietary catalysts have been developed that utilize additional promoter elements that modify both the acid and metal functions to increase yields, lower coke make, or allow higher throughput (Lapinski et al. 2006). The criteria for selection of the best promoters include the impact on coke make, catalyst stability, ability to function correctly over many oxidation-reduction cycles, ability to remain on the catalyst (not volatile), and to not detrimentally affect other catalyst properties (Lapinski et al. 2010).

The process of moving catalyst through the reactors and from the reactors to the regenerator and back requires the use of spherical catalysts, rather than cylindrical extrudates. This is needed to minimize catalyst abrasion and breakage from interactions with other catalyst particles, reactor internals, and piping. Some breakage over time is unavoidable, and small amounts of makeup catalyst are typically added to the unit. The typical spherical diameters range between 1.5 and 1.9 mm with densities in the range of 0.5–0.7 g/cm^3. The catalyst is circulated at a rate corresponding to about one regeneration per week or greater if needed based on the deactivation under the selected operating conditions.

Catalyst Suppliers

For detailed up-to-date lists of catalysts and suppliers, the Oil and Gas Journal periodically publishes a comprehensive review. The main suppliers of reforming catalyst are currently Honeywell UOP LLC, UOP CH S.à.r.l., Nikki-Universal Company, Ltd., and Axens IFP Group.

Deactivation and Regeneration

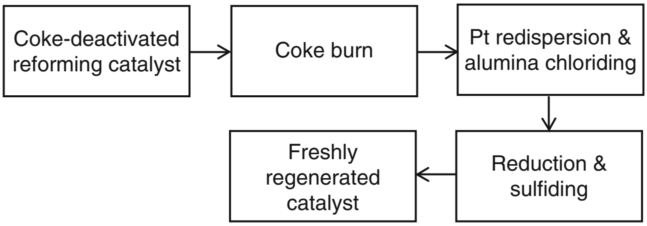
The deactivation mechanisms for reforming catalysts include poisoning, coking, and agglomeration of the platinum. First, poisoning of metal and acid sites is prevented or minimized by making sure that the naphtha hydrotreater is always operating properly to remove N and S compounds and that the naphtha hydrotreating catalyst is replaced before exceeding its capacity for adsorbing metal poisons such as Si, As, and Pb. Fe is a corrosion product in the reforming unit that builds up on the reforming catalyst over time. At higher Fe levels, Fe can plug catalyst pores and/or negatively impact the selectivity of the metal function leading to poorer yields. If the metal contaminants on the reforming catalyst become excessive, a catalyst change-out is required.

Next, under normal reforming operating conditions, coke accumulates on the reforming catalyst and activity is lost, and selectivity is debited at higher coke levels. When the coke is burned in the regeneration step, if the Pt is not properly redispersed, then some of the Pt will remain agglomerated. This results in some of the Pt sites becoming inaccessible which can lead to non-optimum performance.

In an SR unit, coke deactivates the catalyst such that, in time, the temperature limit of the reforming unit will be reached, or the selectivity to desired products is too much reduced, or the octane of the liquid product is declining. When this occurs, the refiner will shut down the SR process unit and regenerate the catalyst in all the reactor positions to return them to their original state. In a cyclic unit, when the coke becomes too high in a particular reactor position, a series of valves are switched putting the deactivated reactor in a separate regeneration system. Meanwhile, a “swing” reactor is substituted for the deactivated reactor so feed processing can continue. In a moving bed reforming unit, some of the catalyst is continually being regenerated outside the process and returned to the reactors such that high selectivity and activity are maintained.

Regeneration Steps

The objective of regeneration is to return the catalyst to its initial, fresh state. If the regeneration is successful, there is no difference in performance between the fresh and regenerated catalyst. To do this, the coke must be burned from the catalyst, the platinum must be well redispersed, the Pt must be reduced, Pt and Pt-Re catalysts must be sulfided, and the alumina must be rechlorided to the correct acidity level. These needs account for the main steps in regeneration: carbon burn, Pt redispersion, chloriding of the alumina, metals reduction, and sulfiding for Pt and Pt-Re catalysts. These steps are outlined below.



The actual chemistry and steps for regeneration for all process units are very similar. In the following discussion, catalyst regeneration for an SR reformer is described in detail. For cyclic or continuous reformers, plant shutdown and start-up are unnecessary, and the remaining steps are accomplished in separate regeneration equipment outside the process stream.

SR Regeneration

In order to conduct regeneration, the heater temperatures and feed rates are reduced gradually. The circulation of recycle gas is continued to strip hydrocarbons from the catalyst, leaving only coke. If the coke is to be burned in the unit, higher temperatures are maintained, and the coke burning procedure is initiated. (If the coked catalyst is to be removed from the unit, temperatures are lowered, to about 100–150 °F before unloading. Since coked catalyst is often pyrophoric, nitrogen blanketing is often used to protect the catalyst from air contact and combustion.)

The coke burning step must be carefully monitored. The combustion of coke to carbon dioxide and water is exothermic, and the oxygen concentration must be kept low to limit the reaction and temperature rise. Excessive temperature can cause agglomeration of the platinum or, in more extreme cases, can cause the alumina to change from the desired phase or crystal structure to a higher temperature phase. The water produced in the combustion also facilitates sintering of platinum. Due to the need to gradually burn coke, the carbon burn is usually the most time-consuming part of a regeneration.

Coke burning is usually done in the range of 400–500 °C at oxygen concentrations initially in the 1–2 mol% range. Oxygen content and temperature are often increased during burning to ensure that all coke has been combusted. Oxygen consumption is monitored to determine the total amount of coke combusted and the extent of the burn.

Since platinum can agglomerate even at relatively moderate exothermic conditions, the platinum must be redispersed after the carbon burn. The temperature is first increased to approximately 500 °C, oxygen content to approximately 5–6 mol%, and chlorine or an organic chloride that breaks down to HCl and Cl_2 is injected into the air/nitrogen stream. Platinum oxychlorides or chlorides form that redisperse platinum over the alumina surface, ensuring that almost all the platinum is exposed for reaction. This also adds chloride to the alumina support to enhance its acidity.

Finally, the last step in the regeneration process is the reduction of the metals on the catalyst and sulfiding, if necessary. This is done in a dry hydrogen atmosphere. At the temperatures required for reduction, greater than 350 °C, high moisture levels can lead to platinum agglomeration. Since water is formed in the reduction process as platinum oxide is reduced to platinum metal, water is drained from the unit during reduction. The reduction hydrogen is recirculated at as high a rate as possible in order to minimize moisture content.

Sulfiding is typically done by injection of H_2S or an organic sulfide into the unit at the end of reduction. Sulfiding is continued until the specified sulfur level is reached or until sulfur is no longer adsorbed by the catalyst as detected at the outlet of the last catalyst bed.

Reforming Process Conditions

The major process variables that affect unit performance are reactor pressure, reactor temperature, space velocity, H_2/HC molar ratio, and catalyst type. The relationship between the variables and process performance is generally applicable to SR, cyclic, and continuous regeneration modes of operation.

Pressure

The reactor pressure affects reformer yields, reactor temperature requirements, and catalyst stability. The average pressure has been defined by the inlet pressure to the last reactor. Practical operating constraints have led to a historical range of operating pressures from 345 to 3,450 kPa (50–500 psig). As a feed passes through the heaters, reactors, and catalyst beds, the overall pressure drop can be as large as 50–60 psig. It is best to minimize the pressure drops in the unit as much as possible so as to operate all the reactors at a lower pressure.

The main benefit of lower pressure is increased aromatic, hydrogen, and reformate yields and decreased temperature requirement to achieve a target product quality (utility savings). However, lower pressure shortens the catalyst cycle because of the increased catalyst coking rate. The higher catalyst deactivation rate associated with operating in the 50–150 psig pressure range requires continuous catalyst regeneration.

Temperature and Space Velocity

The primary control for product quality in catalytic reforming is the temperature of the catalyst beds. Reforming catalysts are capable of operating over a wide range of temperatures. By adjusting the heater outlet temperatures, a refiner can change the octane of the reformate and the quantity of aromatics produced.

The reactor temperature is usually expressed as the weighted average inlet temperature (WAIT). The WAIT is the summation of the product of the fraction of catalyst in each reactor multiplied by the inlet temperature of the reactor. Typically, SR units operate over a WAIT range of 490–525 °C (914–977 °F), while continuous units operate over a WAIT range of about 525–540 °C (977–1,004 °F). CCR Platforming units can operate at even higher temperatures to produce a more aromatic-rich product.

Because the main reforming reactions are endothermic, there is a significant drop in temperature along the catalyst beds. The temperature drop is largest in the first reactor position due to the dehydrogenation of the naphthenes contained in the naphtha feed. The temperature drop is still substantial in the second reactor position but smaller for each successive reactor. It is convenient to also define a weighted average bed temperature (WABT) which accounts for the temperature drops. The WABT is the summation of the weight fraction of catalyst in a bed multiplied by the average of the inlet and outlet bed temperatures.

The amount of naphtha processed over a given amount of catalyst over a set length of time is referred to as space velocity. Space velocity corresponds to the reciprocal of the residence time or time of contact between reactants and catalyst. Since most refiners define their charge rate by volume such as barrels, it is most common to define a liquid hourly space velocity (LHSV, h^{-1}) which is calculated by dividing the volumetric charge rate per hour by the total volume of reforming catalyst in the reactors. The typical commercial LHSVs range from about 1 to 3. Alternatively, a weight hourly space velocity (WHSV, h^{-1}) can be defined by dividing the weight of naphtha feed per hour by the total weight of catalyst in the reactors.

The combination of space velocity and reactor temperature is used to adjust the conversion of the naphtha feed in order to achieve the target product octane or aromatic yield. The greater the space velocity, the higher the temperature required to achieve a given product target. It is important to note that as the conversion of the naphtha is increased producing higher octane reformate, the yield of C_5+ reformate declines due to paraffin cracking reactions forming C_4− products. However, the yields of aromatics and hydrogen will typically continue to rise as the conversion level is increased.

Hydrogen-to-Hydrocarbon Ratio

The hydrogen-to-hydrocarbon (H_2/HC) mole ratio is the ratio of moles of hydrogen in the recycle gas to moles of naphtha charged to the unit. The recycle gas is a mixture of hydrogen and light hydrocarbon gases, typically 75–92 mol% hydrogen. The ratio of total recycle gas to hydrocarbon is sometimes called the gas-to-oil ratio. Recycle hydrogen is necessary to maintain catalyst life stability by removing coke precursors from the catalyst. A proposed mechanism is that the hydrogen allows hydrogenation of the coke precursors and inhibits polymerization to coke.

Because the rate of coke formation on the catalyst is a function of the hydrogen partial pressure, increasing the H_2/HC ratio reduces the coking rate and increases stability with only a small effect on product quality or yields. Lower H_2/HC ratios can provide higher C_5+ and hydrogen yields although this benefit is difficult to measure in commercial units. Since SR units do not regenerate continuously, the cycle length between regenerations can be lengthened by operating under milder conditions which include a higher H_2/HC ratio (i.e., a higher hydrogen partial pressure) and lower reactor temperatures. Continuous units can operate under more severe conditions including lower H_2/HC ratio because catalyst is being continuously removed from the last reactor and sent to the regenerator while fresh catalyst is continuously being fed back to the first reactor.

Process Flow Schemes

Fixed-Bed SR Reforming Units

A simplified SR Platforming flow diagram is shown in Fig. 9. The feed to the unit is mixed with recycled hydrogen gas and heated to reaction conditions by passing through a combined feed-effluent heat exchanger followed by a fired heater. Because most of the reactions that occur in a reforming process are endothermic, the reactor section is separated into several stages or reactors. Inter-heaters are installed between these stages to maintain the desired temperature range across the catalyst in the reactor section. Effluent from the last reactor is cooled by the feed-effluent heat exchanger for maximum heat recovery. Air or water cooling provides additional cooling to near-ambient temperature.

The effluent is then charged to the separation section, where the liquid and gas products are separated. A portion of the gas from the separator is compressed and

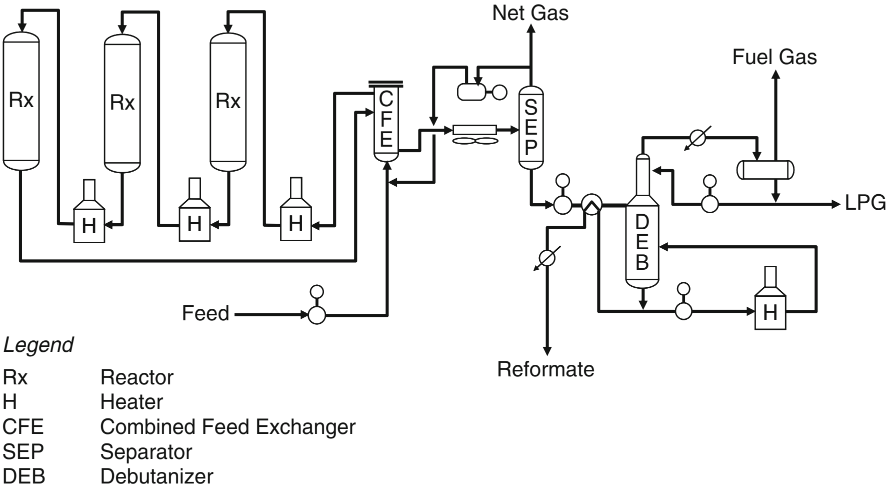


Fig. 9 Semiregenerative reforming process (Reprinted with permission of UOP LLC)

recycled back to the reactor section. The net hydrogen gas produced is sent to hydrogen users in the refinery complex or for use as fuel. The separator liquid is pumped to a product stabilizer (debutanizer) to remove the C_4- hydrocarbons creating the high-octane C_5+ liquid product reformate. The other streams from the debutanizer are fuel gas consisting mostly of C_1 and C_2 hydrocarbons and liquefied petroleum gas (LPG) consisting mostly of C_3 and C_4 hydrocarbons.

Cyclic Reforming Units

The process flow diagram for a cyclic reforming unit is very similar to SR reforming, but an additional “swing” reactor is used to replace one of the primary reactors while that reactor is being regenerated in a separate regeneration system. The frequency of regenerating for a particular reactor position depends on the rate of coke buildup. The regeneration sequence is typically set where the tail reactors are regenerated more often than the lead reactors due to the higher average temperatures and therefore higher coking rates in the tail positions. The swing reactor is regenerated after the tail reactor and then is used in one of the upstream reactor positions.

The swinging of the reactors between the process side and the regenerator side is accomplished by a series of large diameter motor operated valves (MOV’s) and large diameter piping. The separate regeneration system consists of the reactor under regeneration, a compressor, a fired heater, and optionally a spray drier and/or an adsorbent bed for lowering the moisture content in the regeneration gas. The regeneration steps are done in the sequence as described in section “Regeneration Steps.”

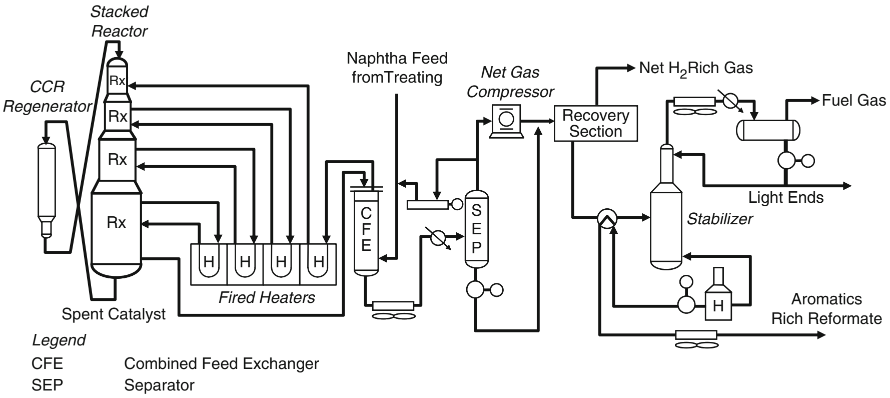


Fig. 10 CCR Platforming process (Reprinted with permission of UOP LLC)

Continuous Catalyst Regeneration Units

Figure 10 shows a simplified flow diagram for the UOP CCR Platforming process. In the CCR Platforming unit, partially spent catalyst in the reactors is continuously replaced with catalyst that has been freshly regenerated in an external regenerator (CCR section) to maintain a low average coke level on the catalyst in the reactors. Thus, the high selectivity and high activity characteristics associated with new catalyst can be maintained at significantly higher severities than with the SR process. For example, an SR unit operates at a severity that steadily builds coke up on the catalyst surface over the length of a cycle (6–24 months), at which point the unit is shut down and the catalyst regenerated. Over the SR cycle, the yields decline. Conversely, in a CCR Platforming unit, the catalyst is regenerated approximately every 3–7 days, and the yields remain constant.

Inside the reactor section, the catalyst flows down by gravity inside an annular space created by reactor internals. The reactors typically employ a profile wire-type center pipe screen and either an outer screen basket or scallop-shaped screens to contain the catalyst. The hydrocarbon and hydrogen flow from the outer baskets or screens across the catalyst and exit to the center pipe. Each reactor effluent is reheated and sent to the next reactor with the last reactor effluent going to the separator and the recovery section.

The ability to continuously regenerate a controlled quantity of catalyst is the significant innovation of the CCR Platforming unit. The catalyst flows by gravity from the last reactor into a catalyst collector vessel. The catalyst is lifted by nitrogen gas through a transfer pipe to a catalyst hopper above the regeneration tower. Catalyst then enters the regeneration tower, where its flow by gravity is controlled through several regeneration zones. The catalyst flows through the coke burn zone, Pt redispersion/chloriding zone, and a drying zone. Regenerated catalyst is returned to the top of the reactor stack by a transfer system similar to that used in the reactor-to-regenerator transfer. The catalyst typically enters a reduction zone before entering into the first reactor. Thus, the reactors are continuously supplied with freshly regenerated catalyst, and product yields are maintained at a constant level. The regeneration and reactor sections of the unit are easily isolated to permit a shutdown of the regeneration system for normal inspection or maintenance without interrupting the processing of naphtha feed.

A few years after the introduction of the UOP CCR Platforming process, another continuously regenerable process design was offered by the Institut Français du Pétrole (IFP). The IFP continuous reforming units designed by the Institut Français du Pétrole employ reactors that are located side by side, and the catalyst transfer is accomplished through a conveying system with piping between reactors.

Secondary Recovery

The need for effective liquid recovery is more critical for the low pressure operations of the CCR unit. The advantage of the increased aromatic, hydrogen, and C_5+ yields at low pressure can be lost if the proper recovery system is not installed. At low pressure in the gas-liquid separator, the flash pressure has been reduced allowing heavier hydrocarbons (C_4–C_6+) to leave with the vapor resulting in lost C_5+ product and lower purity hydrogen gas.

One improved separation scheme involves first separating the reactor effluent in the separator into vapor and liquid followed by recompressing the vapor with a net gas booster compressor with discharge into a drum or absorber vessel. The liquid from the separator is also pumped into the same drum/absorber for recontacting at higher pressure. This will allow a better gas-liquid separation leading to increased liquid recovery and higher purity hydrogen. Another method involves chilling the net separator gas with a refrigeration system and performing vapor-liquid separation at a low temperature. Other proprietary systems have been developed such as UOP's Recovery Plus^{TM} system (Lapinski et al. 2004).

Unit Improvements

The design of reforming units has been constantly improved over time with innovations in equipment and process features. After many decades in operation, many reforming units need replacement of equipment to maintain good reliability. Improved design features include updated reactor internals including improved inlet distributors and higher strength center pipes, logic systems that minimize mechanical stresses during start-ups and shutdowns, improved valves in the catalyst transfer lines for lower catalyst abrasion and attrition, and improved catalyst lift lines to reduce impact of the catalyst pills with the reactor walls. Another improvement is the replacement of older electronic systems that control the regeneration

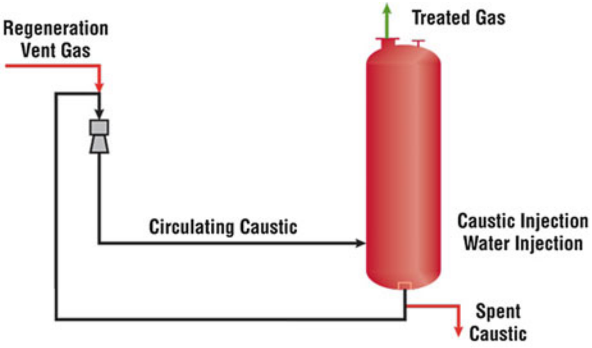


Fig. 11 Caustic scrubber for vent gas treating

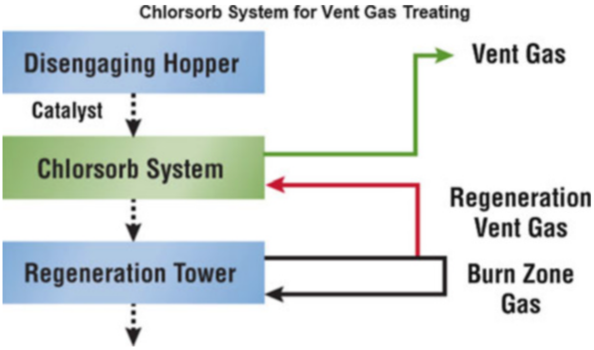


Fig. 12 Chlorsorb system for vent gas treating

system. Replacement with the latest software and hardware platforms can enable longer trouble-free on-stream operations.

Since reforming catalysts contain chlorided alumina catalysts, some Cl can leave the regeneration system in the regen vent gas. Earlier CCR reforming designs employed a caustic wash system (Fig. 11) to remove all Cl before venting to the atmosphere. A more recent innovation that replaces the caustic wash system is UOP's Chlorsorb^{TM} process (Poparad et al. 2011) introduced in 1998. In this process (Fig. 12), the reforming catalyst in the unit is used to adsorb chloride from the regeneration tower vent gas and is then passed to the regeneration vessel as Cl on catalyst. This reduces the Cl injection requirements for Pt redispersion and chloriding as well as removing Cl from the regenerator vent gas. With its ability to remove more than 97 % of chlorides, the Chlorsorb system is accepted by the USA EPA (under RMACT II) as an approved solution for waste gas chloride management. The Chlorsorb system has demonstrated that it can meet between 1 and 30 vppm of total chlorides in the vent gas. The savings are achieved from the significant reduction in chloride usage, the elimination of caustic usage, and the associated treatment of spent caustic as well as reduction in overall utilities costs.

Process Comparison and Economics

From both an economic and technical perspective, continuous reforming processes are superior to the SR and cyclic reforming processes. Thus, the CCR Platforming unit allows for significantly lower pressure operation leading to higher yields. At CCR conditions, the SR catalyst would be completely deactivated after only a few days of operation. The total aromatics, hydrogen, and C_5+ yields are maximized with the CCR Platforming process. Since the number of cyclic reformers is small relative to CCR Platforming process units and SR process units, the following comparison will focus on contrasting CCR Platforming units and SR units.

Obtaining high yields that are constant over time is important in the economics of reforming. As the catalyst is deactivated by coke deposition in the SR Platforming process, the yields begin to decline. With the CCR Platforming process, the reformate, aromatics, and hydrogen yields remain consistent and constant. This is particularly important for downstream users. The CCR section ensures proper redispersion of the metals and chloride balance to maintain fresh catalyst activity. CCR Platforming units have higher on-stream efficiency and are able to handle upset scenarios without long-term shutdown or significant decline in performance.

Table 7 compares the operating parameters for SR and CCR Platforming units. The CCR Platforming unit operates at higher conversions (higher RONC) and lower reactor catalyst inventory (higher LHSV). In addition, the CCR unit runs continuously compared to an average 12-month SR cycle length.

Table 8 shows the product yields for the SR and CCR Platforming units operating at the conditions presented in Table 7. The CCR Platforming unit produces significantly more hydrogen which is also at a higher purity. As discussed

Table 7 Relative severities of CCR versus SR Platforming units

Operating mode	SR	CCR
Charge rate, barrels/day	20,000	20,000
LHSV, h^{-1}	Base	Base × 1.8
H_2/HC	Base	Base × 0.5
RONC	97	102
Reactor pressure, psig	Base	Base – 150
Separator pressure, psig	Base	Base – 145
Cycle life, months	12	Continuous

Table 8 Yield comparison of CCR versus SR Platforming units

	SR	CCR	Delta
Hydrogen yield, SCF/bbl	1,085	1,709	+624
Hydrogen purity, mol%	80	92.6	+12.6
C_5+ yield, lv%	79.3	79.4	+0.1
C_5+ yield, wt%	85.2	88.2	+3.0
Octane-barrel, 10^6 bbl/year	513	583	+80

Table 9 Economic summary

Description	SR	CCR
Gross key product value, \$MM/year	120	141
Raw materials less by-products, \$MM/year	98	103
Consumables, \$MM/year	0.3	0.75
Utilities, \$MM/year	2.8	6.2
Total fixed costs, \$MM/year	5.5	6.5
Capital charges, \$MM/year	3.5	5.2
Net cost of production, \$MM/year	110	122
Pretax profit, \$MM/year	10	20
Pretax ROI, %	30	41
Payout period (gross) years	1.5	1.3

previously, raising the RONC will lead to a lower C_5+ reformate yield at constant pressure, but since the CCR unit operates at much lower pressure, the C_5+ wt% yield is actually significantly higher for the CCR unit at 102 RONC versus the SR unit at 97 RONC. In addition, the reformate from the CCR unit contains more aromatics making the liquid product more dense. However, in the example case, the liquid reformate volume (lv%) of the CCR reformate is still slightly larger than the liquid reformate volume from the SR unit. Taking into account both the higher octane value and the increased on-stream efficiency of the CCR Platforming unit, 80 million more octane-barrels, or 11.4 million more metric octane-tons, are produced per year with the CCR unit than with the SR unit.

An economic summary including operating costs and revenues is shown for the SR and CCR units in Table 9. Both unit types are favorable with a payback period of less than 2 years. However, the economics of the CCR unit are superior because the CCR unit produces more valuable reformate and hydrogen at 102 RONC versus the SR unit reformate at 97 RONC. Although the CCR Platforming utility costs are higher than those for the SR unit, these costs are offset by the increase in both product quantity and value as demonstrated by pretax profit and return on investment (ROI).

References

S.M. Augustine, G.N. Alameddin, W.M.H. Sachtler, J. Cata, J. Catal. **115**(1), 217–32 (1989)

American Petroleum Institute Research Project 45, Sixteenth Annual Report (1954)

Euro fuel specifications, website: http://ec.europa.eu/environment/air/transport/fuel.htm

A.L. Huebner, *Tutorial: Fundamentals of Naphtha Reforming*, AIChE Spring Meeting 1999. American Institute of Chemical Engineers (AICHE), Houston, TX, 14–18 Mar 1999

IHS CERA, *Annual Long-Term Strategic Workbook, Refining and Product Markets* (2014)

M. Lapinski, L. Baird, R. James, in *Handbook of Petroleum Refining Processes*, ed. by Meyers, 3rd edn. (McGraw-Hill, New York, 2004), p. 4.19

M.P. Lapinski, M.D. Moser, R.G. Proffitt, Hydrocarb. Eng. **11**(11), 59–63 (2006)

M.P. Lapinski, M.J. Wier, S. Metro, G. Li, Hydrocarb. Eng. **45**(11), 48–54 (2010)

E.L. Marshall, K. Owen (eds.), *Motor Gasoline* (The Royal Society of Chemistry, London, 1995), p. 8

G.A. Mills, H. Heinemann, T.H. Milliken, A.G. Oblad, Ind. Eng. Chem. **45**, 134–137 (1953)

M.D. Moser, D.H. Wei, R.S. Haizmann, Chemtech, **26**(10), 37–41 (1996)

A. Poparad, B. Ellis, B. Glover, S. Metro, *Reforming Solutions for Improved Profits in an Up-Down World*, AM-11-59 (2011)

C.M. Sorrentino, R.J. Pellet, R.J. Bertolacini (to Standard Oil Company – Indiana), U.S. Pat. 4,469,812 (1984)

D.R. Stull, E.F. Westrum, G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Wiley, New York, 1969)

US EPA MSAT program regulations, 40 CFR 80 subpart (2014). Web: http://www.epa.gov/otaq/fuels/gasolinefuels/MSAT/index.htm

J.A. Weiszmann, in *Handbook of Petroleum Refining Processes*, ed. by Meyers (McGraw-Hill, New York, 1986), p. 31

Fluid Catalytic Cracking (FCC) in Petroleum Refining

Warren Letzsch

Contents

Abstract

The catalytic cracking process, commercialized in 1942, has undergone numerous changes. It is the most important refinery process in that it converts the heavy portion of the crude barrel into transportation fuels. The main changes in catalysts, equipment and operations are covered along with the versatility of the process to handle a wide variety of feeds and produce the desired products. The FCCU is the bridge between refining and petrochemicals and the new FCC processes that fill this gap are presented here.

W. Letzsch (✉)
Technip-Stone & Webster, Houston, TX, USA

Warren Letzsch Consulting PC, Ellicott City, MD, USA
e-mail: wletzsch@verizon.net

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_2

Keywords

Fluid catalytic cracking • Catalytic cracking • Development of catalytic cracking • Catalytic cracking equipment and operation • Cracking catalysts and additives

Introduction

Crude oil comprises hundreds of molecules that boil over a wide temperature range. The lighter products can be separated directly by distillation into LPG, gasoline, naphtha, kerosene, and diesel fuels. Heavier products (BP >650 °F/344 °C) include vacuum gas oils and resids. Thermal and catalytic cracking processes in petroleum refining reduce the molecular weight of these heavier constituents and produce more valuable lighter products such as LPG, gasoline, and diesel fuels.

Catalytic cracking was first commercialized in 1936 by Eugene Houdry. This fixed bed process was a major improvement over the thermal cracking processes it replaced due to the improved yield distribution and superior product properties. Multiple vessels were utilized that alternated between cracking, stripping, regeneration, and purge cycles. This configuration was quickly replaced by a moving bed reactor and a separate regenerator or kiln that first used a bucket lift to move the pelleted catalyst followed later by a pneumatic air lift system. The last of these units was built around 1960.

Standard Oil of New Jersey developed their own cracking process rather than pay the large royalty being asked at the time. They commercialized the fluid catalytic cracking (FCC) process in 3 years, starting in 1939 and culminating in 1942 with the start-up of PCLA#1 at their Baton Rouge, Louisiana refinery. The inherent superiority of the fluid process to transfer both heat and catalyst ultimately made it the catalytic cracking process of choice.

Many different designs of fluid catalytic crackers have been introduced over the years. Table 1 is a list of the various FCCU configurations and the approximate year of their commercial introduction.

Fluid catalytic cracking has evolved considerably over the more than 70 years since its inception. As seen in Fig. 1, these changes have encompassed all aspects of the process as it has adapted to meet ever-changing environmental and performance demands and to accommodate new technologies.

The initial units (1940s) were tall, had dense bed reactors, and were made of carbon steel. Dilute phase catalyst coolers and regenerator steam coils were employed to limit the regenerator temperatures. Recycle rates of 100–150 % were needed to achieve acceptable conversions. Later designs (late 1940s to early 1950s) were undertaken to reduce the height of the crackers, make them more compact, and cater to the many small refiners around the United States.

In the late 1950s, side-by-side designs with straight feed risers were introduced to improve gasoline selectivity. Residue cracking in fluid cracking units was first practiced in the early 1960s. This unit was designed for 100 % atmospheric bottoms and had large amounts of heat removal.

Table 1 Evolution of fluid catalytic crackers

	Commercial fluid catalytic crackers
1942	Model I upflow
1943	Model II downflow
1945	Sinclair design
1947	Model II side by side
1951	Kellogg orthoflow A
1952	Exxon model IV
1953	Kellogg orthoflow B
1955	Shell two-stage reactor
1956	UOP straight riser (SBS)
1958	Exxon riser cracker
1961	HOC cracker (Phillips)
1962	Kellogg orthoflow C
1967	Texaco design
1971	Gulf FCC process
1972	Exxon flexicracker
1972	Amoco ultracracking
1973	UOP high-efficiency design
1973	Kellogg orthoflow F
1981	Total petroleum resid cracker
1982	Ashland/UOP RCC unit
1985	IFP R2R
1990	Kellogg/Mobil HOC
1991	Deep catalytic cracking (RIPP and Stone & Webster)
1993	Exxon flexicracker III
1995	MSCC UOP/Coastal
2005	Superflex Kellogg
2007	PetroFCC UOP
2010	Catalytic pyrolysis process (Sinopec)
2011	ACO Advanced catalytic olefins (SK Korea)
2011	HS-FCC Nippon/Aramco

Catalytic cracking was truly revolutionized in the early 1960s with the advent of zeolite-containing fluid cracking catalysts. Catalyst activities were raised by an order of magnitude and units needed to be redesigned to take full advantage of the new catalyst technology. These design changes included the elimination of reactor dense beds and the use of the feed riser as the sole conversion vessel. Recycle was greatly reduced and replaced with more fresh feed. It was found that coke left on the regenerated catalyst impaired the catalyst's activity and selectivity, and the average carbons on regenerated catalyst were reduced from 0.3–0.5 to 0.1 wt% or less. Complete CO combustion in the regenerator was introduced to provide the needed regenerator burning conditions which necessitated higher regenerator temperatures. Alloy internals replaced the carbon steel and chrome-moly hardware in the regenerator and the regenerated catalyst standpipe. Catalyst inventories were minimized due to the favorable coke burning kinetics and modifications in the regenerator design (1970s).

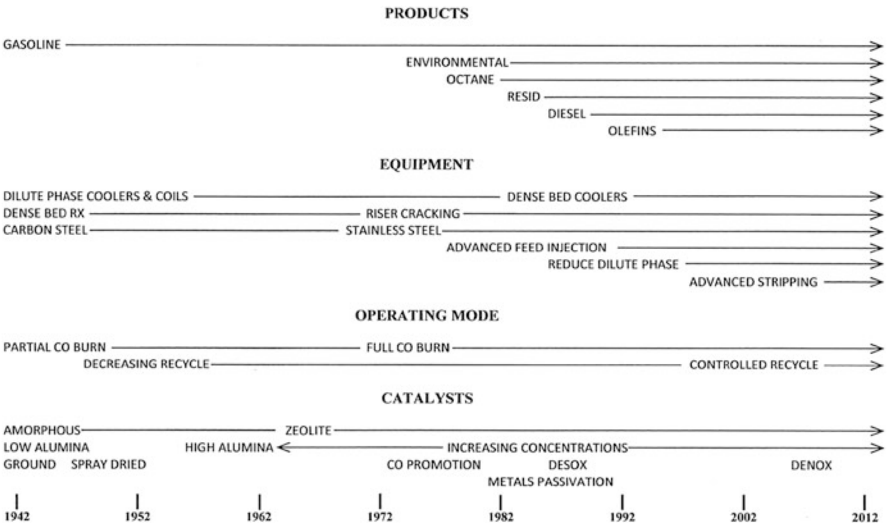


Fig. 1 Fluid catalytic cracking development

In the early 1980s, several new resid cracking designs were introduced. The spent catalyst regeneration was staged in these designs and dense bed catalyst coolers were optional. These coolers have also been used with single-stage regenerators for residual catalytic cracking units. The growth of this segment of the catalytic cracking process is shown in Fig. 2. Over three million barrels per day of on-purpose resid crackers have now been licensed, and another million barrels of FCC capacity process some resid along with their normal gas oils. Typical yields from resid cracking along with the feedstock properties are given in Table 2.

While the olefins in gasoline have become a concern in the gasoline pool, the light olefins for petrochemicals are a valuable product, often exceeding the revenue obtained for transportation fuels. As a consequence, distinctive processes for making much higher amounts of propylene than a normal FCC unit have been developed. The Deep Catalytic Cracking Process (1991) was the first commercial-scale process that was designed to maximize propylene. Specially formulated catalysts, more severe process conditions, and equipment made to handle the unique product distribution are all components of this technology. Table 3 compares the yields from the DCC technology with those obtained.

Even more severe cracking conditions are used in the catalytic pyrolysis process (2002), where the desire is to produce all petrochemical products, i.e., ethylene, propylene, butenes, and aromatics. This process is really a substitute for a steam cracking furnace in an ethylene plant. It allows the operator to use cheaper feedstocks and vary the ratio of ethylene to propylene over a wider range than is possible with only thermal cracking. Further discussion of FCC units designed for petrochemicals is covered later in this chapter.

A diagram of the reactor-regenerator of a modern fluid cracking unit is shown in Fig. 3. Hot-regenerated catalyst contacts the oil near the base of the reactor riser.

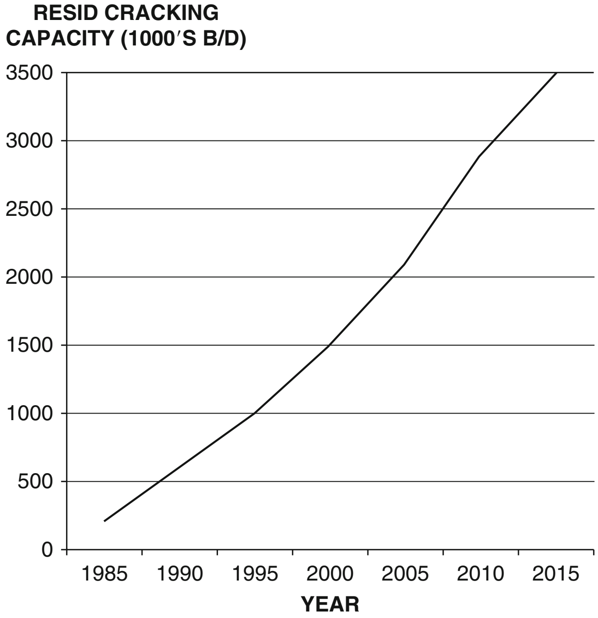


Fig. 2 Growth in resid cracking worldwide

Table 2 Typical resid cracking yields

	Unit A	Unit B
Feed properties		
API gravity	0.922	0.963
Conradson carbon	3.8	8.0
Ni + V	4	7.5
	wt%	wt%
Conversion	70.0	70.0
Dry gas	2.1	3.4
LPG	15.3	14.4
Gasoline	46.2	43.1
LCO	16.3	16.0
Decant oil	13.7	14.0
Coke	6.5	9.1

Virtually all of the cracking takes place in the feed riser which connects to a catalyst/vapor separator. The hot catalyst is discharged into the catalyst stripper while the vapor is routed through secondary cyclones to remove any remaining catalyst and then to the main fractionator and gas plant for separation of the products.

The spent catalyst enters a multistage stripper where the absorbed hydrocarbons are displaced with steam and leave with the product from the overhead of the reactor. This prevents unwanted hydrocarbons from entering the regenerator, consuming air, and possibly causing excessive catalyst deactivation. Staging is

Table 3 Deep catalytic cracking (DCC) versus FCCU

Process	FCC	DCC type 1	DCC type 2
Yields, wt%			
Dry gas	3.5	11.9	4.0
LPG	17.6	42.2	34.5
C5 + gasoline	55.1	27.2	41.6
LCO	10.2	6.6	9.8
DO	9.3	6.1	5.8
Coke	4.3	6.0	4.3
Ethylene	1.1	6.1	1.6
Propylene	4.9	21.0	14.3
Butylenes	8.1	14.3	14.7

Feedstock: Chinese waxy VGO

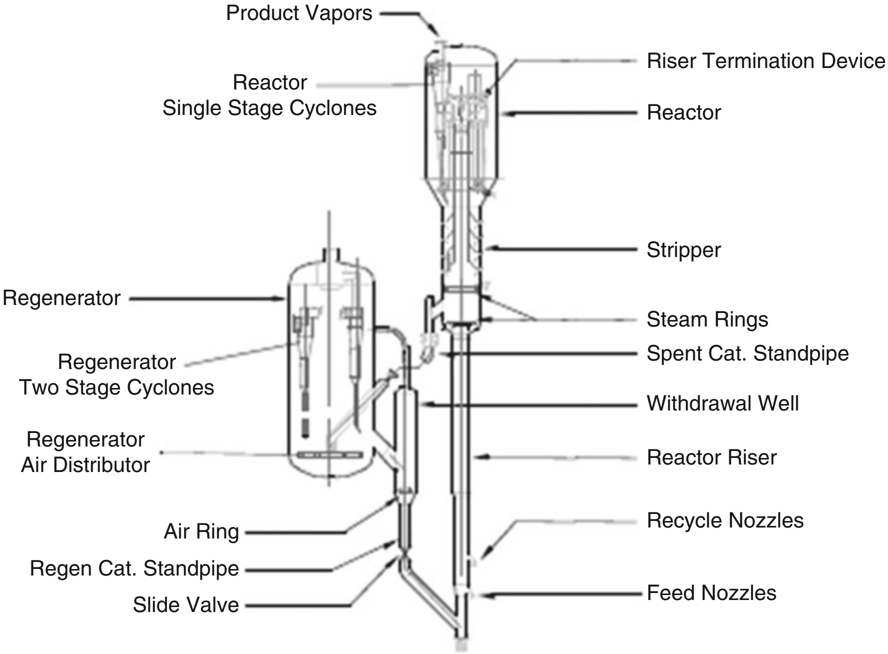


Fig. 3 Reactor-regenerator of a modern FCCU

accomplished by the use of baffles or packing and is similar in concept to a multi-tray distillation tower.

Spent-stripped catalyst enters the regenerator where the coke is burned off the catalyst to restore its activity. The heat generated in the combustion process can supply all of the needed heat for the process. If excess heat is produced, it can be removed by external catalyst coolers. The regenerated catalyst flows back to the base of the riser where the cycle is completed. Typical catalytic cracking units undergo 100–400 of such cycles a day.

Table 4 Major advances in fluid catalytic cracking

1942	First FCC unit on stream (Exxon)
1947	Stacked configuration (UOP)
	Compact with small inventory
1948	Spray-dried catalyst (improved fluidization)
1952	Synthetic high alumina (higher stability)
1955	Reactor riser cracking (Shell)
1959	Semisynthetic catalyst (addition of clay)
1960	Improved metallurgy (Higher regenerator temperatures)
1961	Heavy oil cracking (Phillips-Kellogg)
1964	Zeolitic catalysts introduced (Mobil)
1972	Complete CO combustion process (Amoco)
1974	Combustion promoters (Mobil)
1975	Metals passivation (Phillips)
1981	Two independent regenerators for unlimited
	regeneration temperature (Total)
1982	High-performance feed injectors
1982	Dense bed catalyst coolers (Ashland/UOP)
1987	Vapor quench (Amoco)
1987	Mix temperature control (Total)
1988	Close-coupled cyclones (Mobil)
1991	Deep catalytic cracking (RIPP/Sinopec)
1996	Enhanced stripping designs (Total/Koch-Glitsch)
2002	Catalytic pyrolysis (RIPP/Sinopec)
2005	Gasoline cracking (Kellogg)
2007	Dual diameter risers (RIPP)
2011	Downflow reactor (Nippon/Aramco/Technip-Stone &Webster/Axens)

There have been many advances in the fluid catalytic cracking process. The high capacities of a cracking unit (typically a third of the crude oil a fuel refinery runs goes to a standard gas oil FCC unit) and its positive influence on overall refinery economics have made it a prime target for innovation. A list of most of the major innovations in the process is given in Table 4. These include catalyst, equipment, and process changes that have occurred on a continual basis over the 70 years that FCCUs have been operating. By being able to both improve its performance and evolve its functions, the catalytic cracking process has remained a staple in the modern refinery.

Fluidization

The basic circulating fluid bed reactor system that is widely used today in many other applications got its start in fluid catalytic cracking. It was the development of the standpipe that made the process possible. The fine powder acts as a fluid when contacted with a gas, and it is the standpipe that allows the catalyst to be circulated

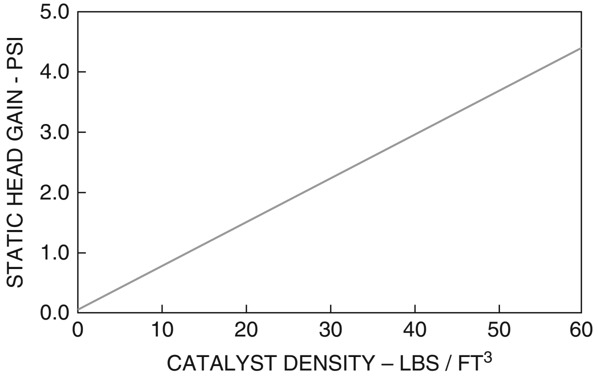


Fig. 4 Static head gain per 10 f. of standpipe versus catalyst density

from a vessel at lower pressure to one of higher pressure, thus completing the circulating catalyst loop.

In Fig. 4, the head gain from the fluidized catalyst is given as a function of the bed density. The latter depends on the catalyst properties, the amount of aeration being used, and the rate at which catalyst is being added to the system.

The change in density of a bed of cracking catalyst with gas velocity is shown in Fig. 5. At very low velocities, the bed is stationary but soon reaches a point where the upward force of the gas balances the weight of the catalyst (minimum fluidization velocity) and the catalyst becomes suspended in the gas. More gas expands the fluidized bed to a point where the next bit of gas enters and forms bubbles. This is the minimum bubbling velocity and the two phases are referred to as the emulsion and bubble phases, respectively. Once bubbles are formed, all of the added gas contributes to this phase. At even moderate velocities, the catalyst is quickly entrained with the gas and must be captured and returned to the bed. This allows operation of the catalyst beds at much higher superficial velocities than would otherwise be possible. Typical velocities in the reactor-regenerator system are given in Table 5.

Bubbles play a key part in the operation of a fluid bed system. They are the “engine” that stirs the bed of catalyst making the high heat and mass transfer rates possible. In the standpipes, bubbles can have a profound effect on the smoothness of catalyst flow, and care must be exercised to avoid over-aerating as well as under-aerating the catalyst. A formula for adding the proper amount of air to a standpipe, Q, was presented by Zenz and is shown below:

$$Q = 2{,}000\left(\frac{P_{\mathrm{B}}}{P_{\mathrm{t}}}\left[\frac{1}{\rho_{\mathrm{f}}} - \frac{1}{\rho_{\mathrm{p}}}\right] - \left[\frac{1}{\rho_{\mathrm{t}}} - \frac{1}{\rho_{\mathrm{p}}}\right]\right) \tag{1}$$

(*for symbols, refer to the* “Nomenclature” *at the end of this section*).

Typically 70 % of the above calculated aeration rate is about optimum, and it should be added at even intervals, around the standpipe, about 6–8 f. apart. Fine-tuning is done once the unit is in operation, and a single-gauge pressure survey can

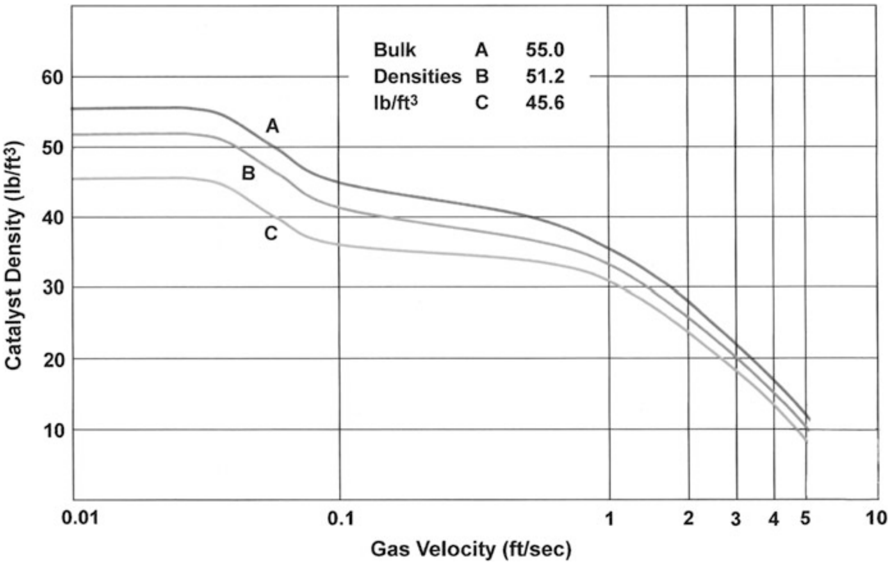


Fig. 5 Fluidization curves for FCC catalysts

Table 5 Superficial velocities for FCC (ft/s)

Minimum fluidization	0.01–0.03
Minimum bubbling	0.05–0.1
Bubbling bed	0.3–2
Turbulent bed	2–4
Fast-fluidized bed	4–10
Pneumatic conveying	12

be taken to aid in the optimization of the system. It is critical that the catalyst be properly fluidized entering the standpipe since refluidizing catalyst is very difficult. Over-aeration is a more common problem than under-aeration in commercial operations.

Process Control

While there are many ways to configure the controls of the cat cracker, Fig. 6 shows the typical scheme used in the industry for a slide valve-controlled unit.

The reactor pressure is controlled by the inlet pressure to the wet gas compressor, but the actual pressure at the top of the reactor in the dilute phase is this pressure plus the pressure drop taken through the main fractionator overhead system, the main fractionator, and the reactor overhead system (cyclones, plenum, and overhead vapor line). At steady state, this pressure should be constant. The regenerator pressure is controlled by the flue gas slide valve and is maintained to

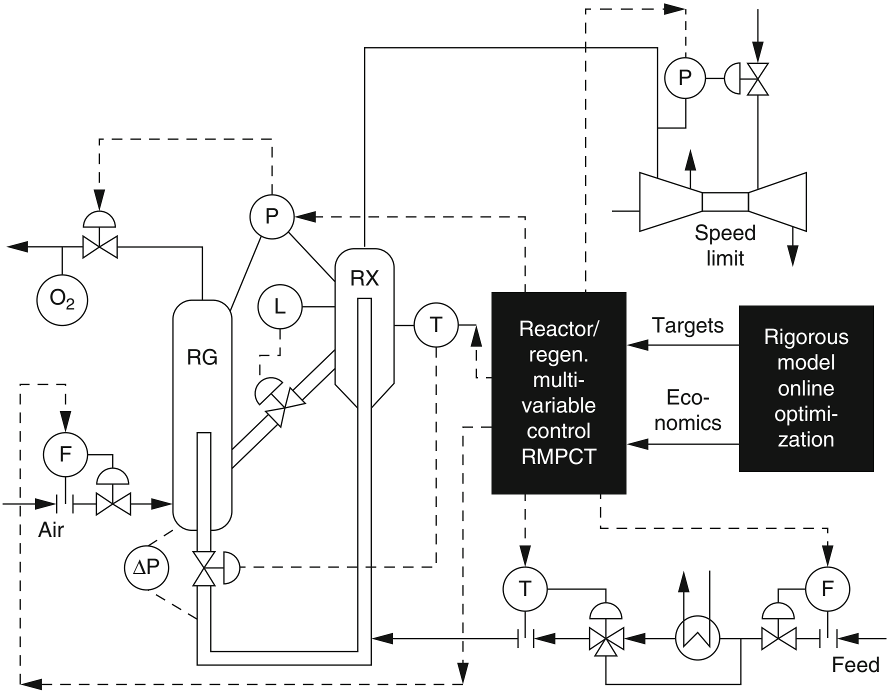


Fig. 6 Advanced FCC process control scheme (Reprinted with permission from hydrocarbon processing, by Gulf Publishing Co., Copyright 2001; all rights reserved)

give a constant differential pressure between the reactor and regenerator. This is adjusted to provide optimum catalyst circulation and adequate pressure drops across the control valves and to balance the wet gas compressor and air blower.

The reactor temperature is controlled by the regenerated catalyst slide valve. More hot catalyst is circulated to raise the reactor temperature or accommodate increased feed rates. The feed going to the unit is preheated by exchange with the hot products and some of the main column pumparounds. While heat exchange is adequate for feed temperatures ranging up to about 550 °F, a fired heater is included for higher temperatures.

The regenerator temperature is a function of the coke on the catalyst entering the regenerator, its composition, and the mode of coke burning. Full combustion or the complete burning of the carbon to CO_2 is most common due to the necessity of limiting the CO concentration in the flue gas to 500 ppm or less to meet environmental regulations. Partial combustion resulting in CO/CO_2 ratios ranging up to one is practiced in units that do not have the needed metallurgy in the regenerator to operate at high temperatures or wish to maximize regenerator coke burning capacity or limit the heat produced in the regeneration process. Such units are equipped with CO incinerators or boilers where the CO is converted to CO_2 before being discharged to the atmosphere. Typical regenerator temperatures in these two operating modes are 1,150–1,250 °F (620–675 °C) and 1,275–1,350 °F (690–732 °C), respectively, for partial and complete combustion.

The spent catalyst slide valve controls the catalyst level in the stripper or reactor bed if one is being used. No direct control of the regenerator catalyst bed level is made, and its level floats depending on the catalyst losses and the catalyst withdrawal and addition policies. Most units are capable of retaining most of the fresh catalyst added daily and must periodically withdraw equilibrium catalyst to keep the regenerator level from getting too high. The regenerator is used as the "floating" vessel because it is larger and it is desirable to withdraw regenerated rather than spent catalyst.

With the advent of computers and advanced process controllers, many refinements to the basic control scheme are possible. The control system has been extended to include the gas plant as well as the reactor/regenerator system. The biggest benefits come from operating closer to several limits at one time. Better analysis of the feedstocks could allow feed-forward control in the future. While these control systems can improve refining profitability from 20 to 40 cents/barrel processed, they require more instrumentation, which must be maintained to achieve the stated benefits.

Reaction Chemistry and Mechanisms

Many studies have been performed elucidating the difference between thermal and catalytic cracking. Two separate reaction mechanisms are attributed to the methods of cracking, i.e., thermal cracking goes through free radicals and catalytic cracking proceeds via carbenium ions. The latter are generally associated with the Brönsted acid sites on the catalyst. In Table 6, the major differences between the two mechanisms are shown. Thermal cracking is minimized as much as possible in current FCC units by the use of advanced equipment such as radial feed injectors, riser termination devices, and post-riser quench. Catalyst selection is also critical.

There are many reactions that occur during the cracking process. These are listed below as primary or secondary reactions (Table 7 and 8). Most of the secondary reactions are undesirable and are controlled through reactor and catalyst design. Numerous cracking reactions occur with the large feed molecules before the desired products are achieved. Typical feeds to a catalytic cracking unit contain molecules boiling above the diesel end point (650–700 °F or 343–371 °C) and may boil as high as 1,500 °F. The consecutive reactions that occur are shown in Eq. 2:

$$\overset{\text{A}}{\text{Gas oil or resid}} \rightarrow \overset{\text{B}}{\text{diesel}} \rightarrow \overset{\text{C}}{\text{gasoline}} \rightarrow \overset{\text{D}}{\text{LPG}} + \text{coke}. \tag{2}$$

While this is an oversimplification of what occurs, it does give an overall view of the cracking process. From the above equation, it is clear that separate processes or applications can center around either product or feed differences.

Table 6 Characteristics of cracking mechanisms

Thermal – free radical	Catalytic – carbenium ion
C_1–C_2 principal products	C_3^+ Principal products
Little skeletal isomerization	Much skeletal isomerization
Cracking at beta position with little preference for free radical type	Aromatics dealkylate at ring if chain is at least three carbons long
Alpha olefins primary product	Cracking occurs at tertiary > secondary > primary carbenium ions
	Products contain an olefin
	Largest molecules crack fastest unless steric hindrance controls

Table 7 Primary cracking reactions for hydrocarbon types

Paraffin		Paraffin + Olefin
$C_n\ H_{2n+2}$	$\longrightarrow$	$C_pH_{2p+2} + C_mH_{2m}$
Naphthene (cyclic paraffin)		Olefin + Olefin
C_nH_{2n}	$\longrightarrow$	$C_pH_{2p} + C_mH_m$
Alkylaromatic		Aromatic (base) + Olefin
ArC_nH_{2n+1}	$\longrightarrow$	$ArH + C_nH_{2n}$
Olefin		Olefin + Olefin
C_nH_{2n}	$\longrightarrow$	$C_pH_{2p} + C_mH_{2m}$
Aromatic	$\longrightarrow$	No reaction

Table 8 Secondary reactions of olefins

Naphthene + Olefin	$\longrightarrow$	Aromatic + Paraffin
Hydrogen + Olefin	$\longrightarrow$	Paraffin
Normal Olefin	$\longrightarrow$	Iso-Olefin
Olefin + Olefin	$\longrightarrow$	Larger Olefin
Aromatic + Olefin →	Alkylaromatic	⟶Cyclization
Multi-ring aromatic (Coke)	← Dehydrogenation	⟵

As such, there are three basic catalytic cracking applications today. These are:

Application	Feedstock	Products
1. Gas oil cracking	Vacuum gas oils	Motor gasoline
		LCO and LPG
2. Resid cracking	Atmospheric resid VGO + vacuum resid	Motor gasoline
		LCO and LPG
3. Cracking for petrochemicals	Vacuum gas oils and added resids	Light olefins – C_2s, C_3s, and C_4s
		Plus aromatics

The driving forces behind these applications are the need for gasoline, the lack of demand for bottom of the barrel, and the increase in demand for light olefins and aromatics. The technologies for each of these process configurations are reviewed in turn.

Gas Oil Cracking Technology Features

Reaction Technologies

All of the reaction systems offered today consist of a feed injection system, reactor riser, riser termination device, and sometimes vapor quench technology. Each licensor approaches the design with different equipment and configurations.

The feed injection system is probably the most important part of the reaction system since it provides the initial contacting between the oil and catalyst. A good system must vaporize the feed quickly, quench the hot catalyst as fast as possible, and provide plug flow of the hydrocarbons and catalyst. Other features are important but are beyond this limited description.

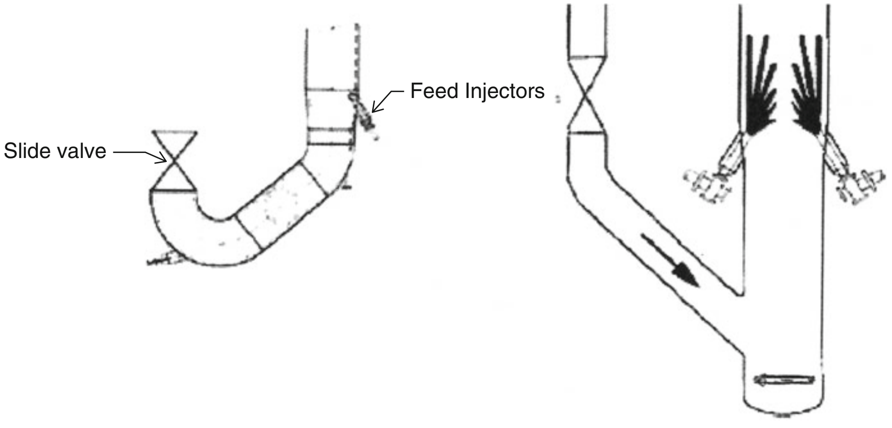
The hot-regenerated catalyst generally comes to the feed riser either through a wye (Y) section or a J-bend depending on the proximity of the regenerated catalyst standpipe and the feed riser (see Fig. 7). Feed nozzles are usually located from 10 to 30 f. downstream of the base of the riser. Since raising the nozzles increases the back pressure on the regenerated catalyst slide valve, lift gas may be incorporated to control the pressure balance and minimize the backmixing of the catalyst. The lift gas is normally light gas from the product recovery section and adds to the load in the main fractionator and wet gas compressor. Steam is sometimes substituted either whole or in part to reduce the processed gas but can cause some catalyst deactivation if the regenerator temperature gets too high.

The feed injection systems (Fig. 8) employed by the various licensors all use different nozzle designs. Oil pressure and dispersion steam rates vary by both licensor and application. Typical oil pressure drops and dispersion steam rates are 30–150 psi and 1–7 wt% and depend on the type of feedstock processed, i.e., vacuum gas oils or residual feeds (BP >1,050 °C (565 °C)).

The feed injection systems being offered by the licensors are shown in Fig. 8.

These all consist of two fluid nozzles that mix an oil feed and steam and distribute them across the riser cross-sectional area. Differences exist in the methods of contacting the steam and oil, in the amount of steam and pressures used, and in the tip design. Refiners are concerned about both performance and reliability when choosing a system.

Reactors are vertical pipes that are generally straight and are about 100 f. long. The diameters at each end are controlled to give adequate lift to the catalyst. Velocities of 20–30 ft/s at the base and 50–65 ft/s at the vapor outlet are typical with vapor residence times of about 2 s based on the vapor outlet velocity. Bends in the riser pipe do not change the vapor residence time but increase the catalyst residence time (or slip) and usually result in poorer oil/catalyst contacting. Riser inserts have been offered that reportedly reduce backmixing in the riser.



J-Bend

Wye Section

Fig. 7 Regenerated catalyst/feed contacting configurations

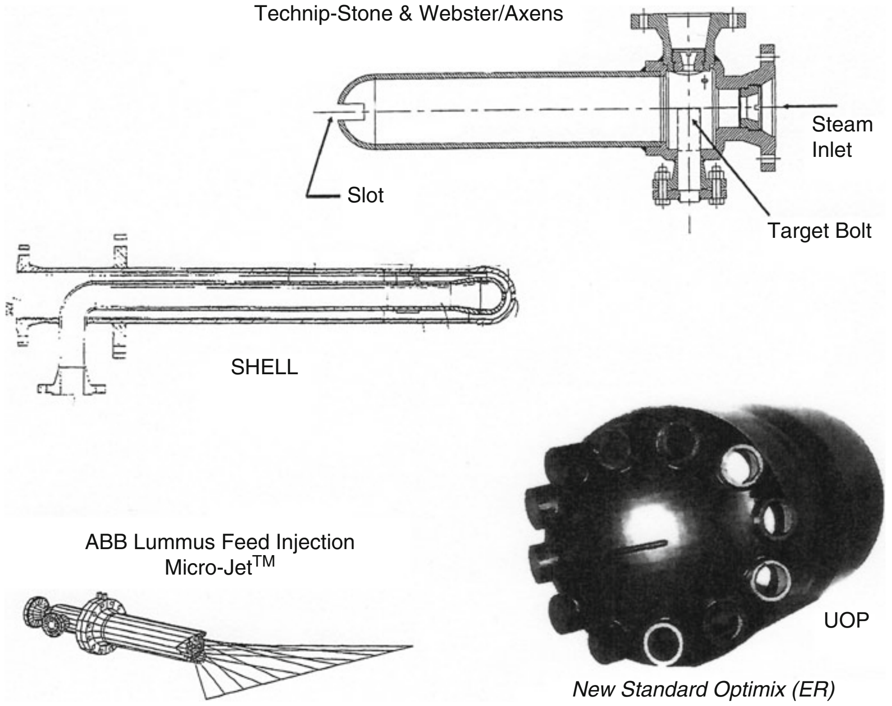
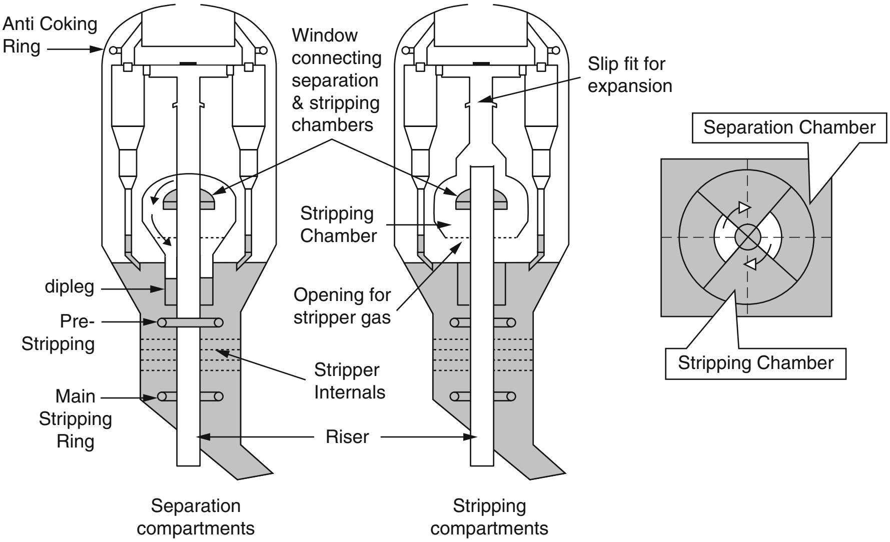


Fig. 8 Commercial feed injection systems



Riser Separation System (RS^2)

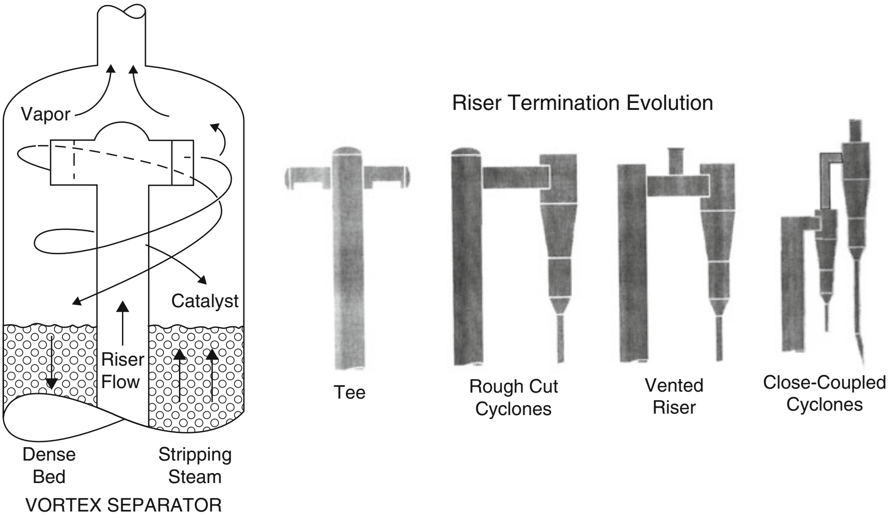


Fig. 9 Riser separators

A termination or separation system is used at the top of the riser. These have been simple tees (T), rough-cut cyclones, or specialized inertial separators. Most recently, the riser termination devices have all been close-coupled systems: connected cyclones, riser separator strippers (RSS), or vortex separators (VSS). These are pictured in Fig. 9 and all are directly connected to the secondary cyclones.

The dilute phase of the reactor-stripper is a place where secondary thermal reactions can occur, and the extent of these reactions can be estimated from Eq. 3:

$$\text{Delta dry gas} = Ke^{\text{E/RT}}t = \left(8.3 \times 10^{12}\right)\left(e^{-93,000/(1.987*T(R))}\right)t. \tag{3}$$

A plot of this equation (Fig. 10) shows that high reactor temperatures and long dilute phase residence times lead to high dry gas yields. At low reactor temperatures, below 505 °C (941 °F), the impact of the dilute phase is small, and the use of advanced termination technology is difficult to justify especially if there is a chance of downtime due to equipment malfunction. The value of K can be determined for an individual unit by measuring the amount of dry gas produced at two different temperatures and measuring the vapor residence time with tracers. A number of factors can add to the dry gas make such as the catalyst type, feed properties, amount of dilute phase catalyst, stripper design and operation, and carbon on regenerated catalyst.

Another approach to reducing the post-gas dry gas make is to reduce the temperature at the end of the riser. This has been done at the end of the riser before the separator and just downstream of the catalyst/vapor separator at the end of the riser. Quenching in the riser will reduce gas make and may be needed if there is a metallurgical limit in the reactor-stripper vessel. However, the amount of quench is high due to the catalyst that is cooled, and the stripper must operate at a lower temperature. The coke make and air requirements are increased since this is a recycle stream from a heat balance perspective.

Downstream quenching only cools the vapor and does not add to the coke yield. It can be applied to any unit that has a rapid/effective catalyst/vapor separator as shown in Fig. 11. The quench material is taken from the main fractionator and from a heat balance perspective acts the same as a pumparound on the main column. It can be adjusted to accommodate changes in the reactor temperature and discontinued at low reactor temperatures or when fuel gas prices are very high. Benefits from three

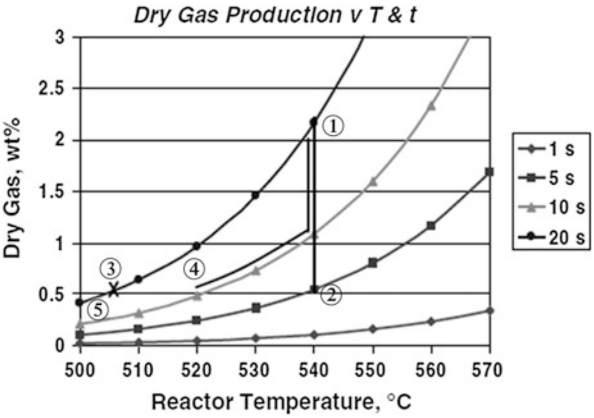


Fig. 10 Post-riser dry gas production

Fig. 11 Reaction systems with post-riser quench

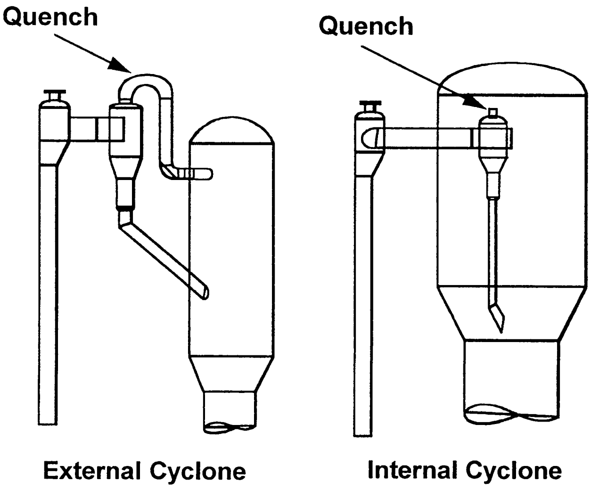


Table 9 Impact of vapor quench on FCC yields

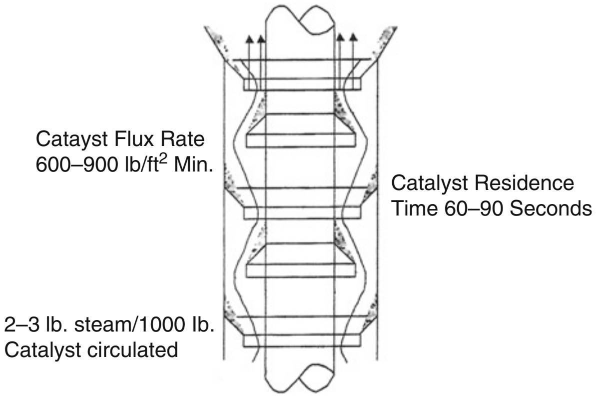
Unit	A	B	C
Temperature (°C)			
Riser outlet	513	549	532
After quench	484	519	494
Yield shifts (wt%)			
Dry gas	−0.23	−0.80	−0.66
Gasoline	+0.43	+1.80	+2.89
LPG	–	–	–1.58
LCO	–	–	+0.25
DO	–	–	–0.86

different units are listed in Table 9. As Eq. 3 implies and Fig. 10 illustrates, the effects of time and temperature are equivalent. However, the vapor quench also reduces the cracking that occurs in the secondary cyclones, plenum changer, and overhead vapor line. Care must be exercised when using quench to avoid coke formation. These precautions include the choice of the quench medium, operating above minimum operating temperatures and automatic shutoffs and purges.

Stripping Technology

After the cracking reactions are completed, the spent catalyst needs to be stripped of the hydrocarbons that would accompany it to the regenerator. This is done in a staged-fluidized bed where steam enters from the bottom and pushes the hydrocarbons in the gas phase out of the top of the bed. Design parameters for new units are given in Fig. 12, which is a common disk-and-donut design.

Fig. 12 Disk-and-donut stripper



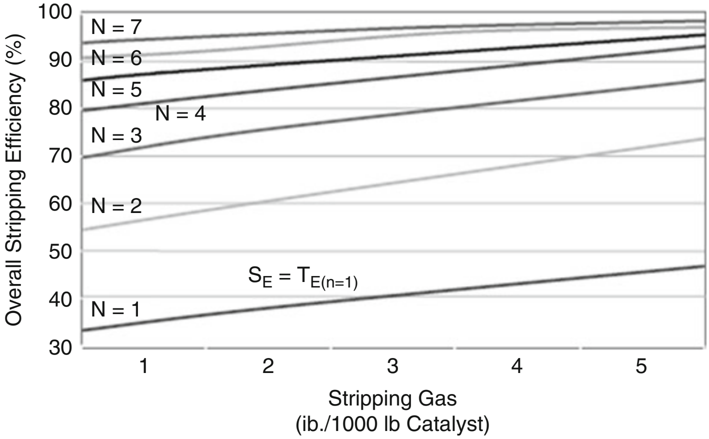
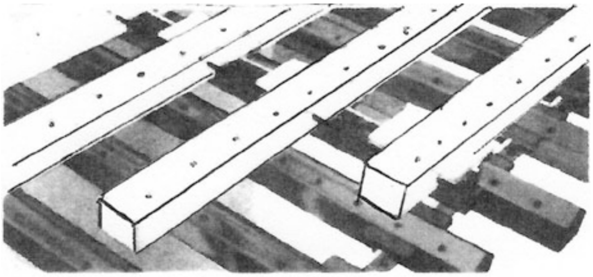


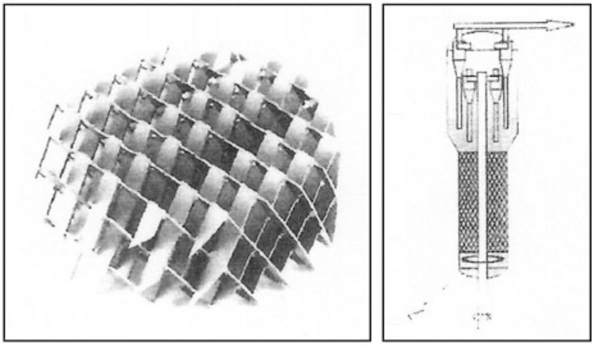
Fig. 13 Disk-and-donut tray efficiency/stage efficiency

The baffles improve contacting between the steam and catalyst and increase the number of contacting stages. As shown in Fig. 13, seven stages of stripping are sufficient to remove at least 95 % of the hydrocarbons. Each of the design parameters is important to the proper operation of the stripper. A minimum amount of steam is necessary to displace the hydrocarbons in the emulsion and bubble phases of the fluid bed. The flux rate determines the catalyst velocity through the bed. If the downward velocity of the catalyst gets too high, it will sweep hydrocarbons and steam with it and adversely affect the stripper performance. The residence time is a function of the stripper's catalyst inventory and the catalyst circulation rate. Overall, stripper efficiency is a function of the number of stages and their efficiencies.

While the disk-and-donut design shown has proven to be both reliable and effective, there are other variations on this design. Holes can be placed in the baffles to improve contacting, the skirts can be lengthened to provide a larger gas ΔP, vent tubes have been used to allow the gas from the bottom of the baffles to pass to the next stage, and rods or shed decks can be substituted as the contacting devices. The use of structured packing has been reported with excellent results. Lower steam usage, better contacting, and utilization of almost the entire cross-sectional area of the stripper are benefits seen with the new designs. Horizontal trays with small holes configured as distillation trays have been tested in the lab and have been put into service in the field. A few of the commercial packing designs are shown in Fig. 14.



Shell high flux Pentaflow™ catalyst stripping



Koch-Glitsch KFBE™ Technology

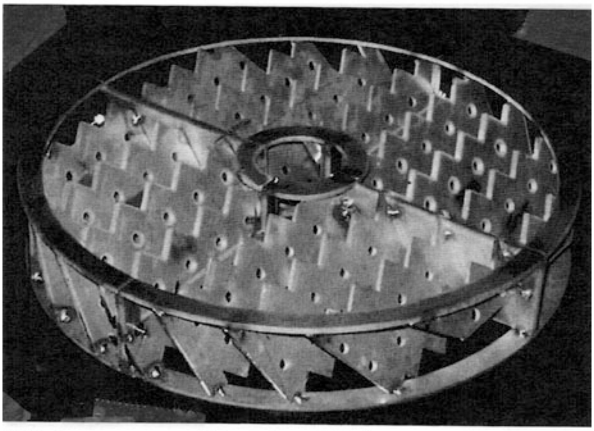


Fig. 14 Commercial stripper packing designs

LUMMUS Modular Grids

Stripping is a mass transfer process. In an analogous fashion to improvements in distillation performance with better tray designs, the improved methods of contacting the spent catalyst with steam have made strippers more effective and lowered the cost of stripper revamps.

Regeneration Technology

The object of the regenerator is to remove the coke that builds up on the catalyst in the reactor without damaging the catalyst. Many studies have been made on the burning rates of coke in a fluidized bed of cracking catalyst. Equation 4 describes the major regeneration operating variables:

$$\frac{dC}{dt} = K \times C_i \times \mathrm{L_m O_2} \times e^{A/RT}. \tag{4}$$

The contacting between the oxygen and catalyst is improved significantly as the air rate or superficial velocity is increased in the regenerator. As the velocity increases, the bed goes through three stages. A bubbling bed occurs at low superficial velocities (up to about 1.8 ft/s or 55 cm/s). Here relatively distinct bubbles are formed and pass through the bed. A turbulent bed (1.8–4.0 ft/s or 55–122 cm/s) exists at higher superficial velocities in which an emulsion is formed and the diffusion rate of oxygen is significantly increased. At higher velocities, a fast-fluidized bed (4–8 ft/s or 122–244 cm/s) exists in which turbulence is maximized. A return line from the recovered catalyst to the combustor is required to provide enough residence time and a sufficient mix temperature for the coke to completely burn. The difference in burning rates between these idealized regenerator designs is shown in Fig. 15.

A few observations can be made from Fig. 14 and Eq. 4. At high temperatures (>1,300 °F or 704 °C), the burning rate is very high. Oxygen availability limits the burning rate, though the small size of the fluid cracking catalyst eliminates or minimizes diffusion as a reaction barrier at normal regenerator temperatures. The plug flow curve moves up, as catalyst is recycled in the combustor since the effect is to increase the residence time. Regenerators with larger inventories will reduce the carbon satisfactorily even if there is a partial malfunction of the air distributor while smaller inventories allow faster change outs of the catalyst inventory. Over the years, the regenerator temperatures have increased due to better metallurgy and the need to burn all of the carbon off the catalyst to restore the zeolite catalysts' activity and product selectivity.

At 1,100 °F (593 °C), the regenerator inventories had to be large to provide enough time to burn the coke. Full CO combustion raised these temperatures to 1,300–1,350 °F (704–732 °C). CO promoters are also frequently employed to assist the carbon burn and prevent the afterburning of CO in the dilute phase or downstream hardware where serious equipment damage can occur. The differences in

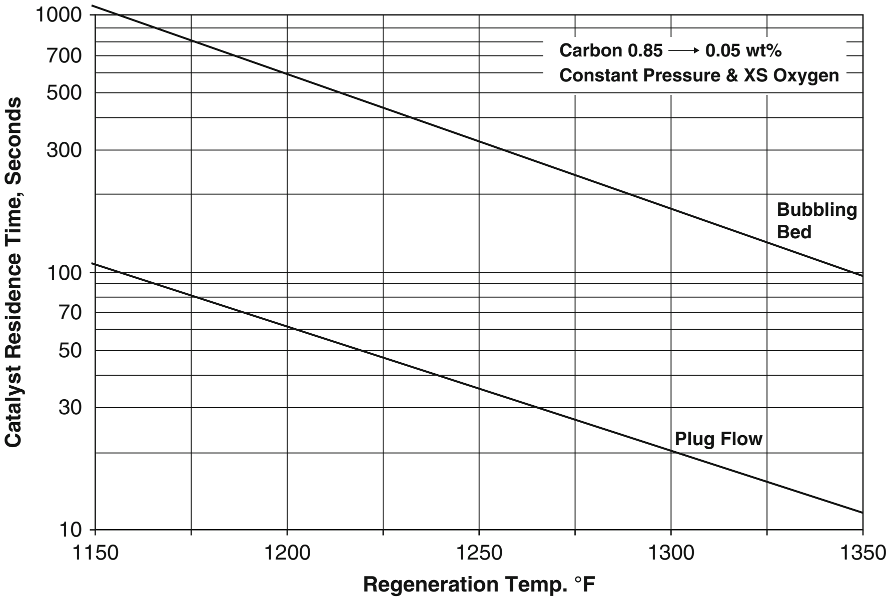


Fig. 15 Comparison of plug flow and backmixed regenerators (ideal)

Table 10 Regenerator parameters (50,000 B/D)

Regenerator type	Residence time (min)	Temperature (°F)	Regenerator inventory (tons)
Bubbling bed	5–20	1,100	300–800
Turbulent bed	3–5	1,250–1,350	200
Fast-fluidized bed	1–3	1,275–1,350	120

catalyst inventory are illustrated in Table 10 for a 50,000 B/D unit that circulates between 30 and 40 t/min of catalyst.

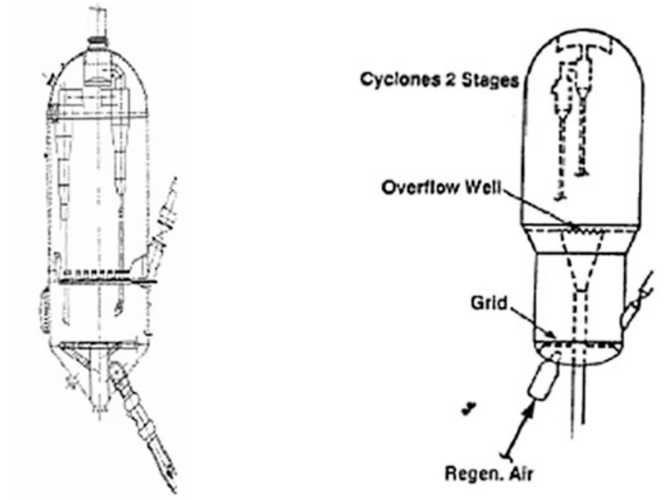
Shorter contact times and smaller catalyst inventories limit operable regeneration conditions and need higher internal catalyst recycle rates for increased throughput or coke burn. Since a catalyst is frequently added on a pound per barrel basis, each of these units would use about 5 t/day of fresh catalyst. Equation 5 relates the catalyst activity to S, the daily fractional replacement rate or age of the catalyst:

$$A = \frac{A_O S}{K_D + S}. \tag{5}$$

This equation implies that the smaller inventory would give the highest equilibrium or unit activity. However, K is also a function of the contacting between the spent catalyst and air, the mix temperature, the catalyst type and activity, and the number of cycles the catalyst makes through the system. This latter fact implies there is an optimum unit inventory for a given processing capacity.

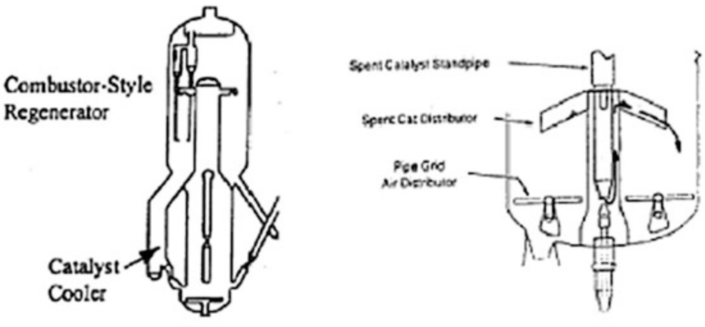
Commercial regenerator designs are shown in Fig. 16. These utilize either turbulent beds or fast-fluidized beds. Cocurrent or countercurrent contacting of the catalyst and air is practiced, and care is taken to prevent short-circuiting of the catalyst from the regenerator inlet to the outlet to ensure an even, low carbon distribution on the regenerated catalyst.

As environmental regulations have become more stringent (recently, NOx has been regulated and CO levels are trending lower), the FCC licensors have modified the spent catalyst entry to the regenerator. Rather than dumping the spent catalyst into one area of the regenerator, the catalyst is preferentially distributed across the entire catalyst bed.



S&W SINGLE STAGE DESIGN

EXXON FLEXICRACKER



UOP HIGH EFFICIENCY DESIGN

M. W. KELLOGG

Fig. 16 Commercial FCC regenerator designs

Table 11 Sources of coke production

Feedstock	Gas oil	Residue
Coke categories		
Catalytic	65	45
Strippable	25	5
Contaminant	5	20
Feed coke	5	20

Resid Catalytic Cracking

Processing heavier feeds poses challenges to the normal FCC design due to the higher coke laydown on the catalyst during the cracking reactions. The coke laid down in the cracking process has been shown to come from four main sources as shown in Table 11.

The catalytic coke comes from the secondary cracking reactions and is caused by polymerization and condensation of hydrocarbons. Strippable coke molecules are the hydrocarbons that are entrained with the spent catalyst that enters the regenerator. Heavy metals that lay down on the catalyst surface promote dehydrogenation and lead to extra coke and hydrogen. Nickel, vanadium, and iron are the main contaminates though occasionally copper, zinc, and lead have been known to cause problems. Feed coke has been associated with the carbon residue in the feed as measured in the Conradson carbon test (ASTM). This has been also referred to as additive coke.

As Table 11 shows, the sources of coke shift dramatically when resid is in the feed. The percentages given in Table 11 are not fixed and shift as the composition of the feed and operating parameters change. The total coke make is different in each case. There are other factors that lead to coke formation that are included in the four categories. Basic nitrogen is known to cause coke since these molecules are strongly adsorbed on the acid sites in the reactor and are burned off in the regenerator.

Some of the very heavy hydrocarbons in resid may not be vaporized and be laid down on the catalyst surface where a portion of them eventually coke. Figure 17 shows that the percentage of Conradson carbon that goes to coke is a function of the feedstock and reactor temperature.

Both desorption of basic compounds and feedstock vaporization would be improved by raising the reactor temperature (and consequently the stripper temperature) so the relationship shown in Fig. 17 is directionally correct. The carbon laydown or delta coke can be represented by Eq. 6. The first term is the Voorhies relationship for carbon laydown for gas oil feedstocks while the second term reflects the feed coke contribution. A, B, and C are constants that depend on operating conditions, feed properties, and catalyst tested:

$$\text{Delta coke} = A\left(\frac{\text{catalyst res. time}}{\text{in the reactor}}\right)^{B} + \frac{C * \text{Conradson carbon}}{\text{catalyst/oil ratio}}. \tag{6}$$

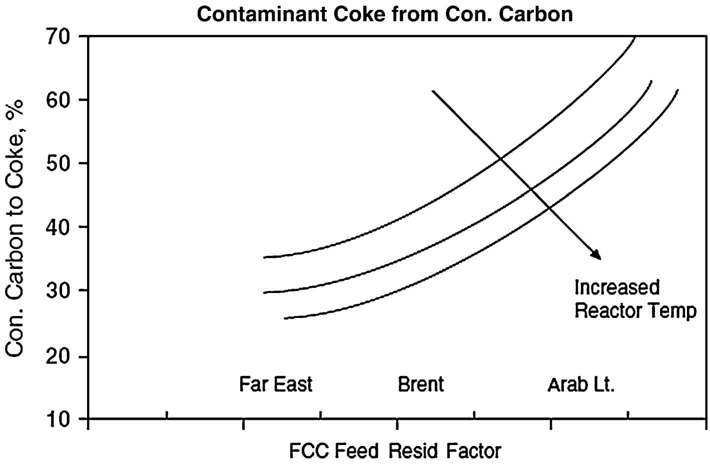


Fig. 17 Percentage of Conradson carbon going to coke (Reprinted with permission from hydrocarbon processing, by Gulf Publishing Co., Copyright 1987; all rights reserved)

The overall heat balance equation for any cracking unit is:

$$\text{wt\% coke} = \text{delta coke} \times \text{catalyst/oil ratio.} \tag{7}$$

The dependent variable is the catalyst/oil ratio, which needs to be high enough to give the desired conversion. Weight percent coke is strictly a function of the operating variables (i.e., fresh feed and recycle rates, feed temperature, reactor temperature, steam rates, heat of cracking, air rates, and carbon burning mode). Since higher delta cokes are caused by heavier feeds, the resulting catalyst/oil ratio becomes too low for medium to high conversion levels. The coke make must be increased to raise the catalyst/oil ratio, and this can be done by any of the means shown in Table 12. For the heaviest feeds, a catalyst cooler will be required.

In Figs. 18, 19, 20, 21, and 22, the commercially offered resid FCC units are pictured.

Much of the reactor-stripper design is the same for resid crackers as it is for gas oil designs. However, there are feed injectors designed specifically to process residual feeds that require more dispersion steam than the normal gas oil models.

On the regenerator side, the two approaches are to use a single-stage regenerator and add a catalyst cooler or split the regenerator into two stages and make the catalyst coolers optional. The two-stage designs offered differ in the sequence of catalyst flow and how the air is introduced and utilized.

The Ashland/UOP design has the first regenerator on top of the second. Spent catalyst flows into regenerator one, is partially regenerated, and flows to the second regenerator where the carbon burn is completed. Air is introduced into both regenerators, but the flue gas from number two passes up through arms into regenerator one. Entrained catalyst is carried with the flue gas. All of the

Table 12 Methods of increasing coke make for resid processing

Modification	Objective	Consequence
Partial burn	Lower regen. temp.	CO emissions rise, carbon on catalyst increases
	Burn more coke	
Mix temp. control	Cool regen.	Higher coke
	Aid vaporization feed	
Water injection	Cool regen.	More coke
		CAT deactivation?
Oxygen enrichment	Increase coke burn	Higher regen. temperature
	Maintain Superficial Air Velocity	
Auxiliary air	Burn more coke	Inc. regen. superficial velocity
Catalyst cooler	Reduce regen.	Higher coke
	Temperature	More air
Second regenerator	Increase throughput and resid	Cost

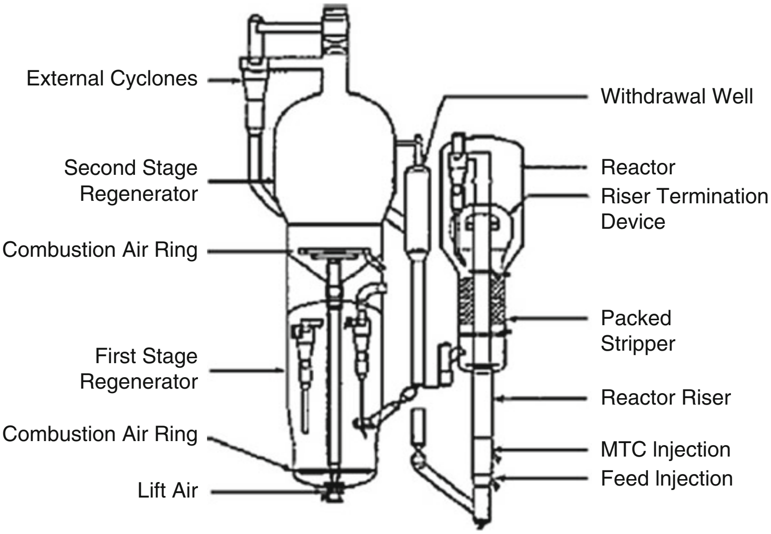


Fig. 18 Technip-Stone & Webster/Axens R2R

regeneration air goes through the top regenerator and a CO boiler to reduce the CO content of the flue gas to permitted levels.

Technip-Stone & Webster/Axens has reversed the regenerators so that the spent catalyst enters the bottom regenerator and the partially regenerated catalyst is vertically conveyed with lift air to regenerator two where the coke burn is finished. Air goes to both regenerators and the catalyst lift line. The flue gas from regenerator one contains CO since the regenerator is run with no excess oxygen.

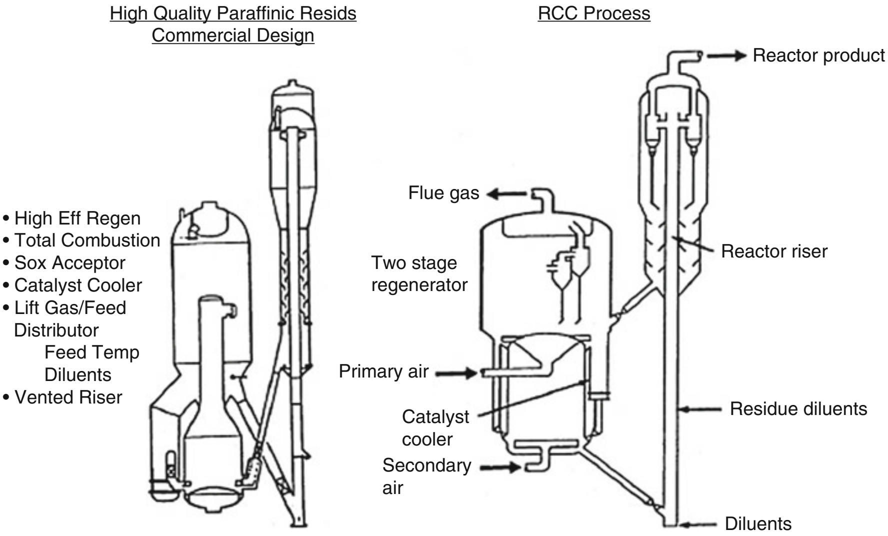


Fig. 19 UOP resid designs

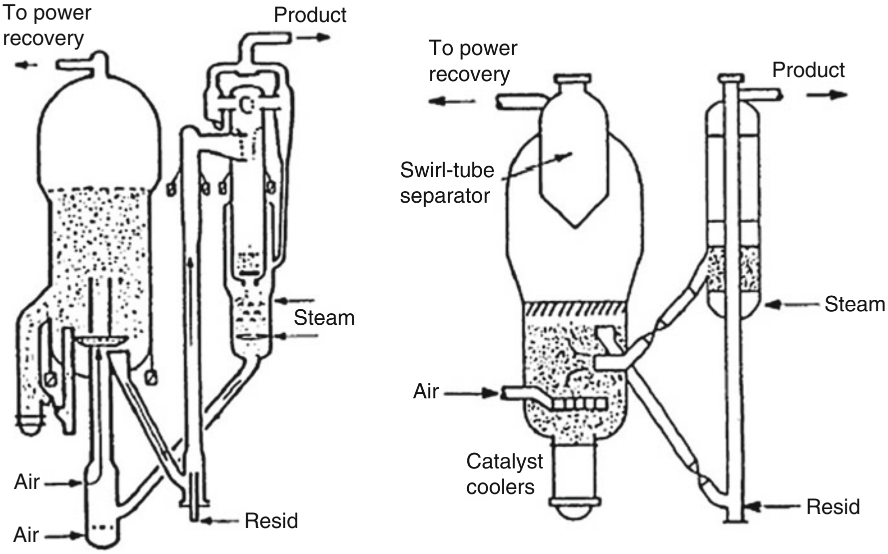


Fig. 20 Shell resid crackers

A CO incinerator or CO boiler is used to produce an acceptable flue gas composition. Lift air and the air to regenerator two are burned and exit the second regenerator and is recombined with the flue gas from regenerator one. Several flue gas combination schemes have been used.

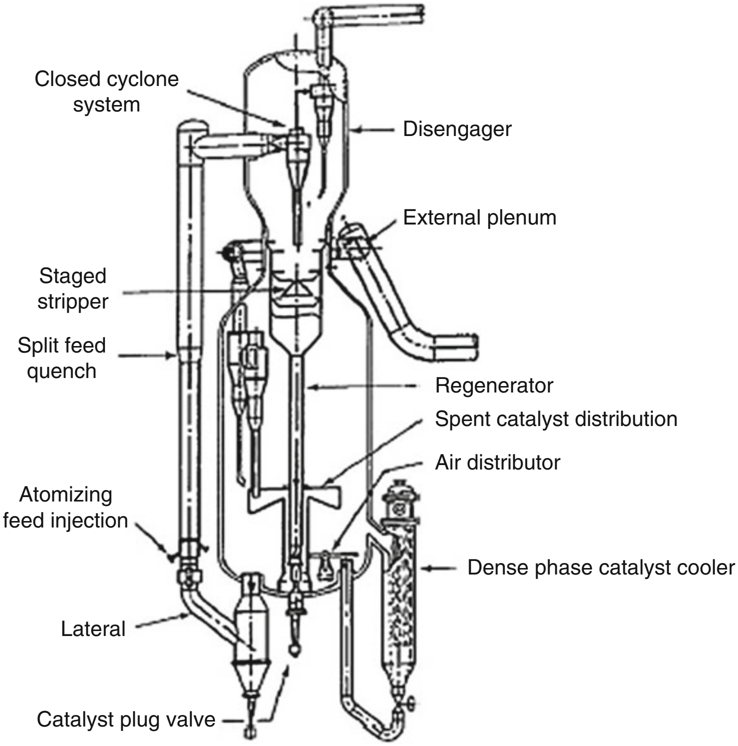


Fig. 21 Kellogg resid cracker

The reason for splitting the regeneration is to produce CO rather than CO_2 so that external heat removal can be eliminated or reduced. Depending on the capacity of the FCC unit, the heat removal by this technique can reach 100 million BTUs per hour. Another benefit is that the hydrogen in the coke burns faster than the carbon as shown in Fig. 23. This hydrogen is the chief source of moisture in the regeneration process that has been shown to deactivate the catalyst. The carbon burn is typically adjusted so that 45–75 % is accomplished in the first stage.

If even more heat removal is required, one or more catalyst coolers can be added to the top regenerator. The two basic designs used are shown in Fig. 24.

Both are dense bed catalyst coolers. Dilute phase coolers were used in the past, but frequent leaks made them too unreliable to use for commercial applications. One of the designs features a shell and tube exchanger while the other has tube clusters that have isolation valves. The latter is more expensive but allows isolation of the leaking cluster without shutting down the catalyst cooler. If steam leaks into the regenerator unabated, excessive catalyst deactivation occurs. The advantage of a catalyst cooler is that its duty can be varied over virtually its entire heat load range. This allows the refiner to adjust the coke make to the feedstock and desired reaction severity.

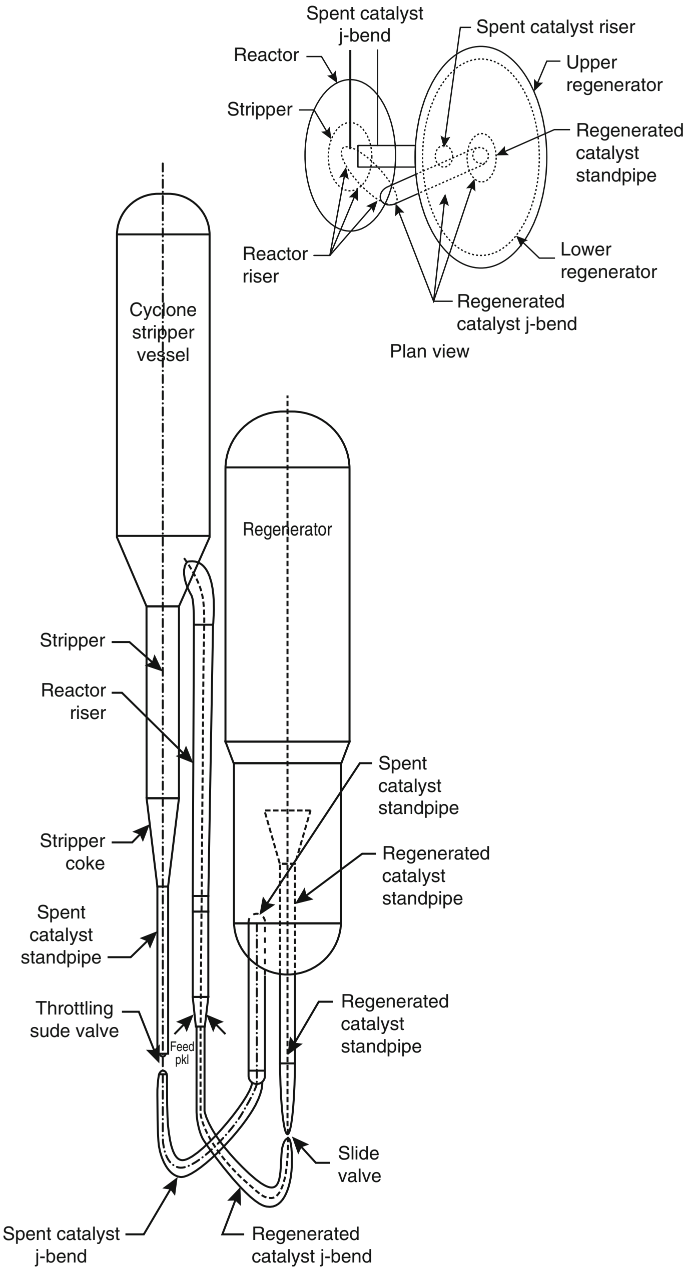


Fig. 22 Exxon flexicracking IIIR unit

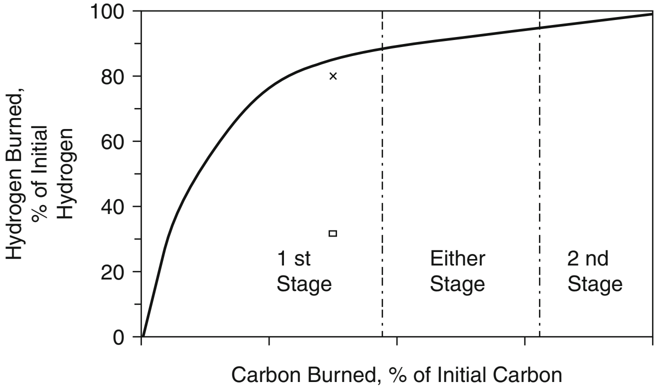


Fig. 23 Carbon and hydrogen burning rates of coke

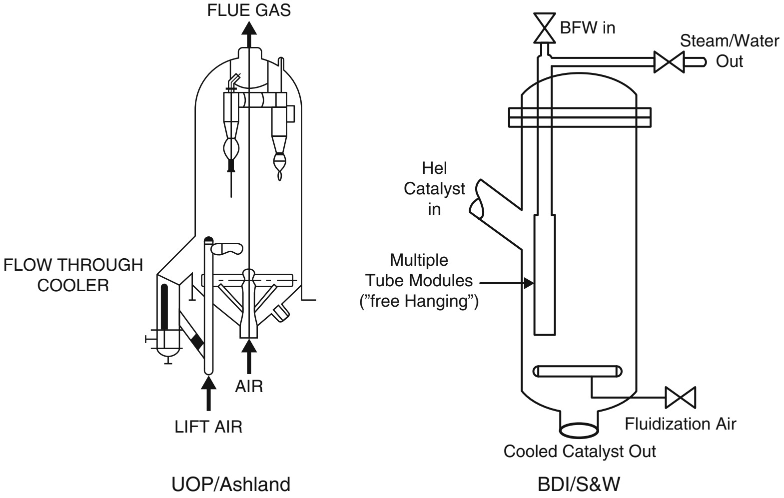


Fig. 24 Commercial catalyst coolers

Many early FCC units had steam coils but these must be run at full load to prevent a mechanical failure. All of these systems require a high water-to-steam ratio to ensure vaporization does not occur in the regenerator coils or tubes, which leads to hot spots and subsequent holes. Older heat removal systems were designed with coils and trim coolers, but this concept has been rejected in modern resid crackers.

The demand for residual fuels has steadily declined and it is unlikely that it will ever return. Consequently, residual catalytic cracking is a high-growth area as shown in Fig. 2.

Not much high-sulfur, heavy fuel oil will be sold in the future. Concern over acid rain and the severe desulfurization required for transportation fuels will focus attention to all the other fuels (off-road diesel, bunkers, etc.) and make desulfurization of these stocks mandatory. High-sulfur fuel (3.5 wt%) currently used for ships will be reduced to 0.5 wt.% in 2020 or 2025. Some ships might use scrubbers to meet the new regulations and others could switch to a diesel fuel. Refiners will find feedstock preparation, while costly, will greatly improve overall yields and install hydroprocessing where the crude warrants. For high metal-laden crude or those deficient in hydrogen, coking will be the preferred bottom processing route followed by hydroprocessing of the coker gas oils or the FCC products.

FCC Reliability and Maintenance

Because of the importance of the FCCU to the profitability of a refinery, considerable effort has been made to improve the reliability and stream factor for the process. Over the years, the average size of the FCCU has steadily increased. Worldwide, the average is over 40,000 B/D while the US value tops 55,000 B/D. Many units are over 100,000 B/D. The cost of a single day of downtime for units this large is from US$1 to 2 million.

In the 1960s, the average unit had a turnaround (TAR) every 2 years. By 1990, this number was 3 years. In 2013, the average FCCU runs about 5 years between scheduled shutdowns. While unscheduled shutdowns use to be common, they are no longer expected or budgeted by refiners.

A survey of US refiners indicated most of the unscheduled shutdowns were due to problems with:

Main air blower
Wet gas compressor
Expansion joints
Power failures
Slide valves
Refractory
Catalyst losses (cyclones)
Interlock trips

Each of these components has been improved over the years to eliminate these unwanted run interruptions.

Rotating equipment uses better alignment techniques such as lasers and more closely measures the temperature, the impurities in the water and oil, and vibrations that signal a potential problem.

Expansion joints have been greatly improved. Better metallurgy is used now that is resistant to failure. Steam purges that were used to keep catalyst from entering the joint have been replaced with packing that better serves the purpose. Dual bellows with leak detectors can give the refiner an opportunity to take steps to avoid a leak to the atmosphere. These factors along with cold-wall designs that greatly reduce the potential movement of the main vessels have made expansion joint leaks a rare occurrence.

Slide valves have gone to cold-wall construction and some designs feature a boltless configuration. Much work has been done to reduce the areas of concern through redesign using finite element analysis. The gas purges have been improved and have made valve failures during the scheduled run unusual.

Refractory has been improved over the years. Dual refractories have been supplemented by monolithic materials that have both insulating properties and abrasion resistance. Better quality control and installation techniques such as vibracast play a vital role in the improvements in performance. Proper curing is essential to trouble-free operation. Much care has to be given to repair methods to avoid premature failures.

Cyclones can run 5 years if they are installed properly, have a proven hanger system, and are run near their design conditions. Regenerator superficial velocities need to be controlled to limit the catalyst loading. Velocities of 3.5 ft/s or higher result in entrainment rates of catalyst to the regenerator cyclones that approach or exceed the rate of catalyst circulation between the reactor and regenerator.

Other factors leading to long run lengths include better equipment designs, improved equipment inspections, better instrumentation, and continuous monitoring of all the unit's components. Smart equipment includes all of the large rotating units as well as pumps. More extensive measurement of temperatures and pressures can identify fouling and allow actions to be taken before a critical failure. Spares can be included in the design to further insure plant reliability.

A list of some of the techniques refiners use to both troubleshoot and monitor FCCU performance are:

Leak detection	Pilot plant testing
RMS (reaction mix sampling)	Infrared scans
Feedstock analyses	Process tomography
Catalyst analyses	Single-gauge pressure surveys
Radioactive tracers	Computational fluid dynamics
Gamma scans	Cold-flow modeling

Problems most frequently occur right after start-up or after an outage such as a power failure. Data are taken with the unit in a distressed condition and are compared to data taken when the operation is normal. Unfortunately, many refiners do not take the data often enough when the operation is routine which makes the location of problems much more questionable. Test runs should be made at least monthly if a refiner wants to evaluate changes in equipment, catalyst, operating variables, and feedstock or the impact of an equipment malfunction.

Monitoring FCC Performance

To monitor FCC performance, the operator needs to have information on the catalyst, the operating conditions, feedstocks being run, and the unit design. The list of factors affecting yields is complex and requires a computer program to

Table 13 Required data for FCCU monitoring

Catalyst	Feedstock	Operating	Design
Activity	Density	Feed temp.	Vessel sizes
Gas factor	H_2 content	Reactor temp.	Cyclones
Surface areas	Aniline point	Regen. temp.	Diplegs
Unit cell size	Refractive ind.	Dispersion steam	Feed system
Metal levels	Aromatics	Stripping steam	Rx terminator
Composition	Distillation	Aerate	Main frac.
Addition rate	Metals	Flue gas anal.	
Additives		Pressures	
		Yields	
		Dilute phase temps.	

examine the many relationships. Some of the required variables in each category are shown in Table 13.

From the operational data, a heat balance is done, and the catalyst circulation rate and heat of cracking is determined. If the heat of cracking is not within certain values depending on the type of catalyst and product distribution, then the data from the regenerator are in error. Other data calculated are the catalyst to oil ratio and the hydrogen content of the coke. The latter should be between 5 and 7 wt% and cannot be less than 4 % or greater than 11 % unless the steam is essentially shut off to the stripper.

Weight balances should be plus or minus 2 % around 100 %. The weight balances and yields should be plotted versus time to insure there are not deviations due to measurements of the various streams.

If the heat and material balances are valid, a number of plots can be made to check on the unit performance. Some of these are:

Individual yields versus conversion
Dry gas versus reactor temp.
Octanes versus reactor temp.
Hydrogen (SCFB) versus Ni, V, Fe
Hydrogen in coke versus stripping steam
Regenerator temp. versus stripping steam
C_3 plus liquid versus conversion
Gasoline versus feed hydrogen content

Many other plots can be made depending on the amount of collected data. A more detailed analysis can be made if an additional variable is used in cross plots of the data.

Over a period of time, an analysis of the data will allow a refiner to optimize the FCC performance, determine the effect of feedstock, evaluate catalyst formulations, and judge the value of equipment modifications.

In Table 14, the effect of increasing the operating variables is shown for many of the variables. Unlike most of the other process units, the FCC has many knobs to

Table 14 The effect of increasing operating variables

Operating variables increased									
Yields	Combined feed temp.	Rx temp.	Feed rate	Catalyst activity	Rx press.	Carbon on catalyst	Combined feed ratio	Contact time in Rx	Coke select. cat
Conv.	Down	Up	Down	Up	Up	Down	Up	Up	Up
Dry gas	Down slightly	Up	Down	Same	Up slightly	Down	Up	Up	Down
LPG	Down	Up	Down	Up	Up	Down	Up	Up	Up
Gasoline	Down	Up slightly	Down slightly	Up	Up slightly	Down	Up	Up	Up
LCO	Up	Down	Up	Down	Down	Up	Down	Down	Down
Coke	Down	Up	Down slightly	Same	Same	Down	Up	Same	Same
RON	Up slightly	Up	Nc	Down	Down	Up	Up	Down	Up
MON	Nc	Up	Nc	Down	Down slightly	Up	Up	Down	Up
Regen. temp.	Up	Up Slightly	Nc	Up	Up	Down	Up	Up	Down
Catalyst/oil	Down	Up	Nc	Down	Down	Up	Up	Down	Up
Delta coke	Up	Down	Down slightly	Up	Up	Down	Up	Up	Down

turn, and the optimization of the unit requires a dynamic model that pushes the cracker to multiple limits. It should be noted that the catalyst is a variable. Activity can be adjusted over a wide range, and product selectivities can be adjusted as needed.

Fluid Cracking Catalysts

The FCC process has been shaped and reshaped to accommodate the advances made in fluid cracking catalysts. Early catalysts were relatively inactive and amorphous in nature and required a lot of recycle of the uncracked feed to achieve the desired conversions. Carbon on regenerated catalyst was usually around 0.3–0.6 wt% and had little effect on unit performance. In the early 1960s, zeolite-containing catalysts were introduced that were much more active and selective than previous catalysts but required the removal of residual coke for optimum commercial performance. This allowed the refiner to substitute fresh feed for the large amounts of recycle being used and resulted in greatly expanded capacity and gasoline yields.

The preferred FCC zeolite is a crystalline silica-alumina compound that has the sodium removed. The type Y or ultrastable Y zeolite commonly employed has a faujasite structure and a produced formula as shown in Fig. 25. The important properties of these zeolites that make them suitable for use in fluid cracking catalysts are:

- High stability (>1,600 °F) to heat and steam
- Three-dimensional structure
- High activity (acidity)
- Large pores (7.5 Å)

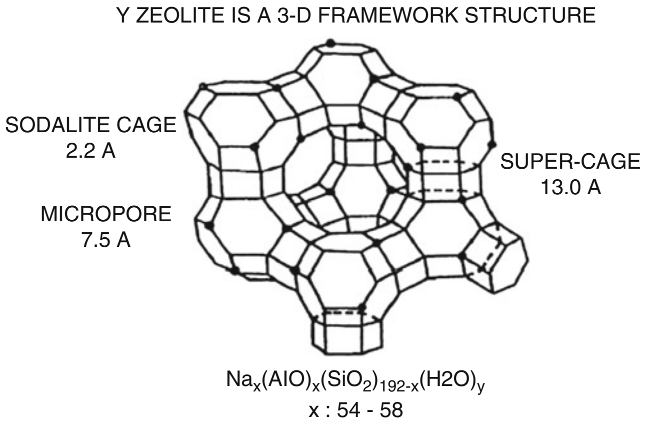


Fig. 25 Faujasite zeolite structure

Without all these characteristics, the zeolite will not stand up to the high temperatures in the regenerator or let in large molecules so that the interior of the crystal can be utilized. Rapid coking is mitigated by the three-dimensional structure. The acidity or activity of the zeolite is associated with the hydroxyl groups attached to the aluminum atoms in the crystal structure.

The types of zeolite contained in fluid cracking catalysts are variations of the basic faujasite or type Y zeolite structure. These are made and characterized as illustrated in Eq. 8. The products are referred to as ultrastable Ys (US-Y), hydrogen Ys (H-Y), calcined rare earth Y (CREY), or rare earth ultrastable Y (RE-US-Y). Each of these has been used as the primary cracking component in commercial cracking catalysts. Variations of the structures and compositions of the above products are made by new methods of zeolite syntheses and secondary treatment. These include controlling the amount of alumina in the crystal structure and occluded in the zeolite pores, substituting other cat ions for alumina in the zeolite framework, and using other cat ions for ion exchange to replace the sodium:

$$\begin{array}{lccccccc} & \mathrm{Na-Y}\xrightarrow{\mathrm{Exc}} & \begin{array}{c}\mathrm{NaHY}\\ \mathrm{NaREY}\end{array} & \xrightarrow[\mathrm{Exc.}]{\mathrm{Cal}} & \begin{array}{c}\mathrm{HY}\\ \mathrm{CREY}\end{array} & \xrightarrow[\mathrm{Stm}]{\mathrm{Cal}} & \begin{array}{c}\mathrm{US-Y}\\ \mathrm{RE-US-Y}\end{array} \\ \mathrm{Na_2O} & 13.0 & 3.0 & & <1 & & <1 \end{array} \tag{8}$$

where

Exc = exchange (NH_3 or RE)
Cal = calcine
Stm = steam

In Table 15, the effect of rare earth exchange of the type Y zeolite used in FCC catalysts is shown. Rare earths stabilize the zeolite and it results in higher activity and more hydrogen transfer. Coke selectivity declines along with the olefinicity of the LPG and catalytic gasoline.

In commercial use, the zeolites undergo dealumination due to contacting with steam at elevated temperatures such as those encountered in the regenerator. This is shown in Fig. 26 where the dealumination is measured by X-ray diffraction to obtain the corresponding unit cell size of the zeolite crystal.

The commercial performance of the cracking catalyst depends on a number of factors, but the equilibrium unit cell size of the catalyst is a principal variable. As illustrated in Fig. 27, many of the important properties of the catalyst are determined by this number. The zeolite types tend to equilibrate around the levels shown, but it should be understood that both hydrogen and rare earth can be used for exchange on the same zeolite to give a mixed result.

As the aluminum atoms are removed from the zeolite structure, the activity goes down, and much more zeolite needs to be used to give an equivalent conversion. Lower unit cell sizes increase C_3 and C_4 olefinicity and gasoline octane and reduce coke formation.

Table 15 Effect of rare earth exchange of Y zeolite on activity and selectivity

Rare earth on zeolite	0	4	8	16
Activity (C/(100-C))	2.55	2.8	3.0	4.0
Conversion	71.8	73.7	75	80
Coke	2.55	3.5	4.8	6.1
C_3=/TC_3	0.81	0.75	0.72	0.65
C_4=/TC_4	0.39	0.32	0.29	0.23

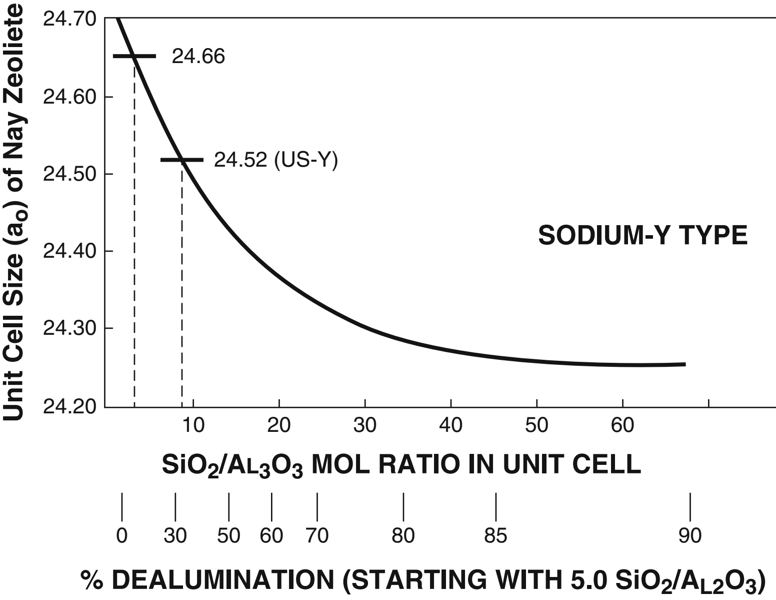


Fig. 26 Unit cell size versus SiO_2/Al_2O_3 ratio for NaY zeolite

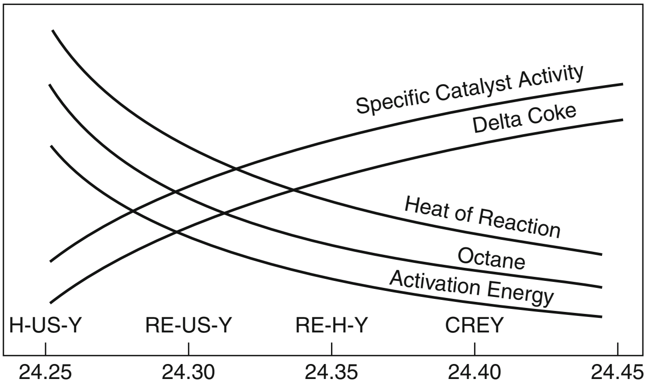


Fig. 27 Effect of unit cell size on catalytic properties

The catalyst's activity is measured by a standard laboratory (MAT) test. The base catalyst without zeolite can have an activity as low as four MAT though numbers ranging from 20 to 45 MAT are more typical. Commercial FCC operations have activities that range from 58 to 77 MAT with 62–72 being the most common range.

The matrix is the rest of the catalyst and contains clay, additives, and/or a binder that holds all the components together. Important properties such as the catalyst's attrition characteristics, density, CO burning rate, coke selectivity, bottom cracking, and dry gas make are a direct function of the matrix composition.

Clay is used as filler and provides some pore structure. Additives such as alumina and silica-alumina are used to increase the matrix cracking activity and crack large molecules. Binders can consist of silica, alumina, or silica-alumina and can also enhance activity. In the new catalysts, more than one additive can be incorporated into the catalyst and small amounts of secondary compounds such as titanium or phosphorus can modify the catalyst's performance.

The ratio of zeolite to matrix is used to vary the yields from an FCC and must be optimized for each matrix and zeolite system. Each feedstock with different properties such as molecular weight and aromaticity requires a unique catalyst formulation. Figure 28a–c shows how the ratio of zeolite to matrix affects yields for a 22.5° API (11.5 K) feed.

In addition to FCC catalysts, there is now a long list of FCC additives to meet specific processing needs. These include products for:

- SO_x removal
- NO_x removal
- Octane enhancement
- Metal passivation
- Bottom cracking
- Fluidization aids
- Olefin generation

A compilation of all the commercially available products is given in Appendix 1.

Cracking for Light Olefins and Aromatics (Petrochemicals)

The demand for propylene as a petrochemical feedstock is outpacing the need for ethylene. As a result, the traditional source of propylene, i.e., as by-product of the steam cracker, is not sufficient for future propylene projections.

Catalytic cracking is the other major source of propylene with the balance being propane dehydrogenation, metathesis, olefin cracking, and MeOH to propylene. Worldwide market shares (2010) are 52:36:12, though catalytic cracking has overtaken steam cracking in the United States as the largest single source of propylene used for petrochemicals. The fracking technology has made large amounts of ethane and propane available to the US market. The ethane is replacing

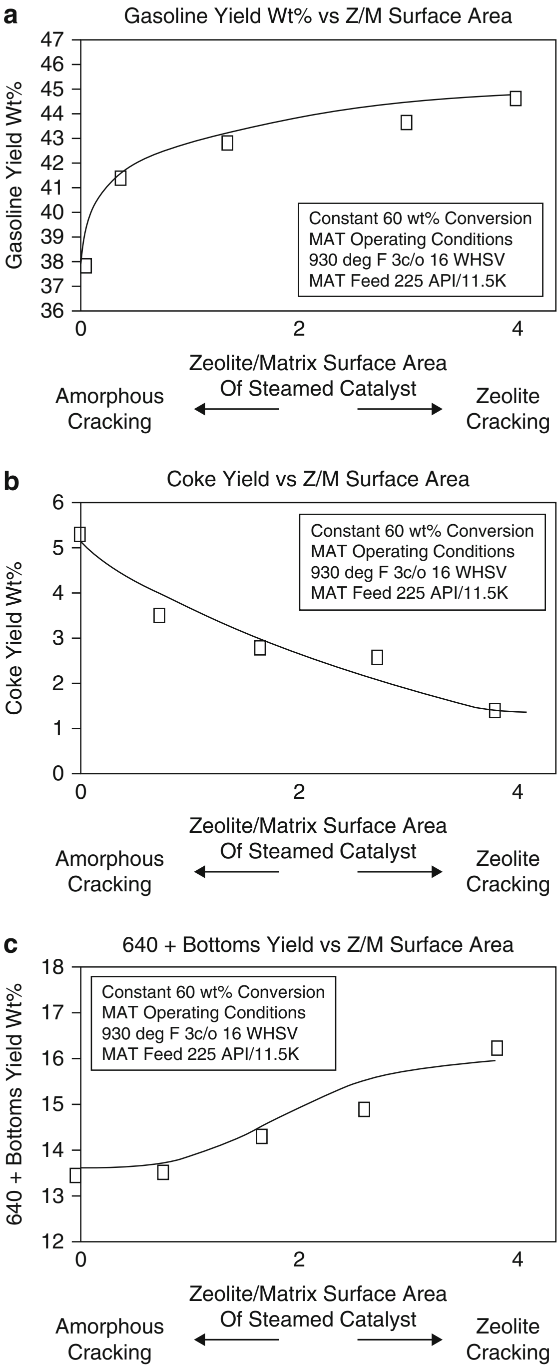


Fig. 28 (**a**–**c**) Effect zeolite/matrix SA ratio on gasoline, coke, and 640+ bottom yields

Table 16 Heavy feed and naphtha propylene processes

Process	Licensor	Feed
Heavy feed propylene processes		
DCC	Technip-Stone & Webster/RIPP	VGO and light ATB
Maxofin	Kellogg, Brown & Root	VGO and ATB
PetroFCC	UOP	VGO
Indmax	Lummus/Indian Oil	VGO and ATB
Resid FCC	Technip-Stone & Webster/Axens	ATB
Milos	Shell Global Solutions	VGO
HS-FCC	Nippon, Aramco, Technip-Stone & Webster	VGO
CPP	RIPP/Technip-Stone & Webster	VGO
Naphtha cracking processes		
Superflex	Kellogg, Brown & Root	Olefinic gasoline
ACO	Kellogg/Brown & Root/Korea	Gasoline streams

naphtha in the steam crackers and propane is being dehydrogenated. This will further increase the percentage of propylene made from FCCUs in the United States.

The deep catalytic cracking (DCC) process was the first commercialized FCC process to make large amounts of propylene as seen in Table 3. Since then, all of the major licensors have offered processes to maximize propylene.

There are two families of technologies to produce propylene in FCC type units. The main processes use heavier feedstocks, i.e., vacuum gas oils and resids, while several others are intended to crack naphthas or various light olefinic streams. The commercial processes being offered are listed in Table 16 along with the feedstocks for each.

Hydrotreating the feed enhances the light olefin yields of all of the heavy oil technologies since increased hydrogen content is necessary to make a product with over 14 wt% hydrogen. The naphtha processes make more propylene since the feedstocks have a much higher percentage of propylene precursors. However, naphtha has a higher value than the heavier feeds so these processes will see more limited application.

Refiners have used gas oil cracking technologies to maximize propylene for downstream petrochemical processes as well as routed the ethane and ethylene from the cat cracker to an adjacent steam cracker gas plant for recovery. This means that C_2 plus recovery is practiced in these FCCUs versus the normal C_3 recovery for a fuel application. This is one of the synergies obtained by combining a refinery and petrochemical operation. Since the propylene is made by overcracking the gasoline, it is important to adjust the unit design, operating parameters, and catalyst formulations for best results.

The product qualities of the naphtha from the deep catalytic cracking process are compared to a conventional FCC unit and a steam cracker in Table 17. The higher aromatic concentration in the naphtha is mostly a result of the concentration of existing aromatics due to the cracking of the paraffins and cycloparaffins rather than

Table 17 Comparison of DCC, FCC, and SC naphthas

	DCC	FCC	SC
Components			
Paraffins	14.3	28.6	3.5
Olefins	32.4	35.3	13.3
Naphthenes	5.0	9.8	4.1
Aromatics	48.3	26.3	79.1
Aromatic breakdown			
Benzene	1.9	0.6	37.1
Toluene	9.4	2.4	18.9
C_8	15.6	6.7	13.5
C_9	12.1	12.5	5.4
C_{10}+	9.3	4.1	4.2
Total	48.3	26.3	79.1

through dehydrogenation of naphthenes or cyclization of paraffins. Xylenes are the major aromatic compounds produced catalytically while benzene is the primary thermal product. Diolefins are low in both of the catalytic processes since these result from the largely absent thermal reactions.

The normal operating conditions of the cracking process are contrasted below:

Typical operating conditions

	FCC	DCC	SC
Reactor temp. (°F)	950–1,020	980–1,100	1,400–1,600
Residence time (s)	1–10	1–10	0.1–0.2
Pressure, ATM	1–2	1–2	1
Catalyst/oil	5–10	8–15	–
Steam (% fd)	0–5	10–30	30–80

A flow diagram of the DCC process is shown in Fig. 29. The catalyst flow and oil vapors and products follow the same path as the gas oil FCC unit described earlier. Considerably, more steam is added and the reactor can be run with a bed level to increase the hydrocarbon residence time and facilitate the overcracking reactions. Other options include recycling naphtha to the same feed riser or the installation of a separate smaller riser to run at higher temperature.

Recracking of naphtha can optionally include the C_4 olefins. Further, the recycled naphtha can be full range or cut to maximize the crackable molecules. The result of the recycle is to increase propylene and the concentration of BTX in the naphtha. The product slates before and after naphtha recycle are shown in Table 18 from the Jinan DCC unit.

A pilot plant test showed that when DCC naphtha with a 150 °C end point was recycled, the aromatic concentration increased dramatically. The total aromatics went from 42 to 81 wt% of the naphtha with the BTX content being 4.4, 28.9, and 40.4 wt%, respectively.

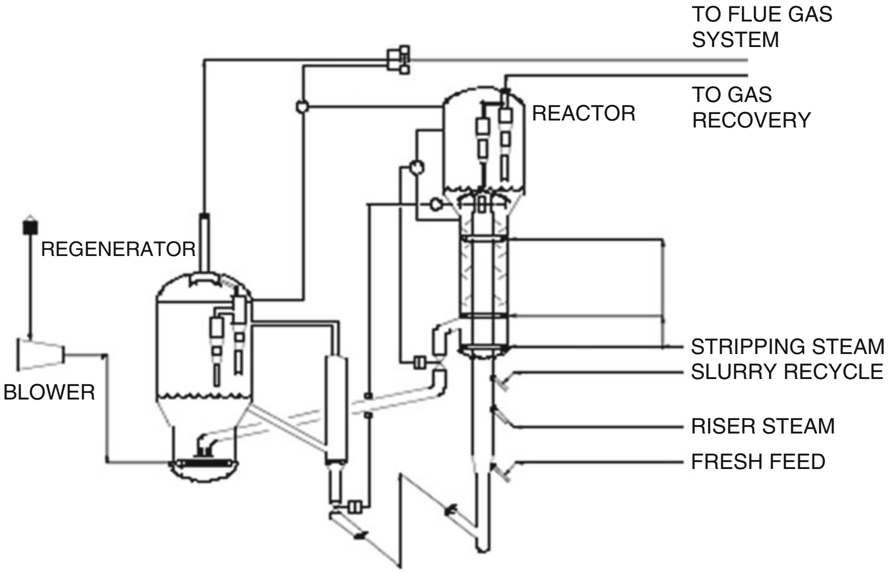


Fig. 29 DCC process

Table 18 DCC operation with naphtha recycle (Jinan DCC unit)

Naphtha recycle	No	Yes
Products (wt%)		
Dry gas	6.8	7.5
LPG	39.2	43.9
Naphtha	27.8	20.9
LCO	16.8	18.2
Coke	8.9	9.0
Loss	0.5	0.5
Olefin yield		
Propylene	17.4	21.0
Butylene	12.4	13.2

Recent advances in the technology have been directed to expanding the feedstock types that can be processed. Successfully run feeds now include:

- VGO
- Hydrotreated VGO
- Deasphalted oil
- Dewaxing wax
- Coker gas oil
- Atmospheric resid

Table 19 DCC light olefin yields

Refinery	Daqing	Anqing	TPI	Jinan	Jinan
Operating mode	DCC + I	DCC-I	DCC-I	DCC-I	DCC-II
Feedstock	Paraffinic VGO + AR	Naphthenic VGO	Arabian VGO + DAO + Wax	Intermediate VGO + DAO	Base
Reaction temp.	545	550	565	564	530
Olefins					
Ethylene	3.7	3.5	5.3	5.3	1.8
Propylene	23.0	18.6	18.5	19.2	14.4
Butylene	17.3	13.8	13.3	13.2	11.4

Table 20 DCC yields for atmospheric resid (Daqing DCC unit)

Daqing ATB		Yields (wt%)	
Density	0.9012	Dry gas	11.7
CCR (wt%)	4.7	$C_3 + C_4$	48.3
Hydrogen (wt%)	12.84	C_5 + naphtha	18.9
Saturates	55.5	LCO	12.1
Aromatics	28.0	Coke	8.0
Resins	15.7	Loss	1.0
Asphaltenes	0.8	Olefins	
Nickel (ppm)	6	Ethylene	6.85
		Propylene	24.83
		Butylene	15.27

Catalyst formulations have had to be altered to match the changing feedstock slate. The DCC catalysts are designed with the following characteristics: high matrix activity for primary cracking of the heavy hydrocarbons and higher metal tolerance, a large quantity of a modified mesopore zeolite with a pentasil structure for cracking the primary product (gasoline), isomerization activity for the light olefins, and minimization of hydrogen transfer. Ten different catalysts have been used commercially in the seven operating DCC installations.

Representative yields from various commercial DCC operations are tabulated in Table 19. Paraffinic feedstocks give high propylene yields, and the isobutylene concentration in the C_4 stream is near the thermodynamic limit. Atmospheric resid makes an excellent feed as long as it is paraffinic. The results from commercial runs on Daqing atmospheric resid are given in Table 20 along with the feedstock analysis. The combination of an ARDS unit in front of a cracking unit designed for heavier feeds would allow a refinery to process a wide variety of crudes and still produce high quantities of petrochemical base stocks. In the last 10 years, over ten units have been configured to process ATB and make at least 9 wt% propylene.

The PetroFCC shown in Fig. 30 has a recycle stream of spent catalyst from the stripper to the base of the feed riser. The principle behind this design, as Table 21

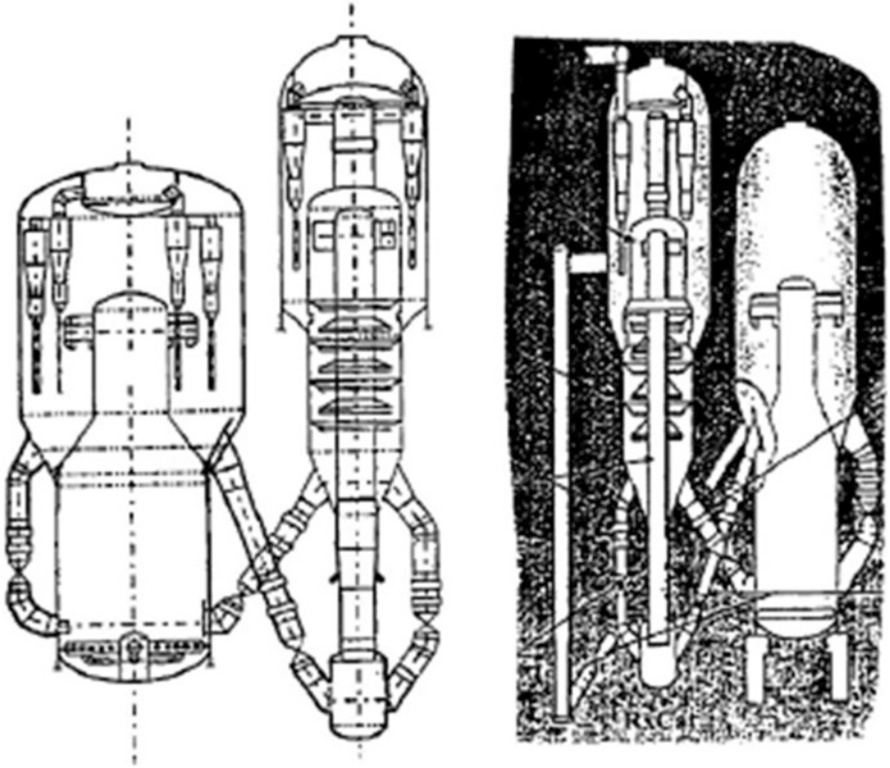


Fig. 30 PetroFCC process (UOP)

Table 21 Selectivity of spent catalyst

	Regenerated	Spent
Initial carbon	0.0	0.91
MAT conversion	64.5	55.0
Yields @ 70 wt% conversion		
C_2 minus	2.0	2.1
Gasoline	49.3	50.0
Coke	2.9	1.6

shows, is that spent catalyst is less active but somewhat more selective than the clean regenerated catalyst at constant conversion.

This makes recycling spent catalyst an option which increases the effective catalyst/oil ratio and reduces the initial regenerated catalyst activity.

The PetroFCC utilizes many of the same technologies that are used in the standard UOP FCC units. This includes both the Optimix nozzles and vortex separator system. A second riser for recracking the naphtha is provided that operates at higher temperature.

Table 22 Pilot yields (wt%) – PetroFCC versus FCC

	PetroFCC	FCC
Propylene	22	4.7
Butylene	14	~6
Ethylene	6	~1
Gasoline	28	53.5

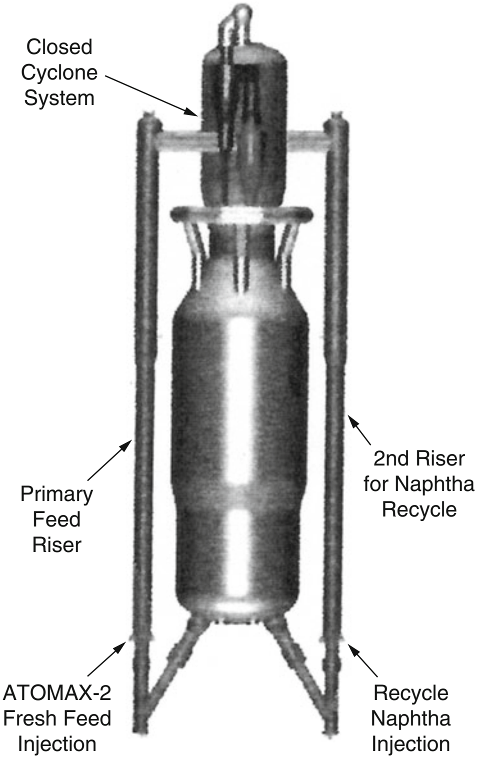


Fig. 31 Maxofin process (Kellogg)

To enhance light olefin production, low hydrocarbon partial pressures (10–30 psia), elevated temperatures (1,000–1,150 °F), and 10–25 wt% of shape-selective (pentasil zeolites) additives are employed. Maximum olefin yields require high conversion since it is the gasoline produced in the cracking process that ultimately is made into propylene and butylene.

Cited yields for the PetroFCC are shown in Table 22.

While the feedstock properties and operating conditions are not known, the feedstock had to be very paraffinic to yield such a high gasoline yield in the regular FCC processing mode.

Another process designed for high olefin yields is the Maxofin FCC. This unit is shown in Fig. 31 and has a second riser for propylene maximization. The process uses the Orthoflow FCC Hardware, e.g., Atomax nozzles and close-connected

Table 23 Yields from a Maxofin unit

	Max $C_3 =$	Intermediate	Max fuels
Recycle	Yes	No	No
ZSM-5	Yes	Yes	No
Riser temp., °C	538/593	538	538
Yields (wt%)			
C_2 minus	7.6	2.3	2.2
Ethylene	4.3	2.0	0.9
Propylene	18.4	14.4	6.2
Butylene	12.9	12.3	7.3
Gasoline	18.8	35.5	49.8
Coke	8.3	6.4	5.9
Conversion	86.4	87.7	85.4

cyclones and the stacked reactor-regenerator configuration. A special ZSM-5 additive is used along with the FCC catalyst.

Pilot yields from the Maxofin process are shown in Table 23. The data are shown for a paraffinic gas oil operating in three different modes.

Some of the other new petrochemical FCC designs listed in Table 16 are shown in Figs. 32 and 33.

The fastest-growing area for FCC petrochemical applications is the cracking of resid to make propylene and transportation fuels. The R2P process was specifically designed for this market. Driving this trend is the high price of crude oil and the shrinking market for heavy fuel oil. With crude prices at $100 US/barrel, it is not economical to burn heavy fuel oil to make electricity. The profit margins for heavy, high-sulfur fuel tend to be negative or marginal at best as demand for these products wane. This induces refiners to minimize heavy oil production.

Both residual FCC processing and delayed coking are being employed to crack the bottom of the barrel. The large size of resid cracking units makes them easy to integrate with petrochemicals since units over 60,000 B/D in feed capacity can make enough propylene for a world-scale polypropylene unit. More than 500,000 B/D of this technology has been licensed in the last 8 years.

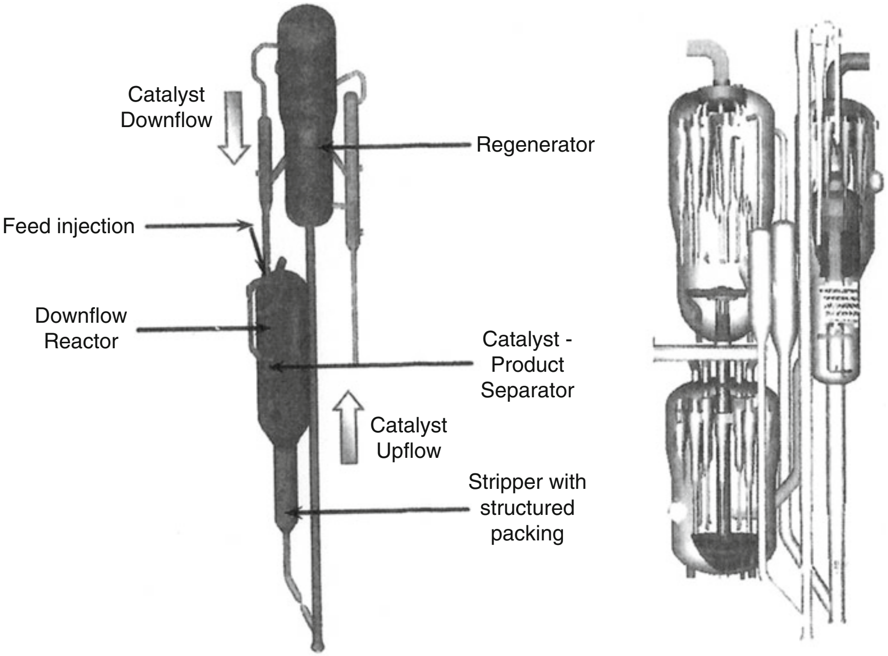
Catalytic cracking is well positioned as we enter a new decade of petroleum refining. The continued demand for gasoline, the need to reduce the residual portion of the crude barrel, the advancements in VGO and ATB hydrotreating technologies, and an ever-increasing thirst for petrochemical base stocks will insure a premier position for the fluid catalytic cracking unit in the refining and petrochemical industry.

Nomenclature

A = activation energy for coke burning

A, A_O = equilibrium and initial catalyst inventories

BP = boiling point



HS-FCC Process R2P

Fig. 32 HS-FCC (Nippon/Aramco) and R2P (Technip-Stone & Webster/Axens) processes

C, Ci = carbon on catalyst and initial carbon on catalyst (wt%)
CO = carbon monoxide
DO = decant oil
E = activation energy for thermal cracking
e = natural exponent
K = rate constant
K_D = deactivation constant
LCO = light cycle oil
L_mO_2 = log mean oxygen concentration
LPG = liquefied petroleum gas
P_B, P_T = pressure at bottom and top of standpipe (psi)
ΔP = pressure difference
Q = aeration requirements for standpipe (scfm)
R = gas constant
S = daily fractional catalyst addition rate (ton/ton)
T = temperature
t = time (seconds)
ρ_{mf}, ρ_t = catalyst densities at minimum fluidization and top of standpipe (lb/ft^3)
ρ_p = skeletal density of catalyst (lb/ft^3)

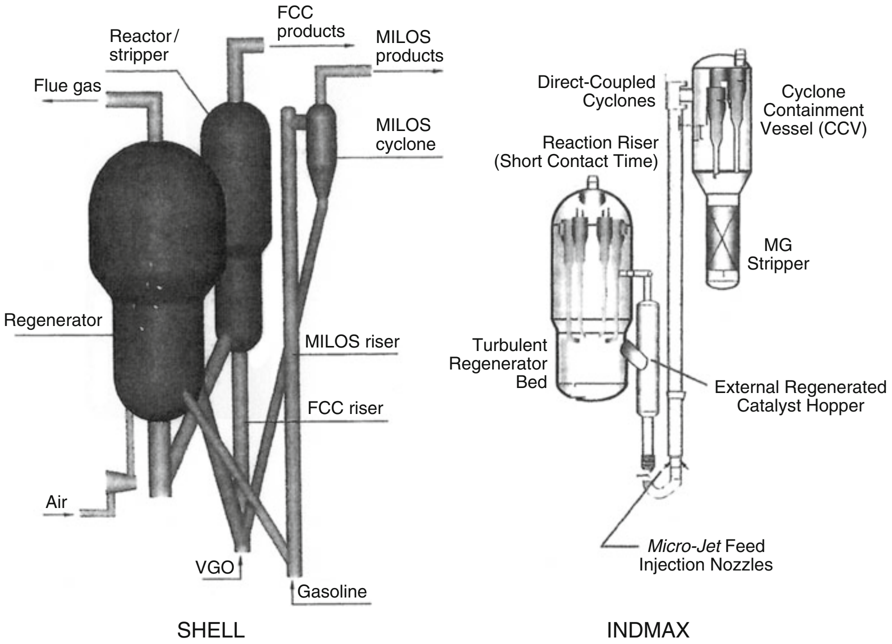


Fig. 33 Shell Milos and Indmax (Indian Oil) processes

Appendix 1: Commercially Available FCC Catalysts and Additives

Note: All catalysts are microspheres with densities from 0.70 to 0.90 g/cc. Matrix binders are silica or aluminum sols or silica-alumina. Clays and other aluminas are added.

Feedstocks		Products	
GO	Gas oils	MDG	Minimum dry gas
R	Resids	MLPG	Maximum LPG
HN	High nitrogen	MG	Maximum gasoline
HNR	High-nickel resid	MLCO	Maximum LCO
HR	Heavy resid	MBC	Maximum bottom cracking
HT GO	Hydrotreated GO	MO	Maximum octane
A	All	MC	Minimum coke
		MLY	Maximum liquid yields
		MOB	Maximum octane barrels
		MIO	Maximum iso-olefins
		MC3=	Maximum propylene
		MC4=	Maximum butylenes

Albemarle

Applications

Catalyst name	Feedstocks	Products	Product features
Action	A	MOB, MLCO, MDG	C4= zeolite, high accessibility
Action T	A	MOB, MLCO, MDG	Same as action, tight oil feeds
AFX	A	MC3=, MBC	C3= zeolite, high accessibility
Amber	GO, HN	MG, MLCO, MBC	Moderate Z and matrix, high access.
Amber MD	GO, HN	MLCO, MBO	High matrix, high access.
Amber T	GO, HN	MG, MLCO, MBC	Amber designed for tight oil
Amber LRT	GO, HN	MG, MLCO, MBC	Mod. Z and M, high access., low RE
Coral	HN, all Rs	MC, MDG, MLY	Low coke, metal tol., higher Z
Coral SMR	HN, all Rs	MC, MDG, MLY	Low coke, xtr metal tol., higher Z
GO-ULTRA	GO, HN	MG, MC	Coke and gaso. select., mod. to hi. Z
GO-LRT	GO, HN	MG, MC	Low RE version of GO-ULTRA
RUBY	GO, HN	MLY, MC	Coke sel., mod. to hi. Z
R-ULTRA	HN, all Rs	MC, MDG, MBC	Coke sel. matrix, metal tol.
Upgrader	HN, all Rs	MCB, MG, MLCO	Hi. M, hi. access., metal tol.
			Upgrader versions for lower coke, max. diesel, tight oils, and low RE are also offered
			LE to all catalysts, low emissions

Sinopec Catalysts Research Institute of Petroleum Processing (RIPP)

Applications

Catalyst name	Feedstocks	Products	Product features
CDOS/RICC-1	R	MLY, MBC	Low coke, high cat stability
DMMC-1	GO, HT GO	MLPG, MC3=	Produces petrochemical feeds
CIP-2	GO, R	MLY, MLPG	Metal tol. and high stability
GOR	GO, R	MC, MBC, MLY	Metal tol. and high stability, low gasoline olefins, min. ON loss

(*continued*)

Catalyst name	Feedstocks	Products	Product features
HGY	HR, R	MG, MLY	Metal tol., high stability, low olefinic gasoline, high RON
MLC-500	A	MBC, MLCO	Low coke, metal tol., high stability
CGP-1	A	MBC, MLY	High C3=, min. coke, high stability

Davison, W. R. Grace and Co.

Applications

Catalyst name	Feedstocks	Products	Product features
Achieve	R, GO	MG, MLCO	Pore structure for metals
Alcyon	GO, HT GO	MG	Max activity
Aurora	GO, HT GO	MG	Attrition resistance
DieseliseR	GO, HT GO	MLCO	Spec. pore structure
Genesis	GO, HT GO, R	MG, MLCO	Low coke, high bottom conv.
Impact	R	MG	Mi metals resist., low coke and gas
Midas	GO, HT GO, R	MLY, MBC	High mesopores, sel. bottom conv.
NaceR	GO, HT GO	MLCO	Mod. matrix acidity, opt. delta coke
Nadius	GO, HT GO	MG	High activity and stability
Nektor	R	MG, MLCO, MC3=	High metal pass., low coke and gas
PMC	GO, HT GO, R	MC3=	Good for most feeds
ProtAgon	GO, HT GO	MC3=	Low coke and gas, Y and ZSM-5 zeolites
ReplaceR	GO, HT GO, R	MG,MLCO, MC3=	Low or no RE catalysts
ResidCrackeR	R	MG, MLCO	Max resid conv., high bottom cracking
SuRCA	GO, HT GO, R	MG, MLY	Gasoline sulfur reduction

BASF

Applications

Catalyst name	Feedstocks	Products	Product features
PetroMax	GO	MCON	High matrix act., max. conv.
NaphthaMax	GO	MCON, MBC, MC	Low coke, good bottom cracking
NaphthaMax II	GO	MCON, MBC, MC	Improved selectivity
NaphthaMax III	GO	MCON, MBC, MC	Max. olefins, low delta coke
HDXtra	GO	MLCO	Low hydrogen transfer
Flex-Tec	R	MCON, MBC, MC	Heavy resids
Defender	R	MCON, MC	Vanadium tolerance
Endurance	R	MCON	Light and hydrotreated resids

(*continued*)

Catalyst name	Feedstocks	Products	Product features
Stamina	HR	MLCO, MDG, MBC	Heavy resid, hi. metal resis.
Aegis	R	MCON, MLCO, MC	Metal tolerance, better yields
Fortress	HNR	MCON, MDG, MC, MBC	Improved metal passivation vs. Flex-Tec
BituPro	GO, R	MCON, MLCO	Bitumen feedstocks
Converter	GO	MCON, NBC	Cocatalyst, conv. enhance
HDUltra	GO	MLCO	Cocatalyst for LCO
HDUltra-R	R	MLCO	Cocatalyst for LCO with R
MPS	GO	MLPG, MLY	Max. C3= with ZSM-5
NaphthaClean	GO	MCON	Max. gasoline

FCC additives

	Product name	Comments
Flue gas SOx reduction		
Albemarle	KDSO$_x$	Standard
	DuraSO$_x$	Max. act., min. dilution
	SO$_x$Master-2	Zero RE
W.R. Grace	DESOX	
	DESOX OCI	
BASF	EnviroSOX	
Sinopec	RFS-C	
Intercat	Super SOxGetter	Full burn units
	Super SOxGetter II	Full burn, low RE
	Super SOxGetter II DM	Middle distillate mode
	Super SOxGetter III	Lowest RE content
	LoSOx-PB Plus	Part. burn and 2 stg units
	LoSOx Special	Units with scrubbers
Flue gas NOx reduction		
Albemarle	ELIMINO$_x$	Non-Pt based
	InsituPro-2	Max. non-Pt dispersion
W.R. Grace	DeNOx	
Intercat	NOxGetter	Reduce NOx and HCN
	NoNOx	
BASF	CLEANOx	
Gasoline sulfur reduction		
W.R. Grace	GSR 5	
	D-PriSM	
BASF	LSA	Gasoline vol. expansion
Intercat	LGS series	
Sinopec	MS011	
Metal passivation		
Albemarle	BCMT-500	Hi. access. and matrix SA
	BCMT-LRT	Same but low RE

(*continued*)

	Product name	Comments
Intercat	Cat-Aid	V and Fe trapping
Nalco	Nickel passivation	Antimony
Fluidization aid		
Albemarle	Smoothflow	Fine part. size dist
	HACTifine	High act., fine PSD
Intercat	FloCAT	
BASF	EZ Flow/EZ Flow Plus	

Bottom cracking		Comments
Albemarle	BCMT-500	High matrix, metal tol.
	BCMT-LRT	Same but low RE
Intercat	BCA-105	Diesel maximization

Octane (pentasil-containing products)

Albemarle	DuraZOOM	Max. LPG olefins, ONs
	IsoZOOM	High C4=, high ONs
	OCTUP-3	
W.R. Grace	OlefinsMax	High sieve content
	OlefinsUltra	
	OlefinsUltra HZ	
BASF	ZIP	Max. activity for lt. olefins and octanes
	MOA	Lt. olefins and octanes
Sinopec	MP051	Higher C3=
Intercat	PENTA-CAT	Moderate to low activity
	Z-CAT HP	Moderate act. for ON and C3=
	Super Z	High activity
	Super Z Excel	High act., maximum C3=
	Super Z Exceed	Higher activity for C3=
	PropylMax	High C3= yield with in situ gasoline olefin make
	ISOCAT	Octane with low LPG
	OCTAMAX	Octane with minimum LPG
	ZMZ	Butylene selective
	ZMX-C HP	Low LPG

	Product name	Comments
CO promoters		
Albemarle	KOC-15	Pt based
	InsituPro	Max. Pt dispersion
	ELIMINO	Non-Pt based
	InsituPro-2	Max non-Pt dispersion
W.R. Grace	CP3, CP5	Pt for CO control
	CP P, XNOx W	Low NOx

(*continued*)

	Product name	Comments
Intercat	COP-NP, COP-NP II	Low NOx
	COP-250, 375, 555, 850	Pt levels on promoters
BASF	COnquer	Minimum NOx
	USP/PROCAT	Pt based
Flush catalyst		
W.R. Grace	ENCORE	Ecat for high metals

References

Additives play important role in FCC development. Oil Gas J. 50–52 (1991). 23 Sept 1991

Advanced catalytic olefins (ACO), in *KBR Technical Brochure* (2013)

Advanced control and information systems 2001, Hydrocarb. Process. 102

American Chemical Society, in *The Fluid Bed Reactor* (1998)

S.V. Anderson, Improved FCCU feed and catalyst contact. Pet. Technol. Q, Spring, 55–59 (1999)

R. D'Aquino, Refiners get cracking on petrochemicals. Chem. Eng. **106**, 30–33 (1999)

L.R. Anderson, H.S. Kim, T.G. Park, H.J. Ryu, S.J. Jung, Operations adjustments can better catalyst cooler operations. Oil Gas J **97**, 53–56 (1999)

A.A. Avidan, M. Edwards, H. Owen, Innovative improvements highlight FCC's past and future. Oil Gas J. 33–58 (1990a)

A.A. Avidan, F.J. Krambeck, H. Owen, P.H. Schipper, FCC closed-cyclone system eliminates post riser cracking. Oil Gas J. 56–62 (1990b)

P.H. Barnes, Tutorial: basic process principles of residue cat-cracking, in *AIChE, 1998 Spring National Meeting*, New Orleans, 8–12 Mar 1998

S. Benton, Advanced technology for increasing LPG and propylene production, in *2nd Bottom of the Barrel Technology Conference (BBTC 2002)*, Istanbul, Turkey, 8–9 Oct 2002

D. Bhattacharyya, Convert resid to petrochemicals, in *International Conference on Refining Challenges and Way Forward*, New Delhi, 16–17 Apr 2012

M.G. Bienstock, D.C. Draemel, P.K. Ladiwig, R.D. Patel, P.H. Maher, A history of FCC process improvement through technology development and application, in *AIChE Spring Meeting*, Houston, 28 Mar–1 Apr 1993

C.A. Cabrera, Recent innovations UOP RCC/FCC technology, Katalistiks Technology Seminar, New Orleans, 15 Dec 1988

R.J. Campagna, A.S. Krishna, Advances in resid cracking technology, in *Katalisticks 5th Annual FCC Symposium*, 23–24 May 1984

I.B. Cetinkaya, UOP PetroFCC process, in *Grace Refining Seminary*, (Singapore), 18–20 Sept 2002

I.B. Cetinkaya, Plug flow vented riser. U.S. Patent 5,449,497

L. Chapin, W. Letzsch, D. Dharia, Deep catalytic cracking for petrochemical and refining application, in *Proceedings Petrotech–95*, India, 1995

L.E. Chapin, W.S. Letzsch, T.E. Swaty, Petrochemical options from deep catalytic cracking and the FCCU. Harts Fuel Technol. Manag. 30–33 (1998)

Y.-M. Chen, D. Brosten, A new technology for reducing NOx emissions from FCC regenerators, in *NPRA Annual Meeting*, Paper AM-08-16

Y. Chen et al., Stripper technology – how to get more profits from FCC units, in *NPRA Annual Meeting*, Mar 2005

Y. Chen et al., U.S. Patent 5,979,799

Complete combustion of CO in cracking process. Chem. Eng. (1975)

K. Couch, FCC propylene production technology integrations to optimize yields, in *Grace 13th European Technology Conference*, Rome, 4–7 Sept 2007

B. Dahlstrom, K. Ham, M. Becker, T. Hum, L. Lacijan, T. Lorsbach, FCC reactor revamp project execution and benefits, in *NPRA Annual Meeting*, paper AM-96-28

R. Dean, J.-L. Mauleon, W. Letzsch, Resid puts FCC process in new perspective. Oil Gas J. (1982a)

R. Dean, J.-L. Mauleon, W. Letzsch, Total introduces new FCC process. Oil Gas J. **80**, 168 (1982b)

D. Decroocq, *Catalytic Cracking of Heavy Petroleum Fractions* (Editions Technip, IFP, Paris, 1984)

E.J. Demmel, H. Owen, U.S. Patent 3,791,962

Exxon Research and Engineering Company, *Flexicracking IIIR State-of-the-Art Cat Cracking Commercial Brochure*, Lummus Engr

A. Fu, D. Hunt, J.A. Bonilla, A. Batachari, Deep catalytic cracking plant produces propylene in Thailand. Oil Gas J. **96**, 49–53 (1998). 1/12/98

FCC as resid processing option, in *Indian Oil R&D Technical Presentation* (2012)

Fluid catalytic cracking technology, in *KBR Technical Brochure* (2013)

Y. Gao, C. Xie, Z. Li, DCC update and its commercial experiences, in *5th Stone and Webster/Axens FCC Forum*, May 2002

W. Gilbert, C.A. Baptista, A.R. Pinho, Exploring FCC flexibility to produce mid-distillate and petrochemicals. ACS Div. Petr. Chem. **51**(2), 417–420 (2006)

P.E. Glasgow, A.A. Murcia, Process and mechanical design considerations for FCC regeneration air distributors, in *Katalistiks 5th FCC Symposium*, Vienna Austria, May 1984

R.J. Glendinning, H.L. MCQuiston, T.Y. Chan, Implement new advances in FCC process technology. Fuel Reformulation 3/4, (45–53) (1995)

R.J. Glendinning, H.L. McQuiston, T.Y. Chan, *New Developments in FCC Process Technology*

J. Haruch, U.S. Patent 5,673,859, Lummus Brochure

C.L. Hemler, *FCC Historical Perspective and Major Process Changes*, CFB-4 FCC Tutorial (1993)

C.L. Hemler, D.A. Lomas, D.G. Tajbi, FCCU reflects technological response to resid cracking. Oil Gas J. **82**, 79–86 (1984)

B.W. Hewrick, J.P. Koebel, I.B. Cetinkaya, Improved catalyst stripping from cold flow modeling. PTQ Autumn, 87–95 (2002)

J.M. Houdek, J Anderson, Market Trends and opportunities in petrochemical propylene production, in *NPRA Annual Meeting*, AM-05-58

R. Hu et al., Effect of hydrocarbon partial pressure on propylene production in the FCCU. Catalagram **103**, 21–30 (2008)

D. Hunt et al., Implementation of state of the art FCC technology for improved reliability, in *AFPM Annual Meeting*, AM-14-28, 23–25 Mar 2014

G.E. Jacobs, C. Santner, W. Letzsch, Regenerator design to minimize catalyst deactivation and reduce emissions, in *NPRA Annual Meeting*, AM-08-18, San Diego, Mar 2008

D.L. Johnson, FCC Catalyst Stripper, Int. Patent WO96/04353

T.E. Johnson, Improve regenerator heat removal. Hydrocarbon Processing 55–57 (1991)

T.E. Johnson, R.K. Miller, New developments in resid FCC technology. Paper presented at the Institute for International Research, Singapore, 9–10 May 1994

F.H.H. Khouw, M.J.P. C. Nieskens, M.J.H. Borley, K.H.W. Roebschlaeger, The shell residue fluid catalytic cracking process commercial experience and future developments, in *NPRA Annual Meeting*, Paper AM-90-42

J. Knight, R. Mehlberg, Maximize propylene from your FCC unit. Hydrocarbon Processing reprint, (2011)

K.V Krikorian, J.C. Brice, FCC's effect on refinery yields. Hydrocarb. Process. 63–66 (Sept 1987)

A.S. Krishna, C.R. Hsieh, A.R. English, T.A. Pecoraro, C.W. Cuehler, Additives improve FCC process. Hydrocarb. Process. **70**, 59–66 (1991)

C. Leckenbach, A.C. Worley, A.D. Reichle, E.M. Gladrow, Cracking-catalytic, in *Encyclopedia of Chemical Processing and Design*, vol 13 (Marcel Dekker, New York), pp. 1–133

W.S. Letzsch, Controlling FCCU dilute phase reactions. PTQ Q2. 49–53 (2005)

W.S. Letzsch, Fluid catalytic cracking in the new millennium, in *NPRA Annual Meeting*, Paper AM-99-15

W.S. Letzsch, P.A. Minton, FCC revamps. Hydrocarb. Eng. 32–35 (2000)

W. Letzsch, R. Blinkhorn, Maintaining the reliability of the FCC unit. PTQ **8**, 1–6 (2003)

W. Letzsch, D. Lawler, Processing resid through FCCUs. PTQ Q2 **11**, 65–69 (2006)

W. Letzsch, J.-L. Mauleon, G. Jones, R. Dean, Advanced residual fluid catalytic cracking, in *Katalistiks 4th Annual FCC Symposium*, Amsterdam, May 1983

W. Letzsch, C. Santner, S. Tragesser, More than 60 ways to improve your FCC operation, in *NPRA Annual Meeting*, AM-09-70, San Antonio, Mar 2009

W. Letzsch, K. Peccatiello, M. Tibbits, Evolution of residual FCC technology, in *NPRA Annual Meeting*, Paper AM-07-34

W.S. Letzsch, D.J. Dharia, W.H. Wallendorf, J.L. Ross, FCC modifications and their impact on yields and economics, in *NPRA Annual Meeting*, Paper AM-96-44

W.S. Letzsch, D. Dharia, J.L. Ross, The future of catalytic cracking, in *NPRA Annual Meeting*, Paper AM-97-65

Z.T. Li, W.Y. Shi, R.N. Pan, F.K. Jiang, DCC flexibility for isoolefins production, in *American Chemical Society 206th National Meeting*, Chicago, 22–27 Aug 1993

M. Lippman, Innovative technology to improve FCC flexibility, in *AFPM Annual Meeting*, AM-12-26, San Diego, Mar 2012

J.S. Magee, M.M. Mitchell Jr., *Fluid Catalytic Cracking Science and Technology* (Elsevier, Amsterdam, 1993)

C.R. Marcilly, R.R. Bonifay, Catalytic cracking of resid feedstocks. Arab. J. Sci. Technol. **21**(48), 627–651 (1996)

J. L. Mauleon, J. C. Courcelle, FCC heat balance critical for heavy fuels. Oil Gas J. 64–70 (1985)

J.L. Mauleon, J.B. Sigaud, Mix temperature control enhances FCC flexibility in use of wider range of feeds. Oil Gas J. **85**, 52–55 (1987)

S.J. McCarthy, M.F. Raterman, C.G. Smalley, J.F. Sodomin, R.B. Miller, FCC technology upgrades: a commercial example, in *NPRA Annual Meeting*, Paper AM-97-10

R.A. Meyers, *Handbook of Petroleum Refining Processes*, 2nd edn. (McGraw-Hill, New York, 1996). Chapters 3 thru 7

R. Miller, FCC's role in refinery-petrochemical integration, in *Grace Refining Technology Conference*, Singapore, 18–20 Sept 2002

R. Miller, Y.-L. Yang, E. Gbordzoe, D.L. Johnson, T. Mallo, New developments in FCC feed injection and stripping technologies, in *NPRA Annual Meeting*, Paper AM-00-08

J.R. Murphy, Designs for heat removal in HOC operations, in *Petroleum Refining Conference*, JPI, Tokyo, Oct 1986

J.R. Murphy, Evolutionary design changes mark FCC process. Oil Gas J. **18**, 49–58 (1992)

P. Niccum, Maximizing diesel production in the FCC-centered refinery, in *AFPF Annual Meeting*, AM-12-43, San Diego, Mar 2012

P.K. Niccum, M.J. Tallman, D.H. Grittman, KBR catalytic olefins technologies provide refinery/petrochemical balance, in *25th JPI Petroleum Refining Conference*, Tokyo, 26–27 Oct 2010

P.K. Niccum et al., Maxofin: a novel FCC process for maximizing light olefins using a new generation of ZSM-5 additive, in *NPRA Annual Meeting*, Paper AM-98-18

P.K. Niccum et al., Future refinery-FCC's role in refinery/petrochemical integration, in *NPRA Annual Meeting*, Paper AM-01-61

M. Nieskens, Milos-Shell's ultimate flexible FCC technology in delivering diesel/propylene, in *NPRA Annual Meeting*, Paper AM-08-54

M.J.P.C. Nieskens, F.H.H. Khouw, M.J.H. Barley, K.H.W. Roebschlaeger, Shell's resid FCC technology reflects evolutionary development. Oil Gas J. **37**, 37–44 (1990)

W.L. Pierce, D.F. Ryan, R.P. Souther, T.G. Kaufmann, Innovations in flexicracking, in *API Div. of Refining 37th Midyear Meeting*, New York, 10 May 1972

A. Pinho, P.P. Neto, J.G.F. Ramos, J.A.M. Castillero, Double riser FCC: an opportunity for the petrochemical industry, in *NPRA Annual Meeting*, Paper AM-06-13

Propylene or diesel fuel? Just change the controls. Chem. Eng. 20 (2008)

J.A. Rabo, Zeolite chemistry and catalysis, in *ACS Monograph 171*, ed. by J.S. Magee, J.J. Blazek, Chapter 11, Preparation and Performance of Zeolite Cracking Catalysts (1979)

M.F. Raterman, U.S. Patent 5, 409,872

J. Ross FCC Technology Seminar Technip/Axens, San Francisco, (2013)

R.E. Ritter, J.C. Creighton, D.S. Chin, T.G. Roberie, C.C. Wear, Catalytic octane from the FCC, Grace Catalagram. No. 74 (1986)

C.Y. Sabottke, Eur. Patent 0444860A1

A.V. Sapre, P.H. Schipper, F.P. Petrocelli, Design methods for FCC feed atomization, in *AIChE Symposium Series*, vol 88, pp. 103–109

P.R. Satbhai, J.M.H. Dirkx, R.J. Higgins, P.D.L. Mercera, Best practices in shell FCC units, in *Akzo Nobel Catalyst Seminar*, Mumbai, India, Oct 1998

M.W. Schnaith, D.A. Kauff, Resid FCC regenerators: technology options and experience, in *NPRA Annual Meeting*, Paper AM-97-13

M.W. Schnaith, A.T. Gilbert, D.A. Lomas, D.N. Myers, Advances in FCC reactor technology, in *NPRA Annual Meeting*, Paper AM-95-36

A.G. Shaffer Jr., C.L. Hemler, Seven years of operation prove RCC capability. Oil Gas J. 62–70 (1990)

W. Shi, C. Xie, Y. Huo, X. Zhong, DCC family technology for producing light olefins from heavy oils. Chin. Petr. Process. Petrochem. Technol. **2**, 15–21 (2001)

D. Soni, Next generation stripper design commercialized, in *Lummus Paper* (2007)

D. Soni et al., Maximize olefins through catalytic cracking Indmax FCC process (2008). www.digitalrefining.com/article/1000205

A.M. Squires, Circulating Fluidized Bed Technology, in *The Study of Fluid Catalytic Cracking: The First Circulating Fluid Bed*

J. Stell, Worldwide catalyst report. Oil Gas J. 56–76 (2001)

Superflex, in *KBR Technical Brochure* (2013)

M.J. Tallman, C. Eng, Catalytic routes to olefins, in *Grace European Technical Conference*, Rome, 4–7 Sept 2007

M.J. Tallman, C.N. Eng, Propylene on purpose. Hydrocarb. Eng. (2010)

M.J. Tallman et al., Advanced Catalytic Olefins (ACO): first commercial demonstration unit begins operations, in *AICHE Spring National Meeting*, Chicago, 14–17 Mar 2011, p. 74b

A.K. Rhodes, Number of catalyst formulations stable in a tough market. Oil Gas J. **95**, 41–72 (1997)

L.L. Upson, H.V.D. Zwan, Promoted combustion improves FCCU flexibility. Oil Gas J. **85**, 65–70 (1987)

I.A. Vasalos, E.R. Strong, C.K.R. Hsieh, G.J. D'Souza, New cracking process controls FCCU SOX. Oil Gas J. **75**, 141–148 (1977)

P.B. Venuto, E.T. Habib Jr., *Fluid Catalytic Cracking with Zeolite Catalysts* (Marcel Dekker, Boca Raton, 1979)

P. Walker, R. Peterman, RFCC units set new standard for propylene production. PTQ Q4, 83–92 (2012)

C.C. Wear, R.W. Mott, FCC catalysts can be designed and selected for optimum performance. Oil Gas J. 71–79 (1988)

J.W. Wilson, Modernizing older FCCU's, in *NPRA Annual Meeting*, Paper AM-00-09

J.W. Wilson, First Stone and Webster/ IFP Licensors' Forum (Osaka Revamp) (1994)

J.W. Wilson, *Fluid Catalytic Cracking Technology and Operation* (Pennwell, Tulsa, 1997)

E.G. Wollaston, W.J. Haflin, W.D. Ford, G.J. D'Souza, FCC model valuable operating tool. Oil Gas J. **87**, 87–94 (1975). 9/22/75

L. Wolschlag, K. Couch, UOP FCC design advancements to reduce energy consumption and CO_2 emissions, in *NPRA Annual Meeting*, AM-09-35, San Antonio, Mar 2009

L. Wolschlag, K. Couch, UOP FCC innovations developed using sophisticated engineer tools, in *NPRA Annual Meeting*, AM-10-109, Phoenix, Mar 2010

R.E. Wrench, P.C. Glasgow, FCC hardware options for the modern Cat cracker, in *AIChE National Meeting*, Los Angeles, 17–22 Nov 1991, Paper 125C

L.C. Yen, R.E. Wrench, A.S. Ong, Reaction kinetic correlation equation predicts fluid catalytic cracking coke yield. Oil Gas J. **86**, 67–70 (1988)

O.J. Zandona, W.P. Hettinger Jr., L.E. Busch, Reduced crude processing with Ashland's RCC process, in *API 47th Midyear Refining Meeting*, New York, 13 May 1982

Hydrocracking in Petroleum Processing

Maureen Bricker, Vasant Thakkar, and John Petri

Contents

M. Bricker (✉) • V. Thakkar • J. Petri
UOP LLC, A Honeywell Company, Des Plaines, IL, USA
e-mail: maureen.bricker@honeywell.com; vasant.thakkar@honeywell.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_3

Abstract

Hydrocracking is a flexible catalytic refining process that can upgrade a large variety of petroleum fractions. Hydrocracking is commonly applied to upgrade the heavier fractions obtained from the distillation of crude oils, including residue. The process adds hydrogen which improves the hydrogen to carbon ratio of the net reactor effluent, removes impurities like sulfur to produce a product that meets the environmental specifications, and converts the heavy feed to a desired boiling range. The chemistry involves the conversion of heavy molecular weight compounds to lower molecular weight compounds through carbon-carbon bond breaking and hydrogen addition. The main products have lower boiling points, are highly saturated, and generally range from heavy diesel to light naphtha. Hydrocracking processes are designed for, and run at, a variety of conditions. The process design will depend on many factors such as feed type, desired cycle length, and the desired product slate. Hydrocracking is a process that is suitable to produce products that meet or exceed all of the present environmental regulations. Hydrocracking reactions proceed through a bifunctional mechanism. Two distinct types of catalytic sites are required to catalyze the steps in the reaction sequence. The cracking and isomerization reactions take place on the acidic support. The acid can be an amorphous silica alumina or a zeolite. The metals provide the hydrogenation function. The metals are typically noble metal (palladium, platinum) or non-noble metal sulfides from group VIA (molybdenum, tungsten) and group VIIA (cobalt, nickel).

Catalyst manufacturing can be done by a variety of methods. The method chosen represents a balance between the manufacturing cost and the degree to which the desired chemical and physical properties are achieved. Many companies are involved in the licensing of the process and the production of a variety of hydrocracking catalysts.

Keywords

Hydrocracking • Hydroprocessing • zeolite • Y zeolite • Beta zeolite • Ni, W • Pt base metals • Base metal sulfide • Noble metal • Single stage • Two stage • Vacuum gas oil (VGO) • Unconverted oil (UCO) • Diesel • Distillate • Gasoline • Cracking • Isomerization • Hydrogenation • Aromatic saturation •

Hydrodesulfurization HDS • Hydrodenitrogenation HDN • Catalyst manufacture • Cetane number • Smoke point • Cold flow properties

Introduction

Hydrocracking is a flexible catalytic refining process that can upgrade a large variety of petroleum fractions. Hydrocracking is commonly applied to upgrade the heavier fractions obtained from the distillation of crude oils, including residue. Tables 1 and 3 show the feedstock used in hydrocracking as well as the products obtained (Scherzer and Gruia 1996; Robinson and Dolbear 2006). The process adds hydrogen which improves the hydrogen to carbon ratio of the net reactor effluent, removes impurities like sulfur to produce a product that meets the environmental specifications, and converts the heavy feed to a desired boiling range. The chemistry involves the conversion of heavy molecular weight compounds to lower molecular weight compounds through carbon-carbon bond breaking and hydrogen addition. The main products have lower boiling points, are highly saturated, and generally range from heavy diesel to light naphtha. Hydrocracking processes are designed for, and run at, a variety of conditions. The process design will depend on many factors such as feed type, desired cycle length, and the desired product slate. However, units generally operate at the following conditions: liquid hourly space velocity (LHSV), 0.5–2.0; H_2 circulation, 5,000–10,000 SCFB (standard cubic feet per barrel); H_2 partial pressure, 1,500–2,000 psia (103–138 bars); and start of run (SOR) temperatures, from 650 °F (288 °C) to 725 °F (385 °C). Hydrocracking is a process that is suitable to produce products that meet or exceed all of the present environmental regulations.

The demand for hydrocracking is predicted to be a stable growth market for the foreseeable future Table 3. The installed hydrocracking capacity is estimated to be between six and seven million barrels per stream day (bpsd). The estimate of current installed catalyst capacity in the world is 30,000 MT. The 2013 OPEC World Oil Outlook Table 3 shows that the demand for hydrocracking increases with

Table 1 Hydrocracking feeds and products from the processing

Feedstock	Products
Straight-run gas oils	LPG
Vacuum gas oils	Motor gasoline
FCC cycle oils and decant oils	Reformer feeds
Coker gas oils	Jet fuels
Thermally cracked stocks	Diesel fuels
Deasphalted oils	Heating oils
Straight-run and cracked naphtha	Olefin plant feedstocks, lube oils, lube plant feedstock, FCC feedstock
Fischer-Tropsch liquids	Distillate fuels
Tar sands	Distillate fuels

Table 2 2013 OPEC World Oil Outlook

Global capacity requirements by process, 2012–2035 mb/day				
	Additional requirements		Total additions	
Existing projects	To 2018	To 2020	2020–2030	To 2035
Hydrocracking	2.2	1	3.2	6.4
Desulfurization	6.9	6.6	13.5	26.9
Vacuum gas oil/resid	0.9	0.7	1.7	3.3
Distillate	2.8	5	9.8	17.5
Gasoline	3.2	1	2	6.1

Table 3 Types of hydrocracking processes

Unit type	Typical conversion	Total pressure, bar/psig	Hydrogen partial pressure, bar/psig	Reactor temperature, °C/°F
Mild (MHC)	20–40	60–100/ 870–1,450	20–55/290–840	350–440/ 662–824
Moderate/medium pressure	40–70	100–110/ 1,450–1,600	50–95/725–1,380	340–435/ 644–815
Conventional	50–100	110–200/ 1600–2,900	95–140/1,390–2,030	340–435/ 662–842
Resid hydrocracking (LC-fining)	65–100	97–340/ 1,400–3,500	73–255/1,050–2,625	385–450/ 725–914
Slurry hydrocracking	80–97	138–241/ 2,000–3,500	103–206/ 1,500–3,000	426–471/ 800–880

a continuing value of distillate products over gasoline products as well as a large increasing demand for desulfurization processes which reflects the lower sulfur requirements in gasoline and diesel around the world. With the changing market and the change in fuel consumption causing the shift from high gasoline demand to high distillate demand, many refiners are conducting modifications to their existing facilities to allow an improved integration of their refinery or another change in the configuration to allow flexible product needs. Since 2009, the worldwide capacity for hydrocracking has grown about 2 %, the global demand for diesel has grown about 2 %, and over the next 3 years, the demand for combined hydrotreating and hydrocracking is projected to grow by 6 % per year (http://www.opec.org/opec_web/static_files_project/media/downloads/publications/WOO_2013.pdf).

Brief History

Modern hydrocracking technology has been in use since 1960. However, there is a long history of hydrocracking that began early in the twentieth century (Scherzer and Gruia 1996; Robinson and Dolbear 2006). Hydrocracking technology was developed in Germany in the 1910s when it was used for coal conversion to secure a supply of liquid fuels from domestic coal deposits. The first plant for the hydrogenation of brown coal began in Germany in 1927. Coal conversion to liquids was a high pressure, 3,000–10,000 psig (207–690 bar) and high-temperature (700–1,000 °F, 371–538 °C) catalytic process (Ministry of Fuels and Power 1947). From 1925 to 1930, I.G. Farbenindustrie in Germany in collaboration with Standard Oil of New Jersey developed hydrocracking technology to convert heavy gas oils to lighter fuels (Heinemann 1981). Other groups did research work to develop technology to upgrade heavier petroleum fractions (Pier 1949). After World War II, the Middle Eastern crudes became available, and their gas oils and cracked stocks were easily processed in FCC. So hydrocracking became less important. Catalytic cracking processes proved to be more economical for converting heavy petroleum fraction to gasoline based on the demands for gasoline and environmental regulations of that time.

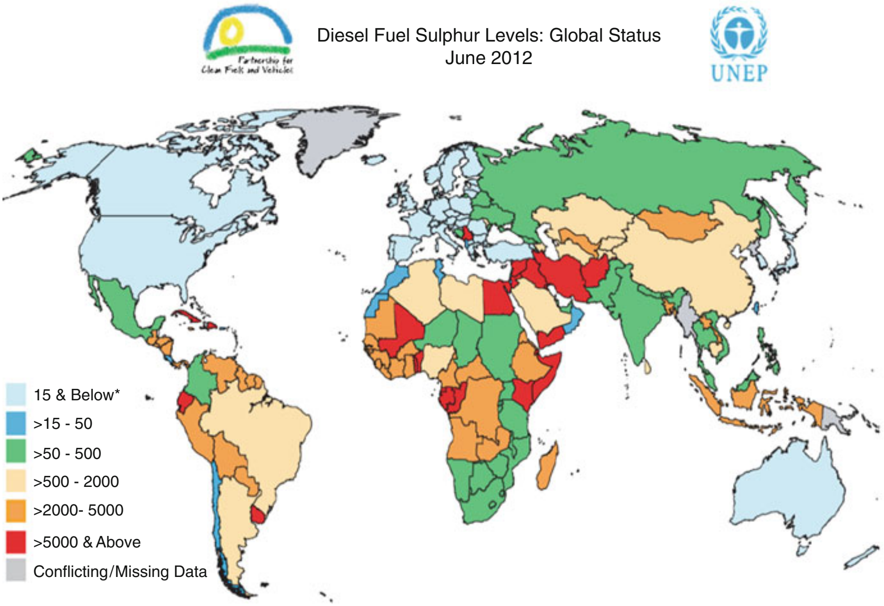
Hydrocracking technology reemerged in the 1950s with the growth of the transportation industries. In the mid-1950s, the automotive industry began to make high-performance cars with engines that required high-octane gasoline. This need caused a large expansion of the catalytic cracking industry to produce gasoline. But the by-products were large quantities of refractory cycle oils that were difficult to convert to gasoline and lighter products. Hydrocracking was able to convert these difficult by-products to desirable gasoline and diesel fractions and so was adopted in some refineries. Simultaneously, railroads switched from steam to diesel engines, and commercial aviation, using more jet fuel, began to emerge as a large industry. All three of these industries increased the demand for refined petroleum products. The flexibility of the newly developed hydrocracking processes allowed the production of fuels from heavier feedstocks.

In early 1960, Chevron Research Co. announced a new hydrocracking process called “Isocracking” (Stormont 1959). Unocal, then known as Union Oil Co., in collaboration with ESSO, introduced the hydrocracking process called “Unicracking-JHC” (Oil Gas J 1960). In the late 1950s, UOP announced the “Lomax” hydrocracking process (Sterba and Watkins 1960). By the mid-1960s, seven different hydrocracking processes were offered for license (Scott and Patterson 1967).

Presently, various environmental regulations stipulate a low level of sulfur and in some cases a low level of aromatics in both gasoline and diesel products; this has spurred a growth in a variety of hydroprocessing complexes around the world. In the United States, the Tier 2 gasoline sulfur program reduced the sulfur content of gasoline by up to 90 % from an uncontrolled level. An average sulfur level 30 ppm was phased in from 2004 to 2007. The final Tier 3 gasoline sulfur program lowers the sulfur level to 10 ppm. This level is planned but it has not yet been mandated (http://www.epa.gov/otaq/standards/fuels/gas-sulfur.htm). However, in Europe an essentially zero sulfur level is the specification, and in Japan, they are moving toward the 10 ppm S specification (http://transportpolicy.net/index.php?title=EU:_Fuels:_Diesel_and_Gasoline#Technical_Standards; http://transportpolicy.net/index.php?title=Japan:_Fuels:_Diesel_and_Gasoline). As the sulfur level required in gasoline and diesel reached low levels, a large growth in both hydrotreating and hydrocracking capacity grew in the world and is expected to continue to grow over the next decade (http://www.hydrocarbonpublishing.com). Even when a refiner in a certain area of the world does not need the stringent specification for their region, the process is designed for the stiffer requirement so that the refiners are able to export their products to any area of the world to improve their economics. Limitations have also been put on the sulfur levels that diesel may contain. As shown in Fig. 1, the level of sulfur in diesel is low in North America, Europe, Australia, and Japan and higher in other areas of the world (Akumu 2012).

Refiners have begun to use heavier sources of crudes to increase their margin on the refined products. One of the new sources is the synthetic crudes and bitumen blends from the Canadian tar sands. This denser, hydrogen-deficient VGO needs more upgrading than hydrogen-rich feeds. Shale deposits will produce a shale oil that will need extensive upgrading to meet the product demands; arsenic is a metal that is found in shale oils that is not commonly found in other typical petroleum fractions (Wier et al.). Today, there is a shift in desired product slate. In the past there was a higher demand for gasoline, especially in the United States as the engines for automobiles were of the gasoline type. In the world, there is less demand for gasoline and more demand for distillate fuel. This change in product distribution has helped spur the demand for flexible hydrocracking processes.

The early hydrocrackers used catalysts based on iron, nickel, or nickel-tungsten metal supported on alumina or amorphous silica-alumina. Zeolite components were



*Information inparts per million (ppm)

Sulpher levels are maximum allowable as of June 2012. For additional details and comments per country,visit WWW.unep.org/transport/pcfv.

Fig. 1 Global levels of sulfur in diesel fuel introduced to the catalysts during the rapid growth of hydrocracking technology during the 1960s. Zeolite-containing catalysts were significantly different than amorphous catalysts; zeolites had higher activity and gasoline selectivity and better ammonia tolerance (Baral and Huffman 1971; Bolton 1976). In the United States, hydrocracking was primarily used in the production of high-octane gasoline, but in the other parts of the world, it was used primarily for the production of middle distillates. Different catalyst formulations are selected depending on the product slate desired by the refiner.

Flow Schemes

Hydrocracking units can be configured in a number of ways. The unit can consist of one or two reactors with either one or multiple catalysts. The process can use one or two stages and be operated in once-through or recycle mode. The choice of the configuration depends on the feed properties and the specific product slate desired by the refiner. The five main types of operating units are mild, moderate/medium pressure, conventional, partial conversion, and resid hydrocracking. These are shown in Table 3.

Once-Through Configuration

Figures 1–3 show a schematic of a once-through hydrocracking unit, which is the simplest configuration for a unit. This configuration is a variation of the single-stage hydrocracking unit with recycle configuration. The feed mixes with hydrogen and goes to the reactor. The net reactor effluent goes to fractionation, with the unconverted oil being removed as the heaviest cut from the bottom of a fractionation column. This type of unit is the lowest cost hydrocracking unit and can process heavy, high-boiling feedstocks and produce high-value products including

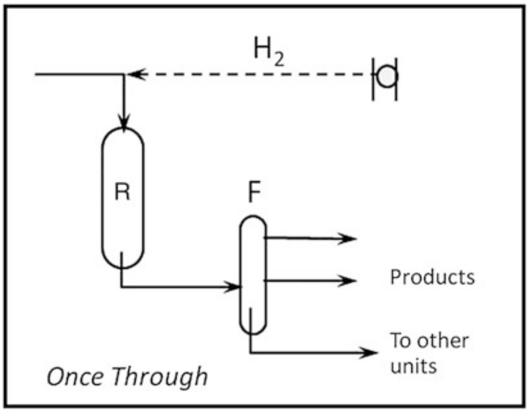
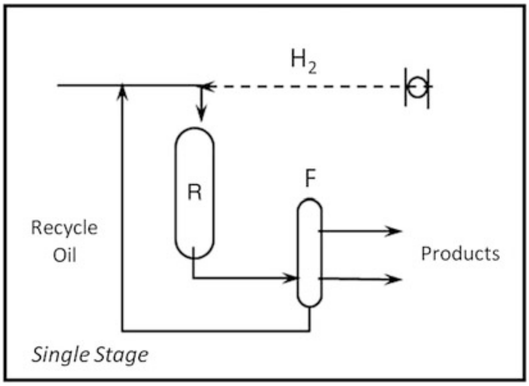


Fig. 2 Once-through hydrocracking unit

Fig. 3 Single-stage hydrocracking unit with recycle



unconverted materials which become feedstock for FCC units, ethylene plant, or lube oil units. In general, the conversion of the feedstock to products is 30–80 vol.%, but a range as high as 90 vol.% is possible with some feeds.

Single Stage with Recycle Hydrocracking

The most widely found hydrocracking unit is the single-stage configuration in which the recycled oil is sent back to the reactor section to maximize conversion at a reduced conversion per pass. Figure 3 depicts this type of unit. It is the most cost-effective design for 100 % conversion and is especially used to maximize the heaviest product cut such as diesel or jet fraction.

A more detailed flow diagram of the reactor section in a single-stage hydrocracking unit (than those shown in either Figs. 2 or 3) is shown in Fig. 4. The fresh feed is preheated to reaction temperature by passing it through heat exchangers and a heater and then passed downward through the catalyst bed in the presence of hydrogen. The effluent from the reactors goes through a series of separators where hydrogen is recovered and, together with makeup hydrogen, is recycled to the reactors. The liquid product is sent to fractionation where the final products are separated from the recycled oil and any unconverted oil. In once-through units, the unconverted oil is sent out of the unit, as previously described. In units designed to operate with recycle, the recycle oil combines with the fresh feed, as shown in Fig. 4.

As described in the Chemistry section (section "Chemistry"), the reaction section fulfills two functions: hydrotreating and hydrocracking. This is shown in Fig. 4 as separate reactors, though both functions can be achieved in a single reactor when using some types of catalysts, e.g., an amorphous catalyst. In most modern configurations, different catalysts are used for the hydrotreating and the hydrocracking sections; however, if both types of catalyst can be loaded in the same reactor, separate vessels are not needed. When using both pretreatment and

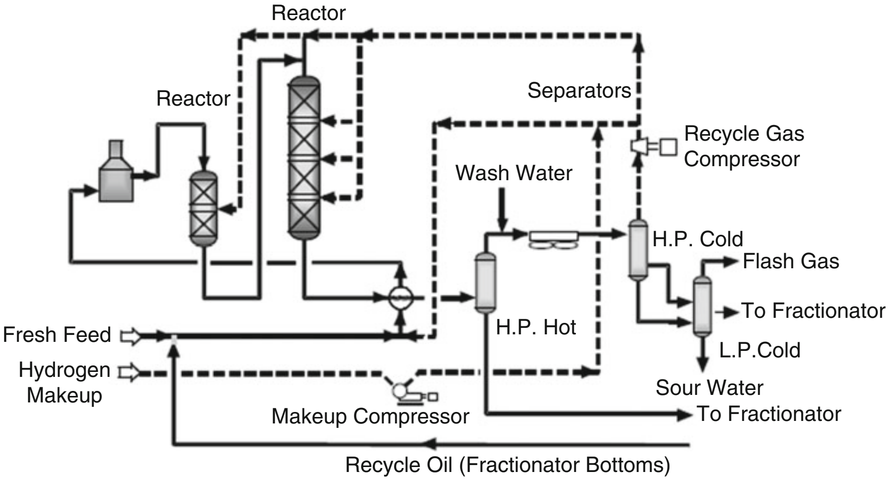


Fig. 4 Typical flow diagram of reactor section of single-stage hydrocracking unit

cracking configurations, the first catalyst (a hydrotreating catalyst) converts organic sulfur and nitrogen from hetero-compounds in the feedstock to hydrogen sulfide and ammonia, respectively. The deleterious effect of gas-phase H_2S and NH_3 on hydrocracking catalysts is considerably less than that of the corresponding organic hetero-compounds in the liquid phase. The hydrotreating catalyst also facilitates the hydrogenation of aromatics. In the single-stage configuration, the products from the hydrotreating reaction zone are passed over a hydrocracking catalyst where most of the hydrocracking takes place. The conversion occurs in the presence of NH_3, H_2S, and small amounts of unconverted amounts of hetero-compounds. The hydrotreating catalyst is designed to convert the hetero-compounds in the feedstock. Typically, such catalysts comprise sulfided molybdenum and nickel on an alumina support. The reactor operates at temperatures varying from 570 to 800 °F (300–425 °C) and hydrogen pressures between 1,250 and 2,500 psig (85–170 bar). Under these conditions, heteroatom elimination, significant hydrogenation, and some cracking also take place. The cracking catalyst operates at the same hydrogen pressures but at temperatures varying from 570 to as high as 840 °F (300–450 °C) for amorphous hydrocracking catalysts and up to 440 °C (825 °F) for zeolite-containing catalysts.

The effluent from the reactor is passed through high- and low-pressure separators, where hydrogen is recovered. The separated hydrogen combined with fresh hydrogen is recycled to the reactor. The liquid product is sent to fractionation where the final products are separated from the recycled oil and any unconverted oil. Fractionation produces the light ends (C_4^-) and liquid products. The liquid products are fractionated into the various product streams. Table 4 shows the product fractions and the application of the product.

Table 4 Product fractions and application of the product from the hydrocracking process

Fraction	Product	Use
Light gases, C_4^-	C_3, C_4	Fuel gas, feed for alkylation, recovered as LPG, petrochemical feedstock
Light naphtha	C_5-80 °C/ C_5-175 °F	Gasoline pool component, feed to isomerization unit
Heavy naphtha	80–150 °C/ 175–300 °F	Reformer feedstock to be converted in high-octane gasoline and hydrogen or aromatics for petrochemicals
Jet fuel/ kerosene	150–290 °C/ 300–550 °F	Fuel for turbine engines
Diesel fuel	290–370 °C/ 550–700 °F	Fuel for diesel engines
Unconverted oil	700 °F^+	Recycle feed or feedstock for lube plants or ethylene plants or FCC plants

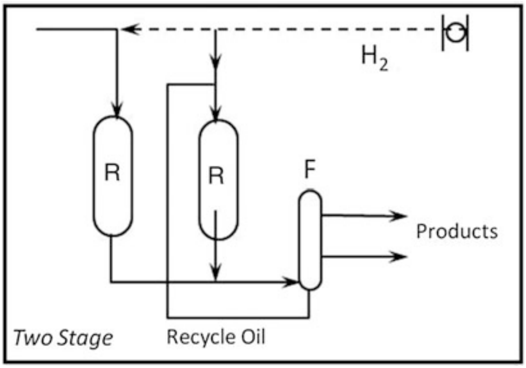


Fig. 5 Two-stage hydrocracking

Two-Stage Recycle Hydrocracking

The two-stage hydrocracking process configuration is also widely used, especially for high-capacity units. In two-stage units, the hydrotreating and some cracking take place in the first stage. The effluent from the first stage is separated and fractionated, with the unconverted oil passing to the second stage for further reaction. The reactor effluent from the second-stage reaction section goes back to the common fractionator. A simplified schematic of a two-stage hydrocracker is shown in Fig. 5. The catalysts in the first stage are the same types as those used in the single-stage configuration. The reaction environment in the second stage may contain ammonia or hydrogen sulfide depending on the unit design. If the recycle gas is scrubbed to low hydrogen sulfide levels, the environment in the second stage is considered “sweet”; if not then the second stage is “sour.” The catalyst in the second stage may be operating in the near absence of ammonia and hydrogen sulfide. Thus the catalysts used in the second stage need to be tailored for that reaction environment to maximize desired product selectivity.

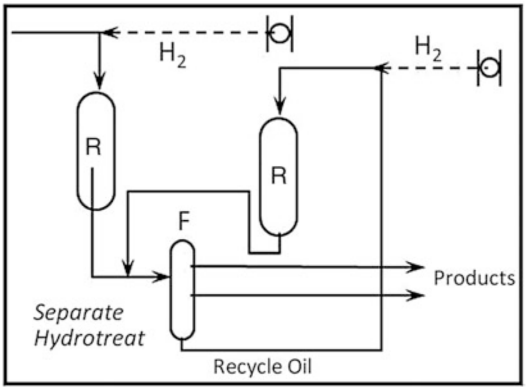


Fig. 6 Separate hydrotreating with two-stage hydrocracking

Separate Hydrotreating with Two-Stage Hydrocracking

A variation of the typical two-stage hydrocracking process occurs when the first stage does not contain hydrocracking catalyst in the first stage. Separate hydrotreating scheme uses common or separate hydrogen circulation loop. Figure 6 shows the flow scheme in which each stage has a separate hydrogen circulation loop, allowing for operation of the second stage in the near absence of hydrogen sulfide and ammonia.

Design and Operation of Hydrocracking Reactors

Hydrocracking reactors are run as downflow, fixed-bed catalytic reactors, generally operating in trickle-flow regime. The reactors are vessels with thick wall constructed from special materials due to the severity of the conditions during hydrocracking, high pressure and temperature, and the presence of hydrogen, ammonia, and hydrogen sulfide. The reactors are usually cylindrical vessels fabricated from 2 ¼ Cr-1 Mo or 3 Cr-1 Mo material with stabilized austenitic stainless steel weld overlay or liner, for added corrosion protection. More specialized materials, in which a small amount of vanadium is added to the 2 ¼ Cr-1 Mo or 3 Cr-1 Mo reactor base metal to increase its strength characteristics, have also been used. A typical drawing of a hydrocracking reactor is shown in Fig. 7.

The size of the hydrocracking reactors varies widely depending on the design conditions and is dependent on the desired mass flux for good flow distribution and acceptable pressure drops. Commercially, reactors with inside diameters of up to 20 f. (6.096 m) have been fabricated. Depending on the design pressure and inside diameter, the thickness of the reactor walls can be as much as 1 f. (30 cm). Since hydrotreating/hydrocracking reactions are exothermic, heat release is a common feature for all hydrocrackers; thus reactor temperature control has to be exercised. As shown schematically in Fig. 7, a hydrocracking reactor will contain several separate catalyst beds in order to manage heat release with quench in between the

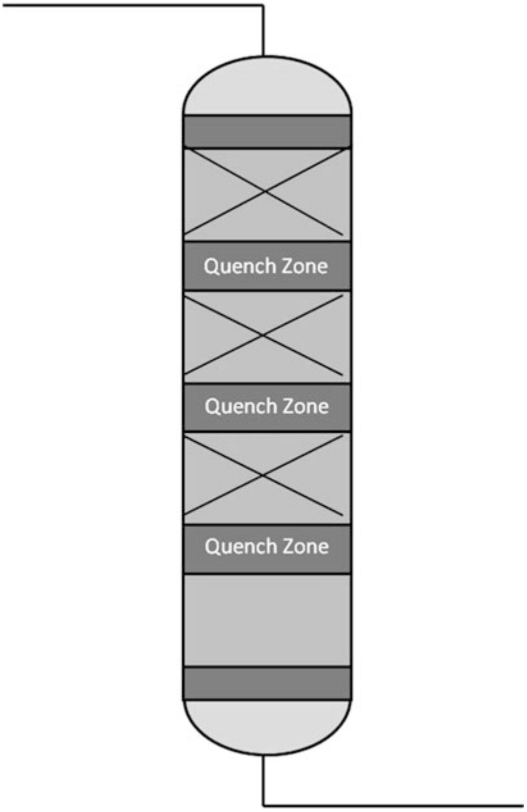


Fig. 7 Typical hydrocracking reactor

beds. The number of catalytic beds in a reactor and their respective lengths are determined for temperature rise profile and flow distribution. The maximum acceptable temperature rise per bed depends on the type of catalyst and operational safety criterion. The heat release is function of feed type, operating severity, and catalyst type. The maximum temperature that determines the end of run depends on the reactor metallurgy and design. A typical reactor operated to maximize conversion to naphtha will have as many as five or six beds. A typical reactor operated to produce middle distillate will have three or four beds. Commercial catalyst beds can be as deep as 30 f. (10 m). A typical hydrotreating reactor will have two or three beds if the feed is straight-run material and up to five beds if the feed contains appreciable amounts of cracked or aromatic material.

Since hydrocracking is an exothermic process, the fluids exiting one catalyst bed have to be cooled prior to entering the next catalyst bed in order to control reaction rate and allow a safe and stable operation. This is accomplished by injecting cool hydrogen for quench. Cold hydrogen gas, introduced in the quench zones, is used to control reactor temperature and improve hydrogen partial pressure. The quench zones which separate successive catalyst beds have the following functions:

- To cool the partially reacted fluids with hydrogen quench gas
- To assure a uniform temperature distribution of the fluids entering the next catalyst bed
- To mix efficiently and disperse evenly the fluids over the top of the next catalyst bed

Furthermore, the temperature distribution in the cooled fluids entering the next catalyst bed has to be uniform in order to minimize the radial temperature gradients in successive catalyst beds. Unbalanced temperatures in a catalyst bed could result in different reaction rates in the same bed. This can lead to different deactivation rates of the catalyst and, in worse cases, to temperature excursions.

It is also important to achieve a good mass flow distribution. The effective vapor/liquid mixing and uniform distribution of fluids over the top of the catalyst bed, accomplished in the quench zone, reestablishes an even mass flow distribution through the catalyst bed. Another important parameter is liquid flux (lb/h/ft^2 of cross-sectional area). While gas mass flux has practically no influence on liquid distribution, liquid mass flux is determinant in avoiding poor distribution in the catalyst bed. Operation at a liquid mass flux of more than 2,000 lb/h/ft^2 is recommended; operation at liquid fluxes lower than 1,500 lb/h/ft^2 is discouraged. Furthermore, if the liquid mass flux is below the recommended limit, increasing the gas mass flux may not improve the liquid distribution.

Hydrocracking Reactor Operation

During operation, the hydrocracking catalyst gradually loses its activity. In order to maintain constant conversion of feedstock to products, the average bed temperature is gradually increased. The temperature increase in many cases is very small, less than 2 °F/month (1 °C/month). When the average bed temperature reaches a value close to the design maximum, the catalyst has to be replaced or reactivated. Because the required temperature increase per unit time is relatively small, the reactor can be operated with the same catalyst for several years before replacement of the deactivated catalyst becomes necessary. Similar changes take place in the pretreating reactor.

The rates of reaction determine the key properties of a hydrocracking catalyst: initial activity, selectivity, stability, and product quality. The temperature required to obtain the desired product at the start of the run measures the initial activity. In general, the catalyst activity is a measure of the relative rate of feedstock conversion. In hydrocracking, activity is defined as the required temperature obtaining a fixed conversion under certain process conditions. Hydrocracking conversion is usually defined in terms of shifting molecules above a specified true boiling point (TBP) to products boiling below the same TBP, commonly referred to as a cut point:

$\%\text{Net Conversion} = \left(\left({\text{EP}^+}_{\text{feed}} - {\text{EP}^+}_{\text{product}}\right)/{\text{EP}^+}_{\text{feed}}\right) \times 100$ where EP^+ indicates the fraction of material in the feed or product boiling above the desired cut point.

Table 5 Chemical basis for product quality measurements

Desired product quality	Chemical basis
High smoke point	Low concentration of aromatics
Low pour point	Low concentration of *n*-paraffin
Low freeze point	Low concentration of *n*-paraffin
Low cloud point	Low concentration of *n*-paraffin
Low CFPP (cold flow pour point)	Low concentration of *n*-paraffin
High octane	High ratio of i-/*n*-paraffin
	High concentration of aromatics
Cetane number	Measure of hydrocarbon type
Cetane index	Estimate of cetane number based on distillation range and density

Catalyst selectivity is a measure of the rate of formation of a desired product relative to the rate of conversion of the feed (or formation of other products). Hydrocracking selectivity is expressed as the yield of desired product at a specific conversion. Yield is determined by the rate of formation of the desired product relative to the feed rate. At 100 % conversion, catalyst yield equals catalyst selectivity. Hydrocracking selectivity is affected by operating conditions. In general, more severe operating conditions cause higher selectivity to secondary products.

Catalyst stability is a measure of change of reaction rate over time. Hydrocrackers are typically operated in the constant conversion mode, with temperature adjustments made to maintain the desired conversion. Hydrocracking activity stability is defined as the temperature change per time required for maintaining constant conversion. Changes in product yield over time also occur. Hydrocracking yield stability is defined as the yield change with time at constant conversion and is usually expressed as a function of temperature.

The product quality is a measure of the ability of the process to yield products with the desired use specification such as pour point, smoke point, or octane. Table 5 shows some of the important product quality measurements and the chemical basis for these measurements.

Chemistry

The chemistry of hydrotreating and hydrocracking is commonly taken together and termed hydroprocessing and is similar for both sections of the hydroprocessing unit. There is not a clear distinction between the hydrotreating and hydrocracking chemistries because there is some hydrocracking that occurs in the hydrotreating reactor especially when high temperatures are used, either at the end of the cycle or when low sulfur in the product is the target. Hydrotreating converts the S heteroatom in organic sulfur-containing compounds to H_2S, the N heteroatom in

Table 6 List of the hydroprocessing reactions

Reaction type	Reaction
Minimal C–C bond breaking	
Hydrodesulfurization (HDS)	$R\text{-}S\text{-}R^* + 2H_2 \rightarrow RH + R^*H + H_2S$
Hydrodenitrogenation (HDN)	$R{=}N\text{-}R^* + 3H_2 \rightarrow RH + R^*H + NH_3$
Hydrodeoxygenation (HDO)	$R\text{-}O\text{-}R^* + 2H_2 \rightarrow RH + R^*H + H_2O$
Hydrodemetallation (HDM)	$R\text{-}M + \frac{1}{2} H_2 + A \rightarrow RH + MA$
Saturation of aromatics	$C_{10}H_8 + 2H_2 \rightarrow C_{10}H_{12}$
Saturation of olefins	$R{=}R^* + H_2 \rightarrow HR\text{-}R^*H$
Isomerization	$n\text{-RH} \rightarrow \text{i-RH}$
Significant C–C bond breaking	
Dealkylation of aromatic rings	$\Theta\text{-}CH_2R + H_2 \rightarrow \Theta\text{-}CH_3 + HR$
Opening of naphthene rings	$\text{Cyclo-}C_6H_{12} \rightarrow C_6H_{14}$
Hydrocracking of paraffins	$R\text{-} R^* + H_2 \rightarrow RH + R^*H$
Other reactions	
Coke formation	$2\ \Theta\text{-}H \rightarrow \Theta\text{–}\Theta + 2H_2$
Mercaptan formation	$R{=}R^* + H_2S \rightarrow HSR\text{-}R^*H$

From Springer Fundamentals of Hydrocracking
Θ aromatic, *R, R** alkyl, *M* Fe, Ni, or V, *A* metal-adsorbing material

nitrogen-containing compounds is converted to NH_3, and if present the O heteroatom in oxygen-containing compounds is converted into H_2O. Hydrocracking converts the higher carbon number feed molecules to lower molecular weight products by cracking the side chains and by saturating the aromatics and olefins. Hydrocracking catalysts will also remove any residual sulfur and nitrogen which remain after the hydrotreating, usually in the heavy molecular weight compounds. Table 6 is a list of the hydroprocessing reactions. The evolution of the reaction profile between the hydrotreating reactor and the hydrocracking reactor is shown in Figs. 8, 9, and 10.

There are two types of reactions taking place in hydroprocessing units: impurity removal (also called pretreating or hydrotreating) and cracking (also called hydrocracking). The conversions in hydroprocessing can be classified into desirable and undesirable reactions. The desirable reactions are desulfurization and denitrogenation, saturation (i.e., hydrogen addition to olefin and aromatic molecules), and cracking (i.e., reaction of side chains to reduce the molecular weight). Undesirable reactions are contaminant poisoning (metals deactivating the catalyst) as well as coking of the catalyst.

Hydrotreating Reactions

The hydrotreating reactions that take place are the removal of sulfur, nitrogen, organometallic compounds, oxygen, and halide. Olefin and aromatic saturation will also occur. Sulfur, nitrogen, and metals are almost always present in any type of feed, and the levels depend on the crude source and/or the conversion unit that

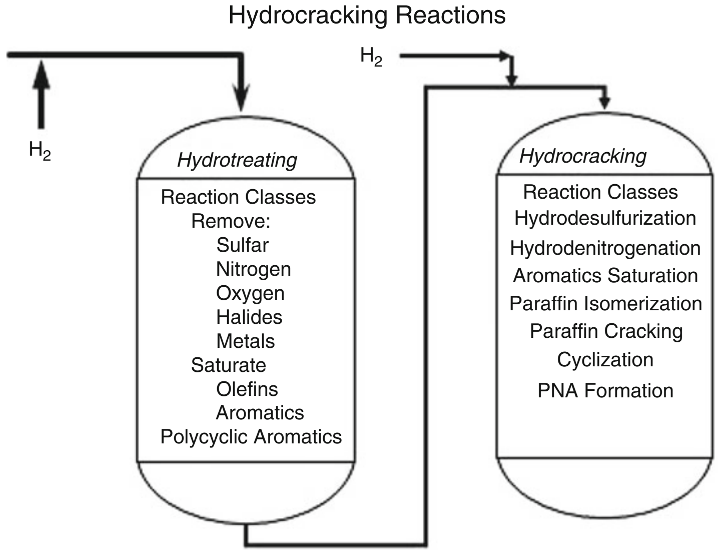


Fig. 8 Summary of hydroprocessing reaction classes in the sections of the hydrotreating and hydrocracking reactors

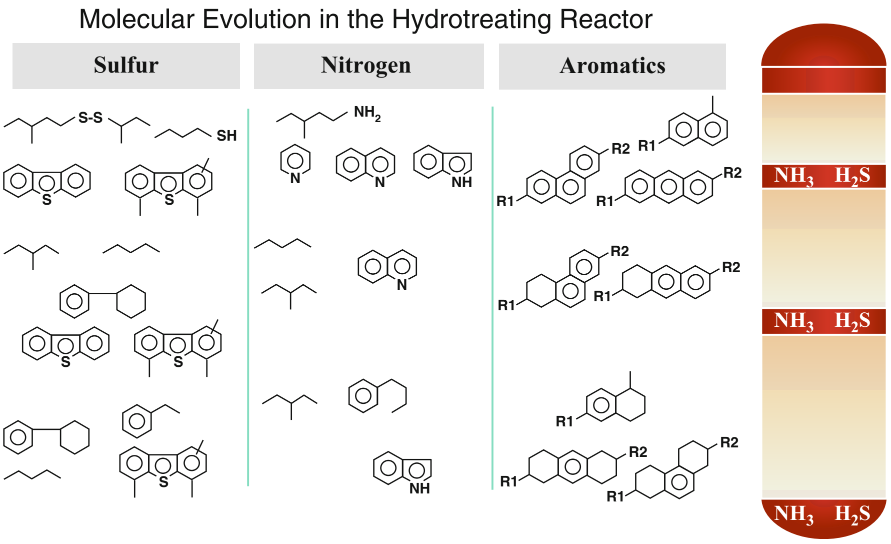


Fig. 9 Evolution of the reactions in the hydrotreating reactor

produces an additional feedstock apart from the crude unit, such as a delayed coking unit, FCC unit, and the like. Oxygen and halides are not always present. The hydrotreating reactions proceed in the following order: metal removal, olefin saturation, sulfur removal, nitrogen removal, oxygen removal, halide removal,

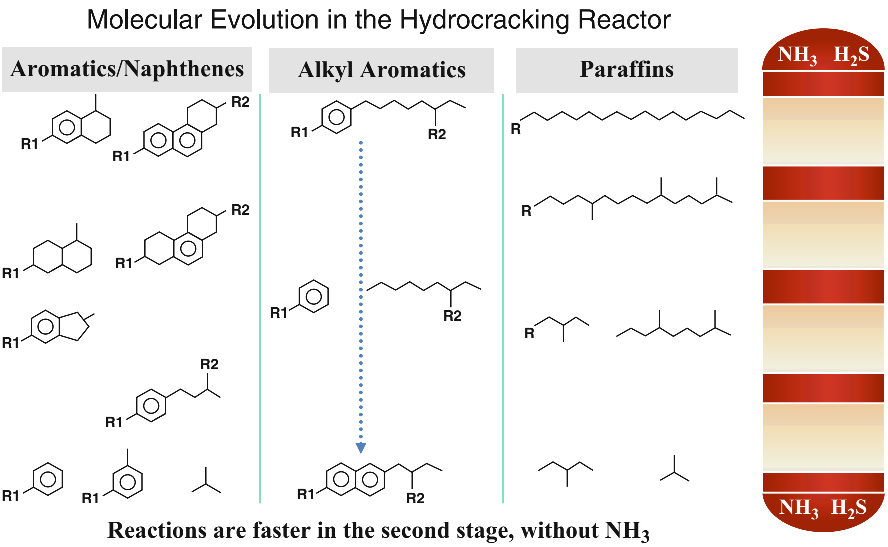


Fig. 10 Evolution of the reactions in the hydrocracking reactor

and aromatic saturation. Figure 9 shows the evolution of the reactions in the hydrotreating reactor. Hydrogen is consumed in all of the treating reactions. As a guideline, the desulfurization reactions consume 100–150 SCFB/wt% S change (17–25 Nm^3/m^3/wt% change), and denitrogenation reactions consume 200–350 SCFB/wt% N change (34–59 Nm^3/m^3/wt% change). Typically the heat release in the hydrotreating section is about 0.1–0.2 °F/SCFB H_2.

Hydrocracking Reactions

Hydrocracking reactions proceed through a bifunctional mechanism (Mills et al. 1953; Weisz 1962; Sinfeld 1964, 1983). Two distinct types of catalytic sites are required to catalyze the separate steps in the reaction sequence. The acid function provides for cracking and isomerization, and the metal function provides for olefin formation and hydrogenation. The cracking reaction requires heat, while the hydrogenation reaction generates heat. Figure 10 shows the evolution of the reactions in the hydrocracking reactor. Overall, there is a heat release during hydrocracking reactions; the heat release is a function of the hydrogen consumption, where higher hydrogen consumption will generate a larger temperature increase. Generally, the hydrogen consumption in hydrocracking is 1,200–2,400 SCFB (200–420 Nm^3/m^3), resulting in a typical heat release of 50–100 Btu/SCFB H_2 (2.1–4.2 kcal/m^3 H_2) which translates into a temperature increase of about 0.1–0.2 °F/SCFB. This amount includes the heat release generated in the hydrotreating section.

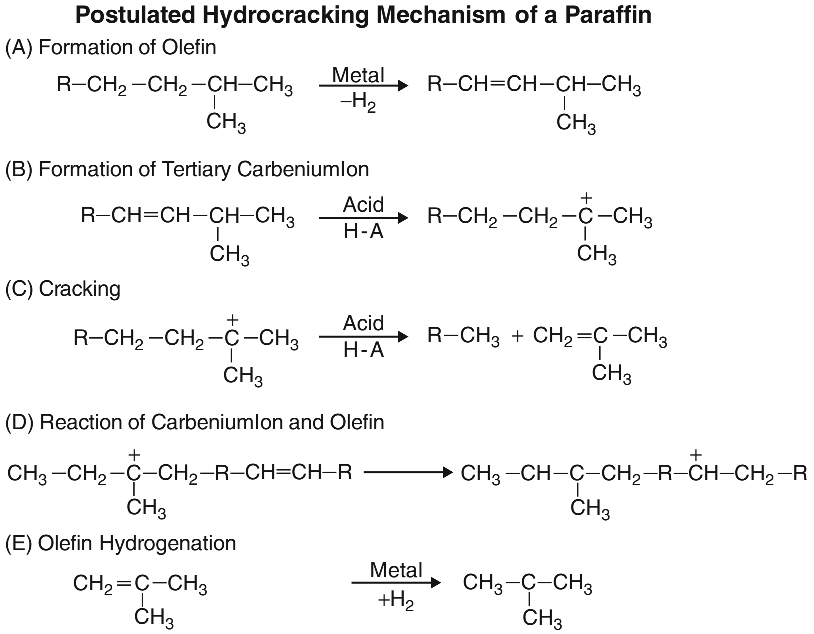


Fig. 11 Steps involved in the hydrocracking of paraffin molecules

In general, the hydrocracking reaction starts with the generation of an olefin or a cycloolefin on a metal site on the catalyst. Next, an acid site adds a proton to the olefin or cycloolefin to produce a carbenium ion. The carbenium ion cracks to a smaller carbenium ion and a smaller olefin. These are the primary hydrocracking products. These primary products can react further to produce still smaller secondary hydrocracking products. The reaction sequence can be terminated at primary products by abstracting a proton from the carbenium ion to form an olefin at an acid site and by saturating the olefin at a metal site. Figure 11 illustrates the specific steps involved in the hydrocracking of paraffins. The carbenium ion typically isomerizes to form a more stable tertiary carbenium ion. Next, the cracking reaction occurs at a bond that is beta to the carbenium ion charge. The beta position is the second bond from the ionic charge. Carbenium ions can react with olefins to transfer charge from one fragment to the other. In this way, charge can be transferred from a smaller hydrocarbon fragment to a larger fragment that can better accommodate the charge. Finally, olefin hydrogenation completes the mechanism.

The hydrocracking mechanism is selective for cracking of higher carbon number paraffins. This selectivity is due in part to a more favorable equilibrium for the formation of higher carbon number olefins. In addition, large paraffins adsorb more strongly. The carbenium ion intermediate results in extensive isomerization of the products, especially to a-methyl isomers, because tertiary carbenium ions are more stable. Finally, the production of C_1 to C_3 is low because the production of these light gases involves the unfavorable formation of primary and secondary carbenium

Table 7 Thermodynamics of major reactions in hydrocracking

Reaction	Equilibrium	Heat of reaction
Aromatic saturation	Unfavorable at high temperature	Exothermic
Hydrocracking	Favorable	Exothermic
HDS	Favorable	Exothermic
HDN	Favorable	Exothermic

ions. Other molecular species such as alkyl naphthenes, alkyl aromatics, and so on react via similar mechanisms, e.g., via the carbenium ion mechanism.

In summary, hydrocracking occurs through a bifunctional mechanism that involves olefin dehydrogenation-hydrogenation reactions on a metal site, carbenium ion formation on an acid site, and isomerization and cracking of the carbenium ion. The hydrocracking reactions tend to favor conversion of large molecules because the equilibrium for olefin formation is more favorable for large molecules and because the relative strength of adsorption is greater for large molecules. In hydrocracking, the products are highly isomerized, C_1 and C_3 formation is low, and single rings are relatively stable.

In addition to treating and hydrocracking, several other important reactions take place in hydrocrackers. These are aromatic saturation, polynuclear aromatics (PNA) formation, and coke formation. Some aromatic saturation occurs in the treating section and some in the cracking section. Aromatic saturation is the only reaction in hydrocracking that is equilibrium limited at the higher temperatures reached toward the end of the catalyst cycle life. Because of this equilibrium limitation, complete aromatic saturation is not when reactor temperature is increased to make up for the activity loss due to coke formation and deposition. Table 7 shows the thermodynamics of the major reactions taking place in a hydrocracker. In general, the thermodynamic equilibrium for hydrocracking is favorable. Cracking reactions, desulfurization, and denitrogenation are favored at the typical hydrocracker operating conditions. The initial step which generates an olefin or cycloolefins is unfavorable under the high hydrogen partial pressure used in hydrocracking. The dehydrogenation of the smaller alkanes is most unfavorable. Nevertheless, the concentration of olefins and cycloolefins is sufficiently high, and the conversion of these intermediates to carbenium ions is sufficiently fast so that the overall hydrocracking rate is not limited by the equilibrium olefin levels.

Polynuclear aromatics (PNA), sometimes called polycyclic aromatics (PCA), or poly-aromatic hydrocarbons (PAH) are compounds containing at least two benzene rings in the molecule. Normally, the feed to a hydrocracker can contain PNA with up to seven benzene rings in the molecule. The PNA formation is an important, though undesirable, reaction that occurs in hydrocrackers. Figure 12 shows the competing pathways for conversion of multi-ring aromatics. One pathway starts with metal-catalyzed ring saturation and continues with acid-catalyzed cracking reactions. The other pathway begins with an acid-catalyzed condensation reaction to form a multi-ring aromatic-ring compound. This molecule may undergo subsequent condensation reactions to form a large PNA.

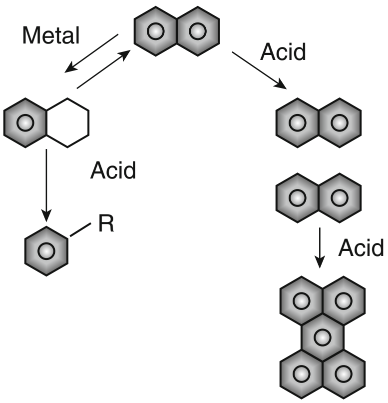


Fig. 12 Possible pathways for multi-ring aromatics

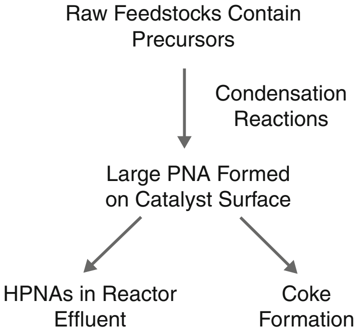


Fig. 13 HPNA formation

The consequence of operating hydrocracking units with recycled oil is the creation of large PNA molecules that can contain more than seven aromatic rings in the molecule. These are called heavy polynuclear aromatics (HPNA) whose formation is shown in Fig. 13. The HPNA produced on the catalyst may exit the reactor and cause downstream equipment fouling, or they may deposit on the catalyst and form coke, which deactivates the catalyst. Their presence results in plugging of equipment. For HPNA mitigation, a stream of 5–10 % of the unconverted material might have to be taken out of the hydrocracker, resulting in much lower than desired conversion of the feed. There is also an option available of adsorbing the HPNA materials on a bed of adsorbent, which reduces the amount of unconverted oil that is needed in the unit.

Catalysts

As stated earlier, hydrocracking catalysts are dual functional (Mills et al. 1953; Weisz 1962; Sinfeld 1964, 1983). Both metallic and acidic sites must be present on the catalyst surface for the cracking reactions to occur as well as some of the other reactions such as hydroisomerization and dehydrocyclization.

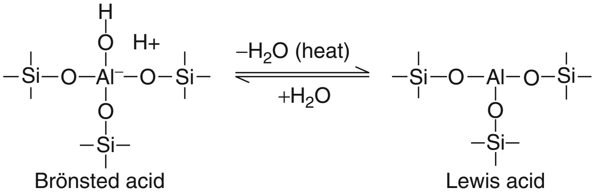


Fig. 14 Silica-alumina acid sites

The metals providing the hydrogenation function can be noble metals (palladium, platinum) or non-noble (also called "base") metal sulfides from group VIA (molybdenum, tungsten) and group VIIIA (cobalt, nickel). As previously discussed, these metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal, as well as reducing the coking rate. They also initiate the cracking by forming a reactive olefin intermediate via dehydrogenation. The ratio between the catalyst's cracking function and hydrogenation function can be adjusted in order to optimize activity and selectivity. For a hydrocracking catalyst to be effective, it is important that there be a rapid molecular transfer between the acid sites and hydrogenation sites in order to avoid undesirable secondary reactions. Rapid molecular transfer can be achieved by having the hydrogenation sites located in the proximity of the cracking (acid) sites.

Acid Function of the Catalyst

Cracking and isomerization reactions take place on the acidic support. Amorphous silica-alumina (ASA) provides the cracking function of amorphous catalysts and serves as support for the hydrogenation metals. Sometimes, ASA catalysts or a combination of ASA and zeolite can be used to produce high-yield distillate hydrocracking catalysts. Amorphous silica-alumina also plays a catalytic role in low-zeolite catalysts. Zeolites particularly Y and beta are commonly used in high-activity distillate-selective catalysts and in hydrocracking catalysts for the production of naphtha. Other acidic support components such as acid-treated clays, pillared clays, layered silicates, acid metal phosphates, and other solid acids have been tried in the past; however, present-day hydrocracking catalysts do not contain any of these materials.

Amorphous mixed-metal oxide supports are acidic because of the difference in charge between adjacent cations in the oxide structure. The advantages of ASA for hydrocracking are their large pores, which permit access of bulky feedstock molecules to the acidic sites, and moderate activity, which makes the metal-acid balance needed for distillate selectivity easier to obtain. Figure 14 is an illustration of silica-alumina acid sites. The substitution of an Al^{+3} cation for a Si^{+4} cation must be balanced by either a cation or by an acidic proton. The removal of water from this Brønsted acid site creates a Lewis acid site. A Brønsted acid site on a catalyst is an acid site where the acidic entity is a protonated hydrogen atom. A Lewis acid site on a catalyst is an acid site where the acidic entity is a positive ion such as Al^{+3} that can accept an electron pair, rather than a protonated hydrogen. Although plausible hydrocracking mechanisms can be written for both Brønsted and Lewis sites, Brønsted acidity is believed to be more desirable because Lewis acid sites may catalyze coke formation.

Zeolites began to be used in hydrocracking catalysts because they provided high activity due to their higher acidity compared to the ASA materials. Zeolites are crystalline aluminosilicates composed of Al_2O_3 and SiO_2 tetrahedral units that form a negatively charged microporous framework structure enclosing cavities occupied by large ions and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. The silicon and aluminum atoms are tetrahedrally coordinated with each other through shared oxygen atoms. Compositionally zeolites are similar to clay minerals as they are both aluminosilicates, but zeolites are crystalline and clays are not. If the mobile cations are exchanged with NH_4^+ (*ammonium ion*), followed by calcination to remove NH_3, a Brønsted acid site is formed. With the right modification, zeolites can be tuned to provide similar yields of the desired products as ASA materials at higher activity. Mobile cations, which are not part of the framework but are part of the zeolites, are readily exchanged.

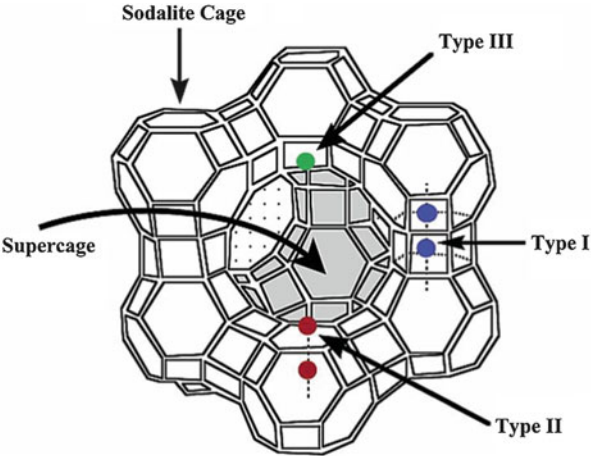
Both Brønsted and Lewis acids are possible in zeolites. The number of acid sites and the strength of the acid sites can be varied in various synthesis steps. These sites are highly uniform, but each zeolite may have more than one type of site. The following factors influence the number and strength of acid sites in zeolites:

- The types of cations occupying the ion exchange sites
- Thermal treatments of the zeolite
- The framework silica to alumina ratio in the zeolite

For example, Y zeolite can be treated to modify the Si/Al ratio; common methods to accomplish this are either a thermal or a hydrothermal treatment. In Fig. 16 is an image after hydrothermal treatment of stabilized Y zeolite. When aluminum is removed, the effect is to decrease the total number of acid sites, because each proton is associated with framework alumina. As can be seen in Fig. 16, there is also a generation of mesoporosity in the zeolite. However, the reduction of the alumina sites increases the strength of the remaining acid sites in the zeolite. As a result, the total acidity of the zeolite, which is a product of the number of sites and strength per site, peaks at an intermediate extent of dealumination. The crystallinity of the zeolite can also be modified depending on the treatment history. The acid site concentration and strength of the zeolite will affect the final hydrocracking catalyst properties. The principal advantage of zeolites for hydrocracking is their high acidity.

One zeolite used in hydrocracking, Y zeolite, is synthetic (Fig. 15). It has a structure nearly identical to the naturally found zeolite faujasite (Baerlocher and McCusker). The Y zeolite has both a relatively large free aperture, which controls access of reactants to acid sites, and a three-dimensional pore structure, which allows diffusion of the reactants in and products out with minimal interference. The

Fig. 15 Y zeolite



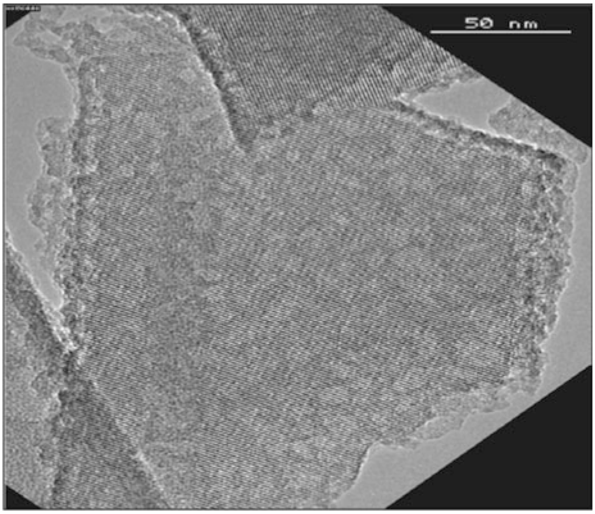


Fig. 16 Stabilized Y after hydrothermal treatment

structure of zeolite, beta, which is used in some hydrocracking catalysts is shown in Fig. 17 (Baerlocher and McCusker). Beta zeolite is another zeolite with a 12-ring structure, similar to faujasite; it also has a three-dimensional structure. The diffusion path length is smaller for beta than for faujasite.

Catalyst Manufacturing

Hydrocracking catalysts can be manufactured by a variety of methods. The method chosen usually represents a balance between manufacturing cost and the degree to which the desired chemical and physical properties are achieved. Although there is a relationship between catalyst formulation, preparation procedure, and catalyst

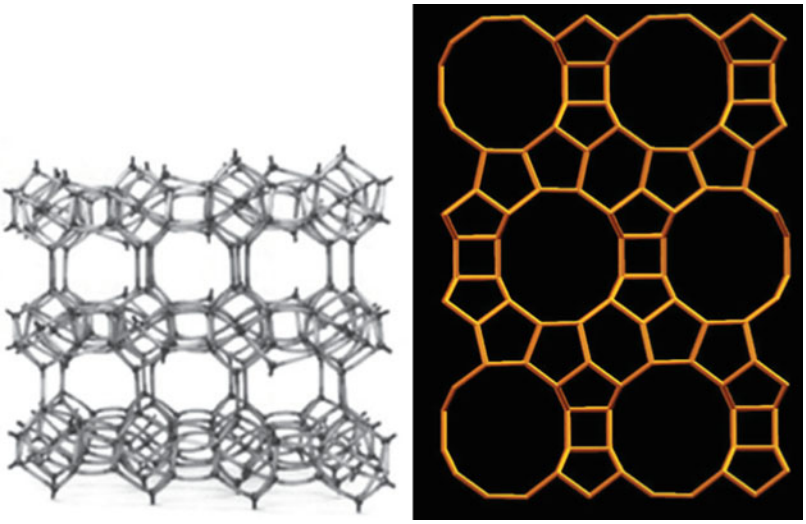


Fig. 17 Beta zeolite

properties, the details of that relationship are not always well understood due to the complex nature of the catalyst systems. The chemical composition of the catalyst plays a critical role in its performance; the physical and mechanical properties also play a major role. The preparation of hydrocracking catalysts involves several steps: precipitation, filtration (decantation, centrifugation), washing, drying, forming, calcination, and impregnation. Other steps, such as kneading or mulling, grinding, and sieving, may also be required. Depending on the preparation method used, some of these steps may be eliminated, whereas other steps may be added. For example, kneading or co-mulling of the wet solid precursors is used in some processes instead of precipitation. When the metal precursors are precipitated or co-mulled together with the support precursors, the impregnation step can be eliminated. Described below are the steps that are an integral part of any hydrocracking catalyst manufacturing process.

Precipitation

Precipitation involves the mixing of solutions or suspension of materials, resulting in the formation of a precipitate, which may be crystalline or amorphous. Mulling or kneading of wet solid materials usually leads to the formation of dough that is subsequently formed and dried. The mulled or kneaded product is subjected to thermal treatment in order to obtain a more intimate contact between components and better homogeneity by thermal diffusion and solid-state reactions. Precipitation or mulling is often used to prepare the support for the catalyst, and the metal component is subsequently added by impregnation or incipient wetting methods.

The support characteristics determine the mechanical properties of the catalyst, such as attrition resistance, hardness, and crushing strength. High surface area and

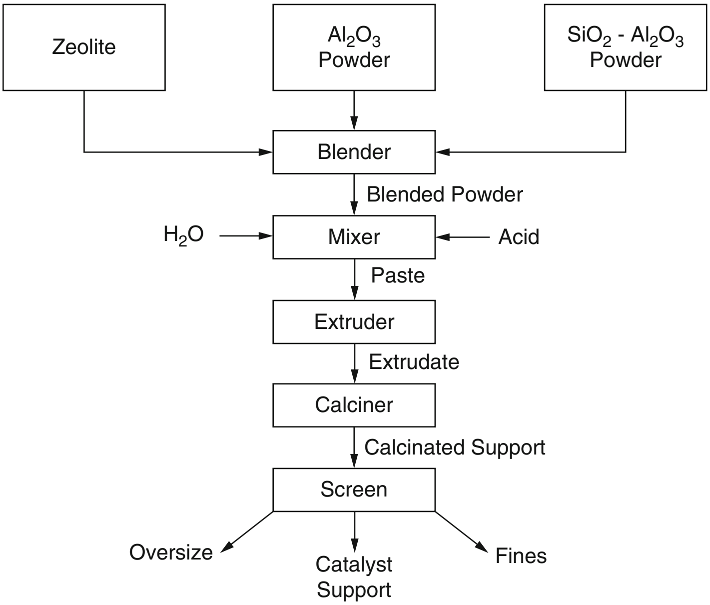


Fig. 18 Extrudate catalyst support manufacturing

proper pore-size distribution are generally required. The pore-size distribution and other physical properties of a catalyst support prepared by precipitation are also affected by the precipitation and the aging conditions of the precipitate as well as by subsequent drying, forming, and calcining.

Forming

The final shape and size of catalyst particles are determined in the manufacturing step. Catalysts and catalyst supports are formed into several possible shapes such as spheres, cylindrical extrudates, or shaped forms such as a trilobe or a quadrilobe. Spherical catalyst support catalyst can be obtained by “oil dropping,” whereby precipitation occurs upon the pouring of a liquid into a second immiscible liquid. Other spherical processes include marmurizing. Generally, because of cost and process considerations such as pressure drop, the majority of catalysts are currently formed in shapes other than spheres. Fewer spherical catalysts are used in modern hydrocracking. Non spherical shapes are obtained by mixing raw materials to form a dough. The dough is then extruded through a die with perforations. The spaghettilike form is then dried, calcined, and broken into short pieces. The typical length to diameter ratio of the catalyst base varies between 2 and 4. Figure 18 shows a typical extrudate support manufacturing.

The shapes of the base produced is varied. The simplest form is cylindrical, but other forms such as trilobes, twisted trilobes, or quadrilobes are also found commercially. Catalysts with multilobed cross sections have a higher surface-to-volume

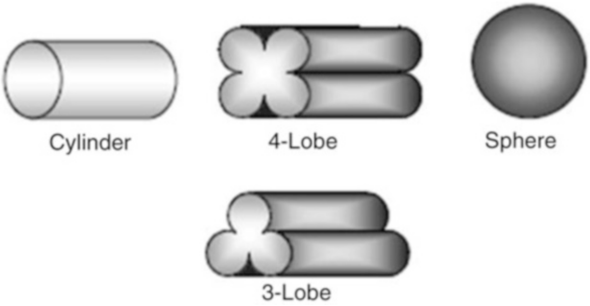


Fig. 19 Commercial catalyst shapes

ratio than simple cylindrical extrudates. When used in a fixed bed, these shaped catalyst particles help reduce diffusion resistance, create a more open bed, and reduce pressure drop. Figure 19 depicts several shapes of commercial catalysts used in hydrocracking.

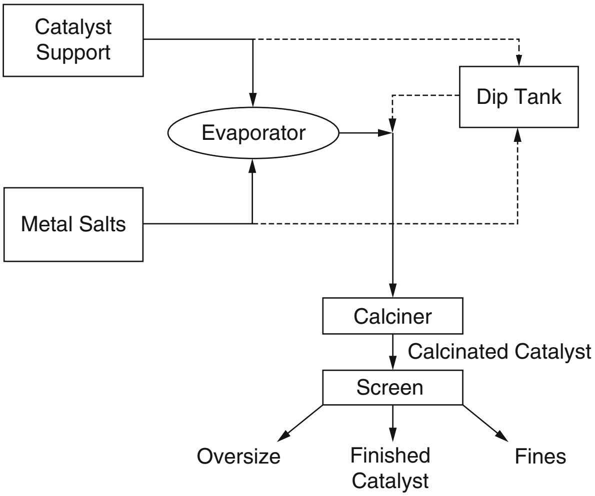
Drying and Calcining

Thermal treatment is applied either before and/or after impregnation of the formed catalyst. For catalysts prepared by precipitation or co-mulling of all the components (including the metal components), only drying may be required prior to forming, with subsequent calcination of the formed product. Thermal treatment of the catalyst or support eliminates water and other volatile matter. The drying and calcination conditions are of critical importance in determining the physical as well as catalytic properties of the product. Surface area, pore-size distribution, stability, attrition resistance, crush strength, and the catalytic activity are affected by the drying and calcination conditions.

Impregnation

Several methods may be used to add the active metals to the base: (a) immersion (dipping), (b) incipient wetness, and (c) evaporative. In the first method, which is the most commonly used, the calcined support is immersed in an excess of solution containing the metal compound. The solution fills the pores and is also adsorbed on the support surface. The excess solution volume is then drained off. Impregnation using incipient wetness is carried out by tumbling or spraying the activated support with a volume of solution having the concentration of metal compound proportioned to get the targeted metal level, and equal to or slightly less than the pore volume of the support. The metal-loaded support is then dried and calcined. Metal oxides are formed in the process; the calcination step is also called oxidation. In evaporative impregnation, the support is saturated with water or with acid solution and immersed into the aqueous solution containing the metal compound. That compound subsequently diffuses into the pores of the support through the aqueous phase. Figure 20 shows an example of catalyst finishing (impregnation).

Fig. 20 Example of metal loading the catalyst base

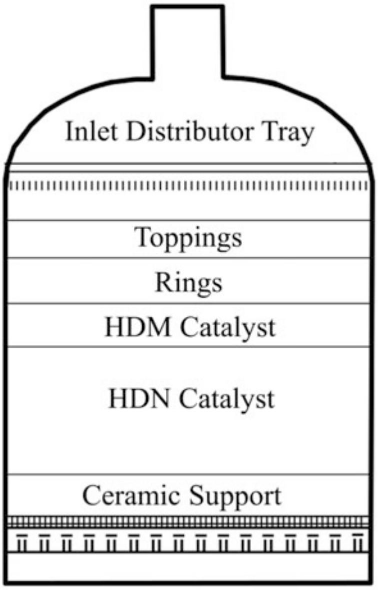


Catalyst Loading (Reactor) and Activation of the Catalyst

Catalyst Loading into Reactor

There are two methods of catalyst loading, sock loading and dense loading. Sock loading is done by pouring the catalyst into a hopper mounted on top of the reactor and then allowing it to flow through a canvas sock into the reactor. Dense loading or dense bed packing is done with the help of a mechanical device. The dense loading method was introduced in the mid-1970s. Catalyst loaded by sock loading will have a higher void fraction than catalyst that was dense loaded. Dense bed packing and the resulting higher-pressure drop provide a more even distribution of liquid in a trickle-flow reactor. Most distillate hydrocrackers are in the trickle-flow regime. If diffusion limitations are negligible, dense loading is desirable in order to maximize the catalyst mass per volume of the reactor and, thus, the reaction rate per unit reactor volume. Another advantage of dense loading is that it orients the catalyst particles in a horizontal and uniform manner. This improves the vapor/liquid distribution through the catalyst beds. Catalyst particle orientation is important especially for cylindrically shaped extruded catalyst in vapor/liquid reactant systems. When the catalyst particles are oriented in a horizontal position in the catalyst bed, liquid channeling is almost completely eliminated. Poor liquid distribution tends to occur when the catalyst loading is done by the sock loading method, which generally causes the extrudates to be oriented in a downward slant toward the reactor walls, increasing bed voids and creating poor liquid distribution. Of all the factors influencing catalyst utilization, catalyst loading has generally proven to be a very important factor. Except for the hydrocrackers that have reactor pressure drop limitations mainly due to operation at higher than design throughputs, the great majority of units worldwide are dense loaded.

Fig. 21 Example of the graded bed



Today catalysts are most commonly loaded in a particular sequence so that the overall reactor can run most efficiently. The reactor loading is done in a way to protect the hydrotreating and hydrocracking catalysts. After the inlet distributor tray, a catalyst bed is loaded that will remove particulates and has been formulated to trap the metals and particulate that are present in the feed. This method of loading is called an activity and particle size-graduated loading or “graded bed” and is depicted in Fig. 21. The graded bed materials are large and an example of graded bed materials is shown in Fig. 22.

Catalyst Activation

Base metal hydrocracking catalysts have to be prepared in the final state through a sulfiding procedure in order to create the active species, the metal sulfides. Several names are used for this treatment, such as sulfiding, pre-sulfiding, and pre-sulfurizing in addition to the term activation. The metals on the greatest majority of catalysts are in an oxide form at the completion of the manufacturing process.

The noble metal catalysts are activated by hydrogen reduction of the finished catalyst, in which the metal is also in an oxide form. Calcination in air prior to reduction is necessary to avoid metal sintering. The presence of water vapors is generally avoided, also to prevent metal sintering. By using an excess of hydrogen, the water formed during reduction can be swept away. The activation of noble metal catalysts by hydrogen reduction occurs at 570–750 °F (300–400 °C).

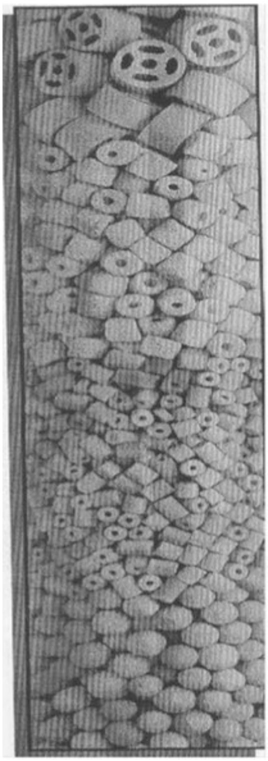


Fig. 22 Images of graded bed catalysts

The active phase is similar for the CoMo or NiMo supported on Al_2O_3 or SiO_2 and by analogy Ni/W on the more complex hydrocracking catalyst (Topsoe et al. 1996). These consist of Co or Ni atoms on the edges of MoS2 slabs and are referred to as CoMoS and NiMoS phases, and by analogy NiWS phase. W and Mo exhibit different behavior with respect to sulfidation. Ni/W is more difficult to sulfide than Ni/Mo, i.e., requires higher temperature. The presence of the Ni enhances the sulfidation of either Ni or Mo. The slabs of Mo or S have a specific length and appear as strands with different levels of stacking. An image (Bricker et al. 2012) of Ni/W in a hydrocracking catalyst is shown in Fig. 23. In this figure the individual atoms of W can be seen.

The non-noble (base metal) catalysts are activated by transforming the catalytically inactive metal oxides into active metal sulfides. This is accomplished mainly in situ though some refiners have started to do the activation outside the unit (ex situ). More and more refiners will opt to receive the catalyst at the refinery site in pre-sulfided state to accelerate the start-up of the unit. In situ sulfiding can be accomplished either in vapor or liquid phase. In vapor phase sulfiding, the activation of the catalyst is accomplished by injecting a chemical which easily decomposes to H_2S, such as dimethyl disulfide (DMDS) or dimethyl sulfide (DMS). The use of H_2S was fairly common until a few years ago, but now it is only rarely used

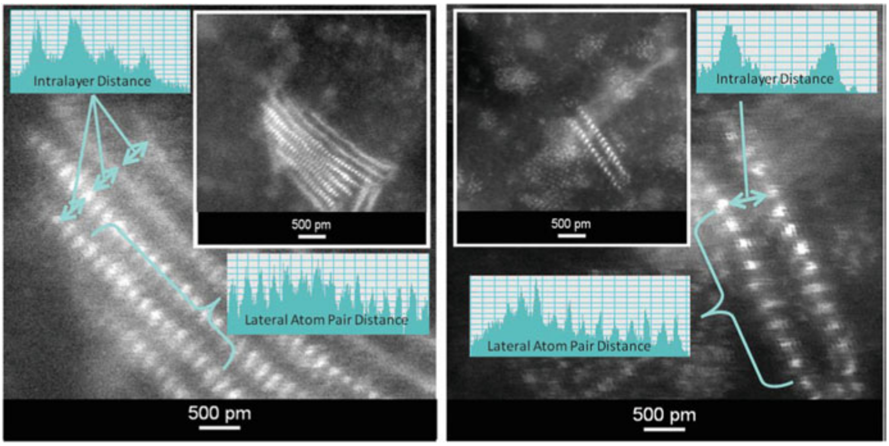


Fig. 23 Image of NiWS active phase using aberration-corrected Titan 80–300 Super X electron microscope

because of environmental and safety concerns. Liquid-phase sulfiding can be accomplished with or without the addition of organo-sulfur compounds such as DMDS in the feedstocks. In the latter case, the feedstock is generally a gas oil-type material that contains sulfur compounds in ranges from a few thousand to 20,000 ppm. The H_2S necessary for the activation of the catalyst is generated by the decomposition of the sulfur compounds.

In the 1960s and early 1970s, the preferred sulfiding procedure in the industry was liquid phase with a sulfur-containing compound such as DMDS or DMS. The addition of the sulfur compounds resulted in saving time when compared to either vapor phase or liquid phase without spiking agents. Another advantage of liquid-phase over gas-phase sulfiding is that all the catalyst particles were wet from the beginning of the catalyst life; there was a small chance of catalyst bed channeling which can occur if the catalyst particles are allowed to dry out. In situ sulfiding occurs at temperatures between 450 °F and 600 °F (230–315 °C) regardless of the method used. Some catalyst manufacturers recommend the sulfiding be conducted at full operating pressure, while others prefer it be done at pressures lower than the normal operating pressure. Ammonia injection is practiced during the sulfiding of high-activity (high zeolite content) catalysts to prevent premature catalyst deactivation.

In the case of ex situ pre-sulfurization of catalyst, sulfur compounds are loaded onto the catalyst. The activation occurs when the catalyst, which has been loaded in the reactor, is heated up in the presence of hydrogen. The activation can be conducted either in vapor or liquid phase. Generally, activation of ex situ pre-sulfurized catalyst is accomplished faster than if the sulfiding is done in situ; however, there is the additional expense due to the need for the ex situ pre-sulfurization step. The economics vary from refiner to refiner; however, ex situ pre-sulfurization is rarely used for hydrocracking catalysts.

Catalyst Deactivation

Catalyst deactivation is the gradual loss of the catalyst's activity to convert the feed conversion. In practical terms, it is the temperature required to obtain a fixed conversion. As the run progresses, the catalyst loses activity. Catalyst will lose activity in several ways described below.

Catalyst Coking

Coke deposition is a by-product of the cracking reactions. The deposition of coke on a catalyst is a function of time and temperature. The longer the catalyst is in service and/or the higher the temperature of the process, the deactivating effect will be more severe. The coking of the catalyst begins with the adsorption of high-molecular-weight, low hydrogen/carbon ratio ring compounds; it proceeds with further loss of hydrogen content and ends with varying degrees of hardness of coke. This coke can cover active sites and/or prevent access to these sites by physical blockage of the entrance to the pores leading to the sites. Coke is not a permanent poison. Catalyst, which has been deactivated by coke deposition, can be, relatively easily, restored to near original condition by regeneration.

Reversible Poisoning/Catalyst Inhibition

Catalyst poisoning is primarily the result of strong chemisorption of impurities on active sites. Hydrocracking catalysts in a first-stage reaction environment such as once-through or single-stage configuration have to operate with high concentrations of both NH_3 and H_2S in the gas phase. This type of poisoning is reversible, i.e., when the deactivating agent is removed, the deactivating effect is gradually reversed. It is possible that if the catalyst temperature is raised, it can compensate for the deactivating effects. However, raising temperatures has to be done cautiously since the rate of coke deposition will accelerate. For example, NH_3 will adsorb strongly on the acidic sites of the catalysts. If there is a temporary exposure to high ammonia, the catalyst will require higher temperature to maintain activity. However, if the NH_3 concentration lowers to the more typical value, the catalyst should return to the normal activity as the ammonia desorbs from the surface. Another example of a reversible poison is carbon monoxide, which can impair the hydrogenation reactions by preferential adsorption on active metal sites. Another example is H_2S, which in moderate to high concentrations can reduce the desulfurization rate constant. In this case, the removal of H_2S from the recycle gas system solves the problem.

Catalytic Metal Agglomeration

Another reversible form of catalyst deactivation is the agglomeration of the hydrogenation component of the catalyst. It can be caused by poor catalyst activation conditions in which a combination of high water partial pressure and high temperature may exist for a prolonged period. Regeneration can restore the catalyst to near original condition.

Non-catalyst Metals Deposition

Some metals may come into the system via additives, such as silicon compounds used in delayed coking unit coke drums to reduce foaming, or feed contaminants such as Pb, Fe, As, P, Na, Ca, and Mg, or as organometallic compounds in the feed primarily Ni and V. Ni and V deposition occurs at the pore entrances and near the outer surface of the catalyst, creating a rind layer which effectively chokes off the access to the interior part of the catalyst, where most of the surface area resides. Metal deposition can damage the acid sites, the metal sites, or both. Deposition of metals is not reversible even with catalyst regeneration.

Catalyst Support Sintering

Catalyst support sintering is another reason for loss of catalyst activity and it also is irreversible. Sintering is also a result of high temperatures and particularly in connection with high water partial pressures. In this case the catalyst support material can lose surface area from a collapse of pores or from an increase in the diameter of pores, with the pore volume remaining approximately constant.

Catalyst Regeneration

A coked catalyst is usually regenerated by combustion in a stream of diluted oxygen or air, although steam or steam-air mixtures have also been used in the past. Upon combustion, coke is converted to CO_2 and H_2O. In the absence of excess oxygen, CO may also form. Except for the noble metal catalysts, hydrocracking catalysts contain sulfur, as the metals are in a sulfide form. In the regeneration process, the sulfur will be emitted as SO_2. In general, sulfur oxide emission starts at lower temperature than CO_2 emission. Regeneration of commercial catalysts can be done in situ or ex situ. The majority of commercial catalyst regeneration is performed ex situ because of environmental considerations. Several companies operate ex situ regeneration by using different equipment for burning off the coke. One company uses a continuous rotolouver, which is a cylindrical drum rotating slowly on a horizontal axis and enclosing a series of overlapping louvers. The spent catalyst passes slowly through the rotolouver, where it encounters a countercurrent of hot air. Another company uses a porous moving belt as a regenerator. The catalyst is moved with the stainless steel belt through a stationary tunnel furnace vessel where the regeneration takes place. Yet a third regeneration company uses ebullated bed technology to perform the catalyst regeneration. Regardless of the regeneration process, the spent catalyst is submitted to de-oiling prior to regeneration. This is to eliminate as much hydrocarbon as possible as well as to remove as much sulfur as possible to prevent formation of sulfates which could deposit on the catalyst and not be removed during regeneration. Sulfates are deleterious to catalyst performance.

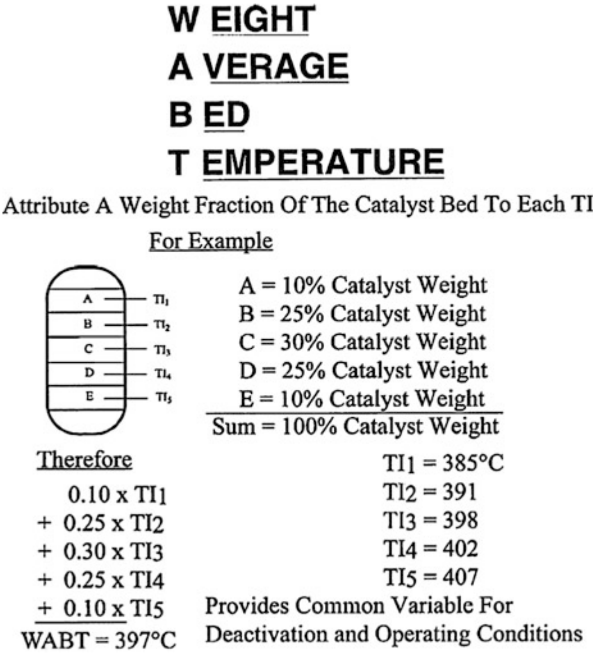
Hydrocracking Process Variables

The proper operation of the unit will depend on the careful selection and control of the processing conditions. By careful monitoring of these process variables, the unit can operate to its full potential.

Catalyst Temperature

The amount of conversion which takes place in the reactors is going to be determined by several variables: the type of feedstock, the amount of time the feed is in the presence of the catalyst, the partial pressure of hydrogen in the catalyst bed, and, most importantly, the temperature of the catalyst and reactants. A high temperature in the reactor causes a fast rate of reaction and, therefore, the high the conversion. Since hydrocracking is exothermic, overall, the temperature increases as the feed and recycle gas proceed through any particular catalyst bed. Maintaining temperature control at all times is very important. More heat can be generated from the reactions than the flowing streams can remove from the reactors. If this happens, the temperature may increase very rapidly. This condition is called a temperature excursion or a temperature runaway. A temperature runaway is a very serious situation since extremely high temperatures can be generated within a short period of time. These high temperatures can cause damage to the catalyst and/or to the reactors. To avoid these situations, temperature guidelines have to be observed. These guidelines are dependent on the type of feedstock, and the type of catalyst, and vary from catalyst supplier to catalyst supplier. But by and large, the temperature rise of catalyst beds loaded with noble metal catalyst is limited to about 30 °F (17 °C). The temperature rise of catalyst beds loaded with high-activity base metal catalysts (for naphtha production) is limited to about 25 °F (14 °C), and of those loaded with low-zeolite content catalyst (for middle distillate production), the temperature rise is limited to 40 °F (22 °C). Finally, maximum bed temperature rises of about 50 °F (28 °C) are recommended for amorphous catalysts. The maximum bed temperature rise of 50 °F (28 °C) is also recommended for most pretreating reactors. To properly monitor the reactions as the reactants pass through the catalyst bed, measuring the temperature of the flowing stream at the inlet and outlet of each bed and/or the reactor is not sufficient. The temperature at the inlet, outlet, and radially throughout the catalyst bed must be observed. A temperature profile plot is a useful tool for evaluating performance of catalyst, effectiveness of quench, and reactor flow patterns. A temperature profile can be constructed by plotting the catalyst temperature versus distance into the catalyst bed or more accurately plotting catalyst temperature against the weight percent of catalyst. The hydrocracking reactor should be operated with equal catalyst peak temperatures for attaining the maximum catalyst operating cycle length. In this manner the total catalyst volume is utilized during the entire cycle. The weight average bed temperature (WABT) is typically used to compare the catalyst activity. Figure 24 gives a general description of how the WABT is calculated for a reactor.

Fig. 24 Calculation of weighted average bed temperature (WABT)



W EIGHT
A VERAGE
B ED
T EMPERATURE

Attribute A Weight Fraction Of The Catalyst Bed To Each TI

For Example

A = 10% Catalyst Weight
B = 25% Catalyst Weight
C = 30% Catalyst Weight
D = 25% Catalyst Weight
E = 10% Catalyst Weight
Sum = 100% Catalyst Weight

Therefore
0.10 x TI1
+ 0.25 x TI2
+ 0.30 x TI3
+ 0.25 x TI4
+ 0.10 x TI5
WABT = 397°C

TI1 = 385°C
TI2 = 391
TI3 = 398
TI4 = 402
TI5 = 407

Provides Common Variable For Deactivation and Operating Conditions

The rate of increase of the reactor WABT to maintain both hydrotreating and hydrocracking functions, in order to obtain the desired conversion level and product quality, is referred to as the deactivation rate. It is one of the key variables used to monitor the performance of the catalyst systems. The deactivation rate can be expressed in °F per barrel or cubic meter of feed processed per pound or kilogram of catalyst (°C per m^3 of feed per kilogram of catalyst) or more simply stated as °F per day (°C per day). The decrease in catalyst activity for hydrotreating catalyst will show up in a decrease in its ability to maintain a constant nitrogen level in the hydrotreating catalyst effluent. For hydrocracking catalyst, a decrease in catalyst activity will generally show up in its ability to maintain a constant conversion to the desired product slate. To hold the same conversion level to the desired product slate, the reactor WABT is gradually increased.

Conversion

Conversion is useful as a measure of the severity of the operation. The operation requires higher severity as indicated by higher catalyst temperature to go to higher conversion levels and higher severity to reduce the endpoint of the product at a constant conversion. Conversion is normally controlled by catalyst temperature.

The term “gross conversion” is usually defined as

$$\text{Gross Conversion, vol\%} = (\text{Fresh Feed} - (\text{Fractionator Bottoms})/\text{Fresh Feed})) \times 100$$

where

Fresh feed = fresh feed rate, barrels per day (BPD) or m^3/h
Fractionator bottoms = net fractionator bottoms product to storage, BPD or m^3/h

Fresh Feed Quality

The quality of the raw oil charged to a hydrocracker will affect the temperature required in the catalyst bed to reach the desired conversion, the amount of hydrogen consumed in the process, the length of time before the catalyst is deactivated, and the quality of products. The effect of the feedstock quality on the performance of the unit is important and should be well understood, especially with regard to contaminants that can greatly reduce the life of the catalyst.

Sulfur and Nitrogen Compounds

In general, increasing the amount of organic nitrogen and sulfur compounds contained in the feed results in an increase in the severity of the operation. The sulfur content of the feed for a normal vacuum gas oil charge stock can be as high as 2.5–3.0 wt%. The higher sulfur levels will cause a corresponding increase in the H_2S content of the recycle gas that will normally have little or no effect on catalyst activity.

The organic nitrogen compounds, which are converted to ammonia, compete with the hydrocarbon for the active catalyst sights. This results in a lower apparent activity of the catalyst as the ammonia concentration increases. Consequently feedstocks with high organic nitrogen contents are more difficult to process and require higher catalyst temperatures or higher catalyst volumes.

Hydrogen Content

The amount of unsaturated compounds (such as olefins and aromatics) contained in the feed will have an effect on the heat released during the reaction and on the total hydrogen consumption on the unit. In general, for a given boiling range feedstock, a reduction in API gravity (increase in specific gravity) indicates an increase in the amount of unsaturated compounds and, therefore, higher heats of reaction and higher hydrogen consumption. Large amounts of unsaturated hydrocarbons can also cause a heat balance problem if the unit has not been designed to process that type of feed.

Boiling Range

The typical charge stock to a hydrocracker for distillate production is a 700 °F+ (370 °C+) boiling range vacuum gas oil or other feedstocks with similar boiling ranges such as heavy coker gas oil from a delayed coming unit. Increasing the boiling range usually makes the feed more difficult to process which can lead to higher catalyst temperatures and shorter catalyst life. This is especially true if the feed quality is allowed to decrease significantly due to entrainment of catalyst poisons in the feed. Higher endpoint feeds also usually have higher sulfur and nitrogen contents, which again make a feedstock more difficult to process.

Cracked Feed Components

Cracked feedstocks derived from catalytic cracking or thermal cracking can also be processed in a hydrocracker. These cracked components tend to have higher contaminants such as sulfur, nitrogen, and particulates. They are also more refractory, with high aromatics content and PNA precursors. These compounds make cracked stocks harder to process and harder to produce quality products.

Permanent Catalyst Poisons

Organometallic compounds contained in the feed will be decomposed, and the metals will be retained on the catalyst, thus decreasing its activity. Since metals are normally not removable by oxidative regeneration, once metals have poisoned a catalyst, its activity cannot be restored. Therefore, metal content of the feedstock is a critical variable that must be carefully controlled. The particular metals which usually exist in vacuum gas oil-type feeds are naturally occurring nickel, vanadium, and arsenic as well as some metals which are introduced by upstream processing or contamination such as lead, sodium, silicon, and phosphorous. Iron naphthenates are soluble in oil and will be a poison for the catalyst. Iron sulfide as corrosion product is normally not considered a poison for the catalyst and is usually omitted when referring to total metals.

The tolerance of the catalyst to metals is difficult to quantify and is somewhat dependent upon the type of catalyst being employed and the severity of the operation, i.e., the higher the severity, the lower will be the metals' tolerance since any impairment of activity will affect the ability to make the desired conversion. It is recommended to keep the total metals in the feedstock as low as possible and protect active catalyst by the use of catalysts designed to remove metals and graded bed strategies.

Fresh Feed Rate (LHSV)

The amount of catalyst loaded into the reactors is based upon the quantity and quality of the design feedstock and the desired conversion level. The variable that is normally used to relate the amount of catalyst to the amount of feed is termed liquid hourly space velocity (LHSV). LHSV is the ratio of volumetric feed rate per hour to the catalyst volume. Space velocity is the inverse of space time or the residence time the feed resides over the catalyst. Hydrocrackers are normally designed for an LHSV that depends on the severity of the operation. Increasing the fresh feed rate with a constant catalyst volume increases the LHSV, and a corresponding increase in catalyst temperature will be required to maintain a constant conversion. The increased catalyst temperature will lead to a faster rate of coke formation and, therefore, reduce the catalyst life. If the LHSV is run significantly higher than the design of the unit, the rate of catalyst deactivation may become unacceptable. LHSV can be defined as

$$\text{LHSV hr} - \text{i} = \frac{\text{Total Feed to Reactor Inlet, m}^3/\text{hr}}{\text{Total Catalyst volume, m}^3}$$

Liquid Recycle

Some hydrocrackers are designed to recycle oil from the product fractionator bottoms back to the reactors. This recycled oil stream is normally material distilled below the heaviest fractionator side-cut product. For a distillate-producing hydrocracker, the recycle stream is normally a 600–700 °F (315–370 °C) heavy diesel plus material.

The liquid recycle rate is normally adjusted as a ratio with fresh feed. This variable is called combined feed ratio (CFR) and is defined as follows:

$$\text{CFR} = \frac{\text{Fresh Feed Rate} + \text{Liquid Recycle Rate}}{\text{Fresh Feed Rate}}$$

If the unit has no liquid recycle from the fractionator back to the reactors, the CFR is 1.0, and the unit is said to operate in a once-through mode. If the amount of liquid recycle is equal to fresh feed, the CFR will be 2.0. An important function of liquid recycle is to reduce the severity of the operation. Consider conversion per pass that is defined as follows:

$$\text{Conversion per pass } = [(\text{Feed Rate} - \text{Fractionator Bottoms Rate to Storage}/(\text{Feed Rate} + \text{Liquid Recycle Rate})] \times 100.$$

If a unit were operating once through (CFR = 1.0) and 100 % of the feed were converted into products boiling below, i.e., 700 °F (370 °C), the conversion per pass is 100 % since the feed only makes one pass through the catalyst. If a unit is designed at a CFR of 2.0 and 100 % of the feed converted into products, the conversion per pass is only 50 %. In this way, as the CFR increases, the conversion per pass decreases. The catalyst temperature requirement is reduced as the CFR is increased (at a constant fresh feed conversion level) at a constant space velocity on a reactor charge basis and gas ratio. Therefore, reducing the CFR below the design value can lead to higher catalyst temperatures and shorter catalyst cycle life. Increasing the CFR above design can be helpful when operating at low fresh feed rates since it does not allow the total mass flow through the catalyst bed to reach such a low value that poor distribution patterns are established.

Hydrogen Partial Pressure

The reactor section operating pressure is controlled by the pressure that is maintained at the high-pressure separator. This pressure, multiplied by the hydrogen purity of the recycle gas, determines the partial pressure of hydrogen at the separator. The hydrogen partial pressure required for the operation of the unit is chosen based on the type of feedstock to be processed and the amount of conversion desired.

The function of hydrogen is to promote the saturation of olefins and aromatics and saturate the cracked hydrocarbons. Hydrogen is also necessary to prevent excessive condensation reactions leading to coke formation. For this reason, running the unit for extended periods of time at lower than design partial pressure of hydrogen will result in increased catalyst deactivation rate and shorter time between regeneration.

Hydrogen partial pressure has an impact on the saturation of aromatics. A decrease in system pressure or recycle gas purity has a sharp effect on the product aromatic content. This will be especially true for kerosene and diesel aromatic content, which will in turn affect the kerosene product smoke point and the diesel cetane number.

A reduction in operating pressure below its design will have a negative effect on the activity of the catalyst and will accelerate catalyst deactivation due to increased coke formation.

Operating at higher than design pressure may not be possible. There will be a practical equipment limitation on most units that will not allow significantly higher pressure than design, such as the pressure rating of the heaters, exchangers, and vessels. The major control variable for hydrogen partial pressure is the recycle gas purity that should be monitored closely to assure it is always maintained above the minimum value. The hydrogen purity can be improved by increasing the hydrogen purity of the makeup hydrogen, venting gas off the high-pressure separator, or reducing the temperature at the high-pressure separator.

Recycle Gas Rate

In addition to maintaining a prescribed partial pressure of hydrogen in the reactor section, it is equally important to maintain the physical contact of the hydrogen with the catalyst and hydrocarbon so that the hydrogen is available at the sites where the reaction is taking place. The physical contact of hydrogen with the catalyst is accomplished by circulating the recycle gas throughout the reactor circuit continuously with the recycle gas compressor. The amount of gas that must be recycled is a design variable again set by the design severity of the operation. The standard measure of the amount of gas required is the ratio of the gas being recycled to the rate fresh feed being charged to the catalyst.

As with hydrogen partial pressure, the recycle gas-to-feed ratio should be maintained at the design ratio or higher. The actual calculation for the gas-to-oil ratio can be defined as

$$\text{Gas to Oil Ratio} = \frac{\text{Total Circulating gas to reactor, SCF/day}}{\text{Total Feed to Reactor Inlet, barrels/day}} = \text{SCFB Feed}$$

As with hydrogen partial pressure, any reduction of the gas-to-oil ratio below the design minimum will have adverse effects on the catalyst life. During normal operations and throughout the cycle length, there will be a gradual increase in the reactor section pressure drop. As the pressure drop increases, there will be a tendency for the gas-to-oil ratio to decrease. When the pressure drop through the system increases to the point where the minimum gas-to-oil ratio cannot be kept, either the unit throughput will have to be decreased to bring the gas-to-oil ratio back above the minimum or the unit shutdown for catalyst regeneration or replacement. Another possibility is to increase the speed on a centrifugal compressor to overcome the increased pressure drop with the obvious limitation of the compressor's rated speed. Gas-to-oil ratio recommendations vary between licensors and/or catalyst vendors, but in general the minimums recommended are 6,000–12,000 SCFB (675 nm^3/m^3).

Makeup Hydrogen

The quality of the hydrogen-rich gas from the hydrogen plant is an important variable in the performance of hydrocrackers since it can affect the hydrogen partial pressure and recycle gas-to-feed ratio and thereby influence the catalyst stability (deactivation rate). Typically pressure swing adsorption (PSA) purified hydrogen is used for high-pressure hydrocracking unit because their purity is near 100 % hydrogen. Other sources of hydrogen such as the net gas from catalytic reforming units are lower purity hydrogen and will reduce the recycle gas purity in the hydrocracking unit.

Hydrogen Purity

The purity of hydrogen in the makeup gas to a hydrocracker will have a major influence on the hydrogen partial pressure and recycle gas-to-feed ratio. Therefore, the minimum purity on the makeup gas should be set to provide the minimum recycle gas purity allowed. If the hydrogen plant is unable for some reason to produce minimum hydrogen purity product, a purge of recycle gas off the high-pressure separator may be possible to maintain the recycle gas purity requirements.

Nitrogen and Methane Content

The total of the nitrogen and methane contained in the makeup gas is only harmful as a diluent, i.e., they will reduce the hydrogen partial pressure. As long as the minimum hydrogen purity is maintained, nitrogen and methane will not affect the unit. However, it should be noted that excessive quantities of molecular nitrogen entering a hydrocracker in the makeup gas stream can cause a buildup of nitrogen in the recycle gas since the nitrogen is not condensable. If this is the case, the nitrogen will have to be removed from the reactor circuit by a small, continuous purge of recycle gas off the high-pressure separator. Nitrogen and methane, however, will increase the molecular weight of the recycle gas and increase the power requirement of the recycle gas compressor.

CO + CO_2 Content

The normal specification for CO plus CO_2 in the makeup gas stream to a hydrocracker is in the range of 20 ppm maximum. Larger quantities can have a harmful effect on catalyst activity. CO is considered the worst impurity due to the fact that it has a limited solubility in both hydrocarbon and water and will, therefore, build up in the recycle gas. CO_2, on the other hand, is much more soluble and is readily removed from the system in the high-pressure separator liquids.

Both CO and CO_2 have similar effects on the hydrocracking catalyst. They are converted on the active sites of the catalyst in the presence of hydrogen to methane and water. This methanation of CO and CO_2 competes with the normal hydrocarbon reactants for the catalyst. Therefore, if CO + CO_2 are allowed to build up, higher catalyst temperatures will be required. In an extreme case where a large quantity of CO or CO_2 would be introduced to the hydrocracker in a short period of time, a temperature excursion is theoretically possible resulting from the highly exothermic methanation reaction. A recommended practice is if the CO + CO_2 content exceeds the maximum design limit, the catalyst temperature should not be increased to compensate for a resulting decrease in conversion. Catalyst temperature should be maintained at the same level or reduced until the problem causing the high CO + CO_2 is eliminated. In this way the catalyst will not be harmed by increased deactivation at a higher temperature, and it will also eliminate the possibility of a temperature runaway due to methanation. In addition, during reactor cooling and shutdown, the presence of CO in the recycle gas at temperatures below 200 °C can lead to formation of nickel carbonyl, which is extremely toxic and can cause death. Therefore, CO concentration should be kept as low as possible (typically less than 10 ppm).

Commercial Suppliers of Hydrocracking Process and Catalyst Technology

Various companies are able to supply the licensing technology for the hydrocracking process, and some companies specialize in the supply of catalyst (http://www.albemarle.com/products—markets/catalyst-solutions/refinery-catalyst-solutions/clean-fuels-technologies-1629.html; http://france.axens.net/fr/component/axensdocuments/872/hydrocracking-brochure/english.html; http://www.cbi.com/technologies/technologies-serviceshydrocracking-technology; http://www.exxonmobil.com/Apps/RefiningTechnologies/Files/sellsheet_hydrocracking.pdf; http://www.fripp.com/en-0301020100.htm; http://www.topsoe.com/business_areas/refining/Hydrocracking/HydrocrackingProcesses.aspx; http://www.shell.com/global/products-services/solutions-for-businesses/globalsolutions/refinery-chemical-licensing/refining-technology.html; http://www.uop.com/products/catalysts/hydroprocessing/; http://www.uop.com/processing-solutions/refining/vgo-fuel-oil-conversion/; https://grace.com/catalysts-and-fuels/en-us/art-hydroprocessing-catalysts; http://www.criterioncatalysts.com/en/products/product-applications/hydrocracking-pretreat.html). The suppliers of the process technology are Axens, Chevron Lummus Global, ExxonMobil, Haldor Topsoe, Shell Global Solution, and UOP.

The providers of catalyst technology are Albemarle, Axens, Chevron Lummus Global, FRIPP, Haldor Topsoe, RIPP/Technip, and UOP.

The suppliers of the catalyst technology are shown in Table 8. There are many types of catalysts used in hydrocracking. Often combinations of catalysts are used in the units. The choice of the catalyst depends on the product slate desired by the refiner.

Table 8 Providers of hydrotreating and hydrocracking catalysts

	Conventional hydrocracking				Mild hydrocracking			
Company	HDS/ HDN	Resid	Max naphtha, jet	Max middle distillates, lubes	HDS/ HDN	Resid	Max naphtha, jet	Max middle distillates, lubes
ABB Lummus Global		x						
Advanced Refining Technology	X	x						
Albemarle	X		X	X	X			x
Axens				X	X			x
Catalyst and Chemical Industries		X	X	X				x
Chevron Lummus Global	X		X	X	X		X	X
Criterion Catalysts and Technologies	X		X	X	X		X	X
ExxonMobil Research and Engineering						X	X	
FRIPP			X	X				
Haldor Topsoe	X			X				X
Kataleuna GMBH Catalysts				X				
RIPP/Sinopec				X				
UOP			X	X				X
Zeolyst International (marketed by Criterion)			X	X			X	X

References

J. Akumu, Sulphur reduction processes in Africa and Global trend, in *From cleaner public transport and low sulphur awareness program*, Accra, Ghana, September 2012. http://unep.org/transport

Ch. Baerlocher, L.B. McCusker, Database of zeolite structures. http://www.iza-structure.org/databases/

W.J. Baral, H.C. Huffman, *Eighth World Petroleum Congress*, Moscow, 4, 119–127 (1971)

A.P. Bolton, *Zeolite chemistry and catalysis*, A.C.S. monograph series no. 117, Washington, DC (1976), p. 714

M. Bricker, M.T. Schaal, S. Bradley, S. Sanchez, *244th ACS National Meeting and Exposition Energy and Fuels Division 8th International Symposium on Hydrotreating/Hydrocracking Technologies*, Philadelphia, PA, August 19–23, 2012 (2012)

H. Heinemann, *Catalysis: Science and Technology*, vol. 1, eds. by J.R. Anderson, M. Boudart (Springer, 1981)

G.A. Mills, H. Heinemann, T.H. Milliken, A.G. Oblad, Ind. Eng. Chem. **45**, 134 (1953)

Ministry of Fuels and Power, *Report on the Petroleum and Synthetic Oil Industry of Germany*, B.I.O.S. Overall report no. 1, section C, Hydrogenation Processes (1947), pp. 46–73

M.J. Wier, D. Sioui, S.Metro, A. Sabitov, M. Lapinski, Optimizing naphtha complexes in the tight oil boom, in *American Fuel and Petrochemical Manufacturers Annual Meeting*, San Antonio, TX, AM-14–35

Oil Gas J. **58**(16), 104–106 (1960)

M. Pier, Elektrochem. **53**, 291 (1949)

Providers of technology in the following websites: http://www.albemarle.com/products—markets/catalyst-solutions/refinery-catalyst-solutions/clean-fuels-technologies-1629.html, http://france.axens.net/fr/component/axensdocuments/872/hydrocracking-brochure/english.html, http://www.cbi.com/technologies/technologies-serviceshydrocracking-technology, http://www.exxonmobil.com/Apps/RefiningTechnologies/Files/sellsheet_hydrocracking.pdf, http://www.fripp.com/en-0301020100.htm, http://www.topsoe.com/business_areas/refining/Hydrocracking/HydrocrackingProcesses.aspx, http://www.shell.com/global/products-services/solutions-for-businesses/globalsolutions/refinery-chemical-licensing/refining-technology.html, http://www.uop.com/products/catalysts/hydroprocessing/, http://www.uop.com/processing-solutions/refining/vgo-fuel-oil-conversion/, https://grace.com/catalysts-and-fuels/en-us/art-hydroprocessing-catalysts, http://www.criterioncatalysts.com/en/products/product-applications/hydrocracking-pretreat.html

P.R. Robinson, G.E. Dolbear, Hydrotreating and hydrocracking: fundamentals, in *Practical Advances in Petroleum Processing* (Springer, New York, 2006), pp. 177–218

J. Scherzer, A.J. Gruia, *Hydrocracking Science and Technology* (CRC Press, 1996) Marcel Dekker NY, NY

J.W. Scott, N.J. Patterson, *Proceedings of the 7th World Petroleum Congress*, Mexico City, 4, 97–111 (1967)

J.H. Sinfeld, Adv Chem. Eng **5**, 37 (1964)

J.H. Sinfeld, *Bimetallic Catalysts: Discoveries, Concepts and Applications* (Wiley, New York, 1983)

M.J. Sterba, C. Watkins, Oil Gas J. **58**(21), 102–106 (1960)

D.H. Stormont, Oil Gas J. **57**(44), 48–49 (1959)

H. Topsoe, B.S. Clausen, F.E. Massoth, *Hydrotreating Catalysis* (Springer, Berlin, 1996)

D.B. Weisz, Adv. Catal. **13**, 137 (1962)

Hydrotreating in Petroleum Processing

Peter Kokayeff, Steven Zink, and Pamela Roxas

Contents

P. Kokayeff (✉) • S. Zink • P. Roxas
UOP, A Honeywell Company, Des Plaines, IL, USA
e-mail: peter.kokayeff@honeywell.com; steven.zink@honeywell.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_4

Abstract

Hydrotreating or catalytic hydrogen treating removes objectionable materials from petroleum fractions by selectively reacting these materials with hydrogen in a reactor at relatively high temperatures and at moderate pressures. These objectionable materials include, but are not solely limited to, sulfur, nitrogen, olefins, and aromatics. The lighter distillates, such as naphtha, are generally treated for subsequent processing in catalytic reforming units, and the heavier distillates, ranging from jet fuels to heavy vacuum gas oils, are treated to meet strict product quality specifications or for use as feedstocks elsewhere in the refinery. Hydrotreating is also used for upgrading the quality of atmospheric and vacuum resids by reducing their sulfur and organometallic levels. Hydrotreaters are designed for and run at a variety of conditions depending on many factors such as feed type, desired cycle length, and expected quality of the products. Until about 1980, hydrotreating was a licensed technology being offered by a fairly large number of companies. From 1980 until the end of the last century, hydrotreating catalysts were becoming more commoditized as the formulations were less differentiated among the various suppliers. Many of the product quality specifications are driven by environmental regulations, and these regulations are becoming more stringent every year. With the advent of ultra-low-sulfur fuel regulations ushering in the first decade of the twenty-first century, however, it was required for hydrotreating research and development to deliver quantum improvements in catalyst performance and process technology. This was accomplished in the form of so-called Type II supported transition metal sulfide (TMS) catalysts, unsupported/bulk TMS catalysts, improved bed grading catalysts and stacking strategies, advanced catalyst loading techniques, improved trickle-flow reactor internals designs, and more effective catalyst activation methodologies.

Keywords
Hydrotreating • Hydrodesulfurization • Hydrodenitrogenation • Resid • Gasoline • Distillate • Upgrading • Desulfurization • Denitrogenation

Introduction

Hydrotreating or catalytic hydrogen treating removes objectionable materials from petroleum fractions by selectively reacting these materials with hydrogen in a reactor at relatively high temperatures at moderate pressures. These objectionable materials include, but are not solely limited to, sulfur, nitrogen, olefins, and aromatics. The lighter materials such as naphtha are generally treated for subsequent processing in catalytic reforming units, and the heavier distillates, ranging from jet fuels to heavy vacuum gas oils, are treated to meet strict product quality specifications or for use as feedstocks elsewhere in the refinery. Hydrotreating is also used for upgrading the quality of atmospheric and vacuum resids by reducing their sulfur and organometallic levels. Many of the product quality specifications are driven by environmental regulations that are becoming more stringent every year. Hydrotreaters are designed for and run at a variety of conditions depending on many factors such as feed type, desired cycle length, and expected quality of the products; in general, they will operate at the following ranges of conditions: LHSV, 0.2–8.0; H_2 circulation, 300–4,000 SCFB (50–675 Nm^3/m^3); H_2 partial pressure, 200–2,000 psia (14–138 bara); and typical SOR temperatures ranging between 500 °F and 740 °F (260–393 °C), with the lower limits representing minimum operating conditions for naphtha hydrotreating and the higher values showing operating conditions used for hydrotreating atmospheric resids. Until about 1980, hydrotreating was a licensed technology being offered by a fairly large number of companies. From 1980 until the end of the last century, hydrotreating catalysts were becoming more commoditized as the formulations were less differentiated among the various suppliers. With the advent of ultra-low-sulfur fuel regulations ushering in the first decade of the twenty-first century, however, it was required for hydrotreating research and development to deliver quantum improvements in catalyst performance and process technology. This was accomplished in the form of so-called Type II supported transition metal sulfide (TMS) catalysts, unsupported/bulk TMS catalysts, improved bed grading catalysts and stacking strategies, advanced catalyst loading techniques, improved trickle-flow reactor internals designs, and more effective catalyst activation methodologies.

The common objectives and applications of hydrotreating are listed below:

- Straight-run and coker naphtha (catalytic reformer feed pretreatment) – to remove sulfur, nitrogen, and contaminants (e.g., Si) that otherwise would poison downstream, noble metal reforming catalysts
- Pyrolysis gasoline and coke-oven light oil – to remove sulfur and nitrogen and to hydrogenate di-unsaturates that would otherwise deactivate/foul downstream equipment and/or catalysts in the aromatics complex
- LPG – to remove sulfur and nitrogen and to hydrogenate di-unsaturates that would otherwise deactivate downstream, noble metal dehydrogenation catalysts
- Kerosene and diesel – to remove sulfur and to hydrogenate unsaturates, resulting in improved properties of the streams (kerosene smoke point, diesel cetane, specific gravity) as well as storage stability
- Shale oil – to remove sulfur, nitrogen, arsenic, and oxygen, resulting in improved properties of the streams as above
- Lube oil – to improve the viscosity index, color, and stability as well as storage stability
- Used lube oil – to remove contaminants and blending package additives, which, for example, may contain zinc and phosphorus, and to at least restore the quality to that of the original base oil
- Vegetable oils and animal tallows – to remove contaminants and to complete one step in the conversion of triglycerides to jet, kerosene, and diesel fuels
- FCC feed – to improve FCC yields especially of gasoline and propylene, to improve the quality of the gasoline and the diesel/light cycle oil, and to reduce catalyst usage and stack emissions
- Hydrocracking – to maximize the yield of ultra-low-sulfur diesel (ULSD) and to improve the properties of hydrocracked fuels (naphtha sulfur and nitrogen, kerosene smoke point, diesel cetane, specific gravity)
- Atmospheric and vacuum residua – to provide low-sulfur, low-metal fuel oils to effect conversion and/or pretreatment for further conversion downstream

Brief History

Hydrotreating has its origin in the hydrogenation of finely powdered, bituminous coal to liquid hydrocarbons, accomplished by Berthelot in 1869 with a nascent hydrogen source, hydriodic acid (Berthelot 1869). In 1897, Sabatier and Senderens published their discovery that unsaturated hydrocarbons could be hydrogenated in the vapor phase over a finely powdered, reduced nickel catalyst (Sabatier and Senderens 1897). Shortly after the turn of the century, Ipatieff extended the range of feasible hydrogenation reactions by the introduction of elevated hydrogen pressures (Ipatieff et al. 1900). At the time, the progress of the automobile industry was expected to entail a considerable increase in the consumption of gasoline. This led to the experimental work by Bergius, started in 1910 in Hanover, Germany, who sought to produce gasoline by cracking heavy oils and oil residues as well as converting coal to liquid fuels. He realized that to remedy the inferior quality of the unsaturated gasoline so produced, the hydrogen removed mostly in the form of methane during the cracking operation has to be replaced by addition of fresh hydrogen. Thus, formation of coke was avoided and the gasoline produced was of a more saturated character. Bergius also noted that the sulfur contained in the oils was eliminated for the most part as hydrogen sulfide. Ferric oxide was used in the Bergius process to remove the sulfur. Actually, the ferric oxide and sulfides formed in the process acted as catalysts, though the activity was very poor. The first plant for hydrogenation of brown coal was put on stream in Leuna, Germany, in 1927 (Stranges 1984). The plant utilized unsupported molybdenum and tungsten sulfides (TMSs) to hydrogenate brown coal. The first TMS catalysts supported on activated γ-alumina were developed and in use during the early 1940s by I.G. Farbenindustrie AG/Badische Anilin- und Soda-Fabrik (BASF) in Ludwigshafen, Germany. Metal shortages while in wartime motivated the idea to disperse a relatively smaller quantity of metals on an activated alumina support (Wu and Storch 1968). Among the first such catalysts utilized industrially were catalysts 7,846 (NiMo) and 8,376 (NiW) (Weisser and Landa 1973; Pier 1949). The past large-scale industrial development of hydrogenation in Europe, particularly in Germany, was due entirely to military considerations. Germany used hydrogenation extensively during World War II to produce gasoline: 3.5 million tons were produced in 1944. The first commercial hydrorefining installation in the United States was at the Standard Oil Company of Louisiana in Baton Rouge in the 1930s. WWII plants were developed by Humble Oil and Refining Company and Shell Development Company, though there was considerably less dependence on hydrogenation as a source of gasoline. Even though hydrogenation has been of interest to the petroleum industry for many years, hydrogen-consuming processes were seldom used industrially due to the lack of low-cost hydrogen. This limitation was relieved in the early 1950s upon the advent of catalytic reforming, making by-product hydrogen more readily available, thus motivating an extensive and increased interest in processes that utilized such hydrogen to upgrade petroleum stocks. As a result of the enormous growth of hydrotreating, as of the beginning of 2001, there were more than 1,600 hydrotreaters operating in the world with a total capacity in excess of 39,000,000 B/D (4,800,000 MT/D).

Flow Schemes

Although the "hydrotreating process" has several different applications (e.g., hydrogenation, hydrodesulfurization, hydrodenitrogenation, hydrodemetallation, etc.) and is used to process a variety of petroleum fractions from LPG all the way to atmospheric residue, practically all units have the same flow scheme. It consists of a higher-pressure reactor section "R" and a lower-pressure fractionation section "F." This is shown schematically in Fig. 1 and is described below in general terms.

Reactor Section

The reactor section consists of the following major pieces of equipment: feed pump, feed/effluent exchangers, reactor charge heater, reactor(s), reactor effluent condenser, product separator, recycle gas compressor, and makeup gas compressors. Additional equipment may be specified in some hydrotreating units: fresh feed filters, reactor effluent hot separator, and recycle gas scrubber. Figure 2 features a typical flow diagram of the UOP Unionfining™ Process, which includes a reactor section and all the equipment described in the preceding section.

Feed Filters

It is preferable to route the feed directly from an upstream unit, bypassing intermediate storage. When storage facilities are used, however, feed filters should be used. The purpose of the filters is to trap corrosion products and other particulate matter entrained by the feed while passing through intermediate storage. The feed filters are either automatic backwash filters operating on a pressure drop setting or manual cartridge (disposable) filters.

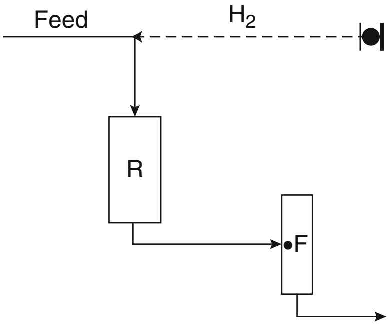


Fig. 1 Schematic flow diagram of a hydrotreater

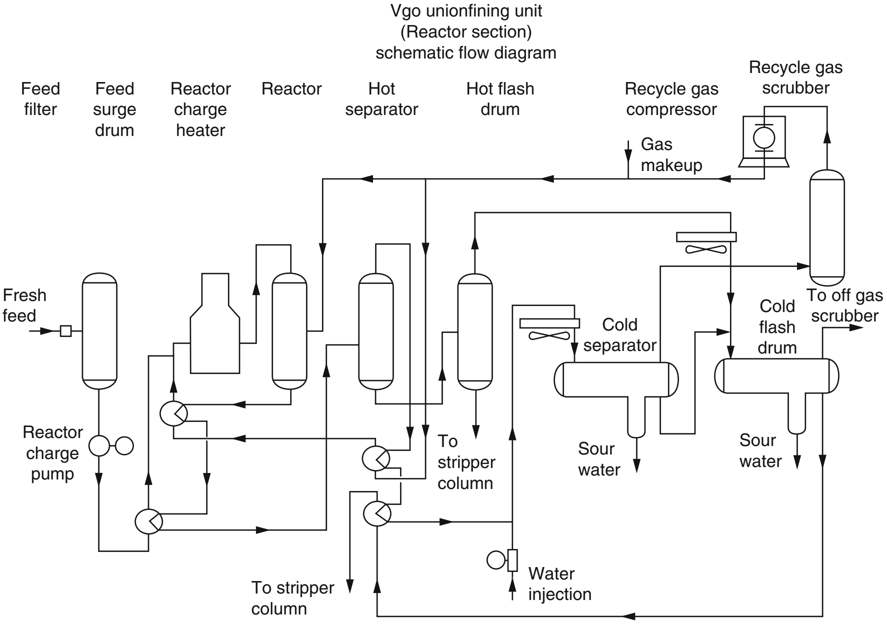


Fig. 2 Schematic flow diagram of a reactor section

Feed/Effluent Exchangers

Via a series of feed/effluent shell-and-tube exchangers, the reactor effluent preheats the reactor charge before entering the reactor charge heater. This recovers as much heat as possible from the heat of reaction and the sensible and latent heats of the reactor effluent. Liquid feed may be preheated separately with reactor effluent exchange before combining with the recycle (treat) gas, depending on the heat integration scheme.

Reactor Charge Heater

In most units, the fresh feed and recycle gas are heated together as “combined feed” to the desired reactor inlet temperature in a combined feed charge heater. In units processing heavy feed, especially the atmospheric residue units, the liquid feed is preheated separately in the reactor feed/reactor effluent exchange, and only the recycle gas is heated in the heater upstream of the reactor.

Makeup Hydrogen System

Makeup hydrogen is typically obtained from hydrogen manufacturing plants, naphtha cracking complexes, and/or naphtha catalytic reforming units. Depending on the pressure of the hydrotreating unit, the makeup hydrogen might have to be compressed before introduction into the unit. Reciprocating compressors are typically used for this service. The makeup gas is introduced into the recycle gas system.

Recycle Hydrogen System

After the reactor effluent's gas and liquid phases are separated, the gas flows to the recycle gas compressor. In some cases, the recycle gas will be sent first to an amine scrubber to remove most of the hydrogen sulfide. Most often, the recycle gas compressor is a separate centrifugal machine, but it could also be a part of the makeup gas compressors, as additional cylinders in a reciprocating compressor. The recycle gas compressor is designed to pump a large volume of gas at a relatively low compression ratio.

Recycle Gas Scrubbing

The recycle gas stream will typically contain hydrogen sulfide. The hydrogen sulfide reduces the reactor hydrogen partial pressure and thus suppresses the catalyst activity. This effect is more pronounced with a high-sulfur feed stream, and for the same feedstock, the heavier the cut, the higher the sulfur content. Recycle gas scrubbing is typically included in the design of selective FCC naphtha hydrotreaters to minimize the temperature severity of hydrotreating, which directly impacts monoolefin hydrogenation and octane retention.

Reactor(s)

Once the feed and recycle gas have been heated to the desired temperature, the reactants enter the reactor inlet. As the reactants flow downward through the catalyst bed, various exothermic reactions generate heat, and the temperature increases. Multiple catalyst beds with interbed quenching may be required, depending mostly upon the feedstock quality and the product specifications. Specific reactor designs will depend upon several variables. Reactor diameter is typically set by the cross-sectional liquid flux. As the unit capacity increases, the reactor diameter increases to the point where two parallel trains would be considered. Reactor height is a function of the amount of catalyst and number of beds required. Depending on the expected heat of reaction, cold recycle gas or cold product separator liquid is brought into the reactor at the interbed quench points in order to cool the reactants and thus control the reaction rate. Good distribution of reactants at the reactor inlet and at the top of each subsequent catalyst bed is essential for optimum catalyst performance. There are many companies that design proprietary internals: reactor inlet diffuser, top liquid distribution tray, quench section which includes quench inlet assembly, quench and reactant mixing device and redistribution tray, as well as the reactor outlet device, or collector. Not all reactors are specified with all the internals described above.

Reactor Effluent Water Wash

Cooling of the reactor effluent is accomplished in the feed/effluent exchangers, which are typically the shell-and-tube design. Final cooling of the reactor effluent is obtained in air fin coolers and/or water trim coolers. Water is injected directly into the stream before it enters the coolers to prevent the deposition of salts. The salts would tend to corrode and foul the coolers. The sulfur and nitrogen contained in the feed are converted to hydrogen sulfide and ammonia in the reactor. These two reaction products combine to form ammonium salts that can solidify and precipitate as the reactor effluent is cooled. Likewise, ammonium chloride may be formed if there is any chloride in the system. The purpose of the water is to keep the salts of hydrogen sulfide and ammonia in solution and not allow them to precipitate. Various companies have slightly different guidelines for the quality of the water injection; in general, boiler feedwater is preferred.

Vapor/Liquid Separation

The exact method of separating vapor and liquid will vary depending on the optimum heat integration scheme. Up to four separate vessels may be used to disengage and individually remove vapor, water, and hydrocarbon liquid. A hot high-pressure separator is sometimes installed after the feed/effluent exchangers to collect the heavier hydrocarbon material from the reactor effluent and send it to fractionation via a hot low-pressure flash drum. The overhead vapor from the hot high-pressure separator continues through an air cooler into a cold high-pressure separator. The two-separator system is depicted in Fig. 2.

Hydrogen Purification

Increasing the recycle gas hydrogen partial pressure will decrease the catalyst deactivation rate. Depending upon the feedstock and type of unit, additional measures may be taken to increase the hydrogen purity. These measures may include hydrogen enrichment and/or membrane separation.

Fractionation Section

A schematic flow diagram of a typical fractionation section is shown in Fig. 3.

The function of the fractionation section is to separate the net reactor effluent into the desired products. This can be accomplished with either a one- or a two-column fractionation scheme, depending on the type of hydrotreating unit.

In the two-column scheme, the flash drum liquids combine and flow to a stripper column. Steam and/or a fired heater reboiler is used to strip naphtha (if desired) and lighter material overhead. The stripper bottoms stream flows to a fractionator where it is further separated into naphtha (if desired) and heavier products. The fractionator feed is typically preheated with fractionator bottoms and a fired heater before entering the column. Stripping steam is used to drive lighter material up the column, and various product strippers are used to pull side-cut products to the desired specifications.

Chemistry

The following chemical steps and/or reactions occur during the hydrotreating process (depending on the impurities present):

- Sulfur removal, also referred to as desulfurization or hydrodesulfurization (HDS) in which the organic sulfur compounds are converted to hydrogen sulfide

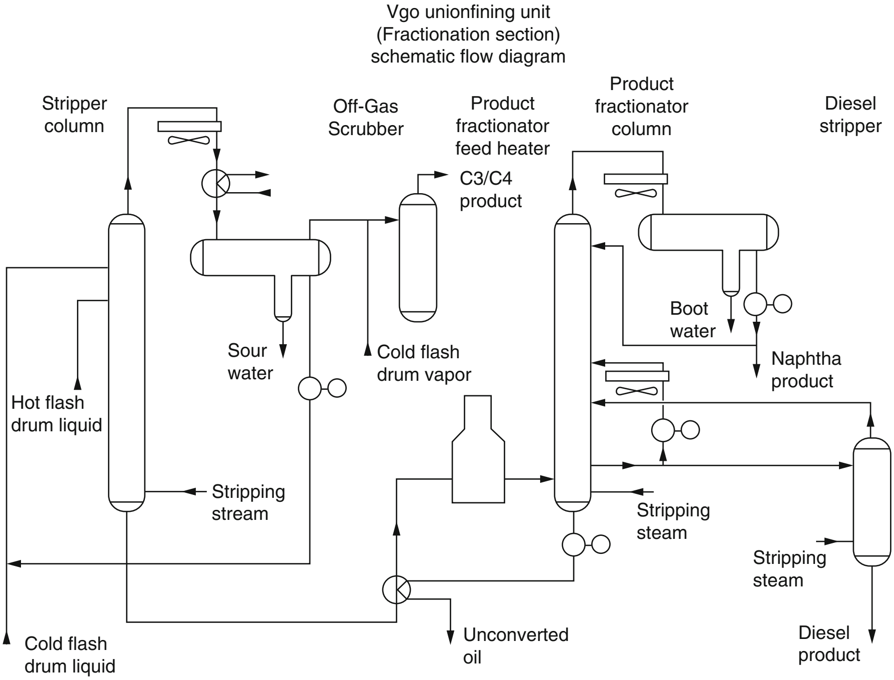


Fig. 3 Schematic flow diagram of a fractionation section

- Nitrogen removal, also referred to as denitrogenation or hydrodenitrogenation (HDN) in which the organic nitrogen compounds are converted to ammonia
- Metal (organometallics) removal, also referred to as demetallation or hydrodemetallation (HDM), in which the organometallics are converted to the respective metal sulfides
- Oxygen removal, also referred to as hydrodeoxygenation, in which the organic oxygen compounds are converted to water
- Olefin saturation, in which organic compounds containing double bonds are converted to their saturated homologues
- Aromatic saturation, also referred to as hydrodearomatization, in which some of the aromatic compounds are converted to naphthenes
- Halides removal, also referred to as hydrodehalogenation, in which the organic halides are converted to hydrogen halides

The first three types of compounds are always present, though in varying amounts, depending on the source of feedstock. For example, naphtha will typically contain extremely low amounts of organometallic compounds, while atmospheric residues may contain levels in excess of 100 wppm. Some crudes contain much more sulfur in all the fractions when compared with other crudes. For example, most middle eastern crudes contain much more sulfur than some crudes from

Indonesia or North Africa. The same is true for nitrogen levels. The other impurities are not always present. In general, the hydrotreating reactions proceed in the following descending order of ease: (organometallic) metals removal, olefin saturation, sulfur removal, nitrogen removal, oxygen removal, and halide removal. The contaminant removal in residue hydrotreating involves controlled breaking of the hydrocarbon molecule at the point where the sulfur, nitrogen, or oxygen atom is joined to carbon atoms. Some aromatic saturation also occurs. The chemistry of residue hydrotreating is essentially that of contaminant removal. Some cracking occurs in residue hydrotreating, but it is normally less than 30 vol% of the fresh feed charge.

In general, the hydrodesulfurization reaction consumes 100–150 SCFB/wt% change (17–25 Nm^3/m^3/wt% change), and the hydrodenitrogenation reaction consumes 200–350 SCFB/wt% change (34–59 Nm^3/m^3/wt% change). Typically, the heat released in hydrotreating is about 0.1–0.2 °F/SCFB H_2 consumed (0.35–0.70 $°C/Nm^3/m^3H_2$).

In general, the “general principles” concerning hydrotreating reaction rates, heats of reaction, and hydrogen consumption are:

- Hydrodesulfurization and olefin hydrogenation are the most rapid reactions.
- Olefin hydrogenation liberates the most heat per unit of hydrogen consumed.
- Hydrodenitrogenation and hydrodearomatization are the most difficult reactions.
- Hydrogen consumption and heat of reaction are related.

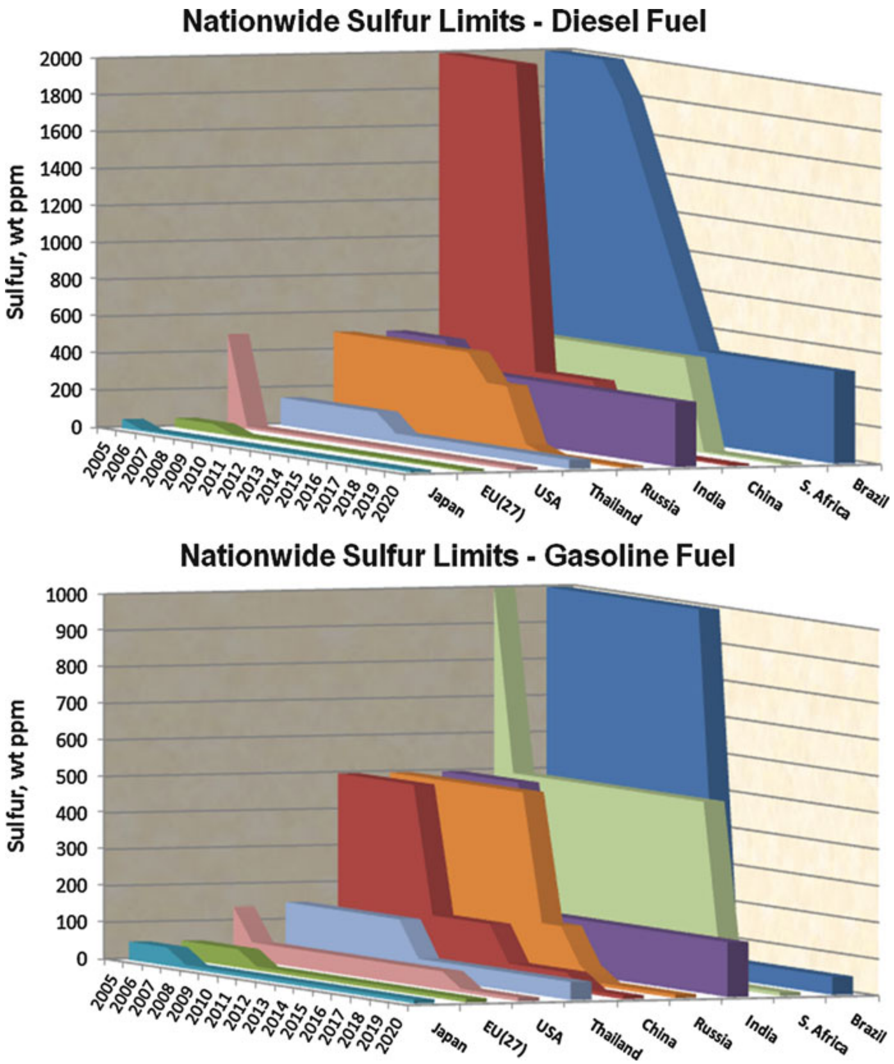
Sulfur Removal

From the end of the last century until now, ultra-low-sulfur fuel specifications continue to tighten. By 2020, it is anticipated that most of the industrialized world will have legislated no more than 10 wppm sulfur in both motor gasoline and diesel products, consistent with the desire to improve fuel economy and reduce vehicle emissions. Timelines for these changes are summarized in Fig. 4 (TransportPolicy.Net 2014).

Sulfur removal occurs via the conversion to H_2S of the organic sulfur compounds present in the feedstock. This conversion is sometimes referred to as desulfurization or hydrodesulfurization (HDS). Sulfur is found throughout the boiling range of petroleum fractions in the form of many hundreds of different organic sulfur compounds which, in the naphtha-to-atmospheric residue range, can all be classified as belonging to one of the following six sulfur types: mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and dibenzothiophenes. Typical reactions for each kind of sulfur compound are shown below.

Mercaptans

$$\text{R-SH} + H_2 \rightarrow \text{R-H} + H_2S$$



Nationwide Sulfur Limits - Diesel Fuel

Nationwide Sulfur Limits - Gasoline Fuel

Fig. 4 Selected timelines for introduction of new sulfur limits for motor fuels

Sulfides

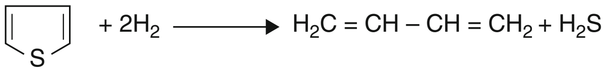
$$\text{R1-S-R2} + 2\text{H}_2 \rightarrow \text{R1-H} + \text{R2-H} + \text{H}_2\text{S}$$

Disulfides

$$\text{R1-S-S-R2} + 3\text{H}_2 \rightarrow \text{R1-H} + \text{R2-H} + 2\text{H}_2\text{S}$$

Thiophene

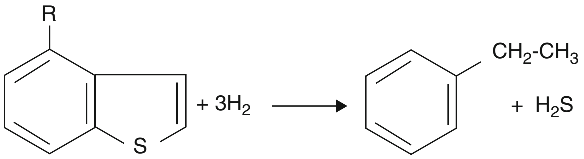
Step (1)



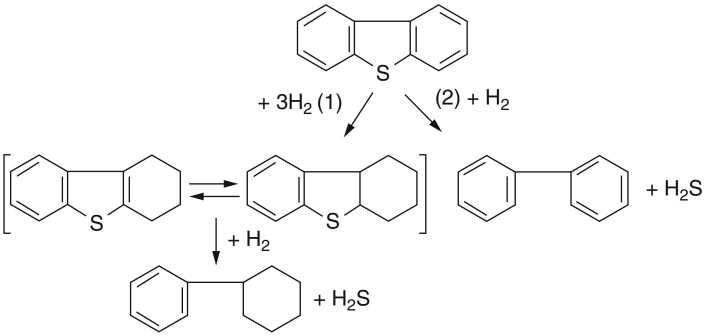
Step (2)

$$H_2C = CH\text{-}CH = CH_2 + 2H_2 \rightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

Benzothiophenes



Dibenzothiophenes



Most of the reactions are straightforward, with the exception of the hydrodesulfurization of aromatic sulfur species. This reaction is more complex, since several routes are possible: direct desulfurization, or hydrogenolysis to a biphenyl species, hydrogenation of one aromatic ring followed by hydrogenolysis, and isomerization of sterically hindering alkyl groups in the 4- and/or 6- positions followed by the preceding pair of reactions. The latter of the three mechanisms is not depicted. The relative rate of hydrogenolysis in the second step is much faster than the hydrogenation in the first step (Dugulan et al. 2008).

Shown below is a ranking of the six sulfur types ranked on the basis of ease of removal:

Easiest to remove → hardest to remove
Mercaptans → sulfides → disulfides → thiophenes → benzothiophenes → dibenzothiophenes

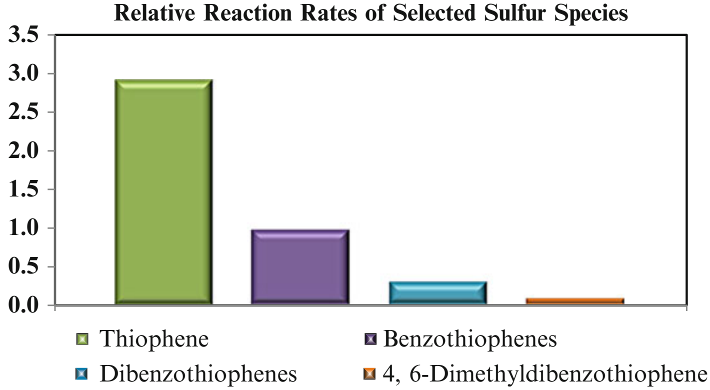


Fig. 5 Relative reaction rates of selected sulfur species

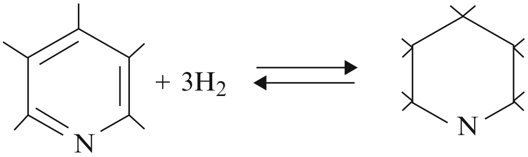
The relative ease of removing sulfur from a particular hydrocarbon fraction depends greatly on the sulfur types present. In naphtha fractions, much of the sulfur is present as mercaptans and sulfides, which makes for relatively easy sulfur removal. In gas oil fractions, the majority of the sulfur is present as benzothiophenes, naphthobenzothiophenes, and dibenzothiophenes. Hence, the sulfur is much more difficult to remove from gas oils than from naphtha fractions. And the more difficult sulfur species are found in the heavier fractions, which means that heavy gas oils are more difficult to treat than light gas oils (Fig. 5).

Nitrogen Removal

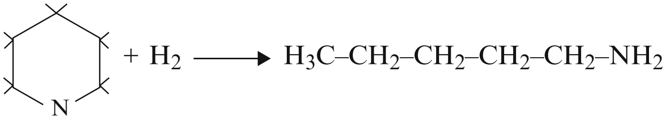
Nitrogen is mostly found in the heaviest end of petroleum fractions in five- and six- membered aromatic ring structures. Both the molecular complexity and quantity of nitrogen-containing molecules increase with increasing boiling range, making them more difficult to convert. The hydrodenitrogenation reaction proceeds through a different path from that of desulfurization. In hydrodesulfurization, the sulfur is removed first and the resulting intermediate olefin is saturated; in hydrodenitrogenation, the aromatic ring is saturated first and then the nitrogen is removed. This is shown below.

Denitrogenation Mechanism

(a) Aromatic hydrogenation



(b) Hydrogenolysis



$$+ H_2 \longrightarrow H_3C\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2$$

(c) Hydrodenitrogenation

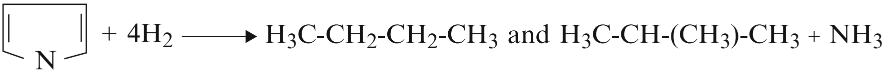
$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_2 \rightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + NH_3$$

Some typical examples of denitrogenation reactions are shown below:

(a) Amine

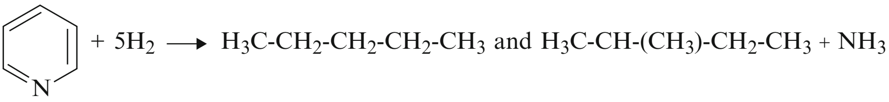
$$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2 + H_2 \rightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3 + NH_3$$

(b) Pyrrole



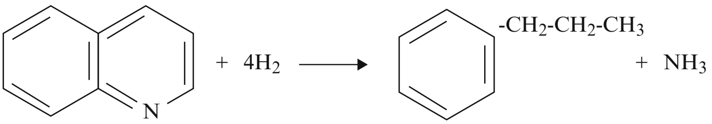
$$+ 4H_2 \longrightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_3 \text{ and } H_3C\text{-}CH\text{-}(CH_3)\text{-}CH_3 + NH_3$$

(c) Pyridine



$$+ 5H_2 \longrightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \text{ and } H_3C\text{-}CH\text{-}(CH_3)\text{-}CH_2\text{-}CH_3 + NH_3$$

(d) Quinoline



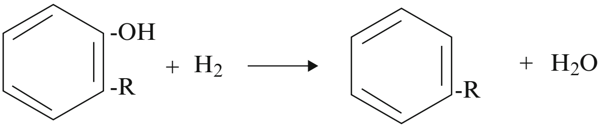
$$+ 4H_2 \longrightarrow \text{-}CH_2\text{-}CH_2\text{-}CH_3 + NH_3$$

Nitrogen is more difficult to remove and consumes more hydrogen than sulfur removal because the reaction mechanism often requires aromatic ring saturation prior to nitrogen removal. Hydrogenation of associated aromatic ring structures is very dependent on hydrogen partial pressure and is the rate-limiting reaction step in nitrogen removal. Nitrogen removal is therefore strongly dependent on hydrogen partial pressure.

Oxygen Removal

Most petroleum crudes contain low levels of oxygen. The oxygen-containing compounds are converted, by hydrodeoxygenation, to the corresponding hydrocarbon and water. The lower-molecular-weight compounds are easily hydrodeoxygenated; however, the higher-molecular-weight compounds – e.g., furans – are more difficult to convert. Shown below are typical examples of hydrodeoxygenation:

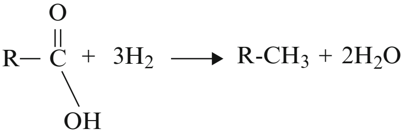
Phenols



Oxygenates

$$(CH_3)_3\text{-C-O-}CH_3 + 2H_2 \rightarrow (CH_3)_3\text{-CH} + H_2O + CH_4$$

Naphthenic acids



$$R-\overset{\overset{\displaystyle O}{\|}}{\underset{\displaystyle \backslash OH}{C}} + 3H_2 \longrightarrow R\text{-}CH_3 + 2H_2O$$

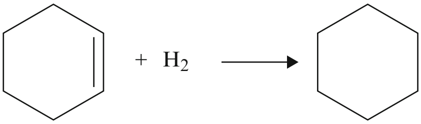
Olefin Saturation

Olefins are not found in petroleum, but are formed when processed in thermal or catalytic units. In general, fractions containing olefins are unstable and thus must be protected from contact with oxygen prior to hydrotreating to prevent the formation of polymer gums. That is especially true of feedstocks derived from thermal cracking operations such as coking and ethylene manufacturing, or naphtha cracking. Typical olefin saturation reactions are shown below:

Hexene

$$C_6H_{12} + H_2 \rightarrow C_6H_{14}$$

Cyclohexene

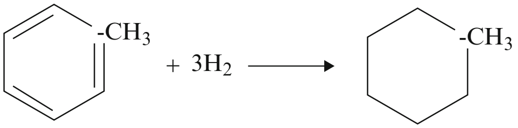


Olefin saturation reactions are very rapid and highly exothermic. While the hydrodenitrogenation reaction shows a heat of reaction of 1 Btu/lb of feed for each 100 ft^3 of hydrogen consumed and the hydrodesulfurization reaction generates 1 Btu/lb of feed for each 10 ft^3 hydrogen consumed, the olefin saturation generates 1 Btu/lb of feed for each 2 ft^3 of hydrogen consumed. If proper care is not exercised during operations, it can result in flow obstructions, such as excessive coking that can lead to pressure drop buildup and/or poor liquid flow distribution through the catalyst bed(s). Diolefins are readily hydrogenated to olefins at low temperatures, e.g., <375 °F.

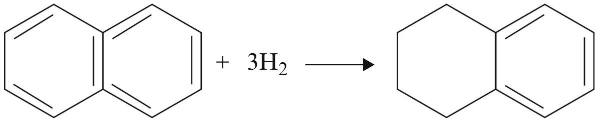
Aromatic Saturation

Saturation of aromatics is desirable for improvement of the properties of petroleum products, e.g., smoke point, diesel index, etc. The aromatics found in the naphtha to gas oil boiling range are present as one-, two-, and three-ring aromatics – often referred to as mono-, di-, and tri-aromatics. Typical reactions are shown below:

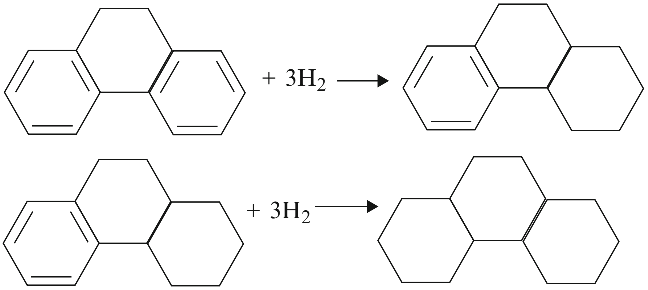
One ring – toluene



Two rings – naphthalene



Three rings – phenanthrene



The reactions shown above provide the mechanism by which polyaromatic compounds saturate, via a stepwise mechanism: from tri-aromatics, to di-aromatics, to mono-aromatics. The end products are naphthenic. Ring opening does not occur in hydrotreating (it does in hydrocracking) because a hydrotreating catalyst's support is not designed with significant acidity, unlike a hydrocracking catalyst. The aromatic saturation reaction is strongly favored by high hydrogen partial pressure. Unlike all the other hydrotreating reactions, the amount of conversion of aromatics becomes equilibrium limited at higher operating temperatures within the commercial operating range, since the naphthene dehydrogenation reverse reaction becomes favored when temperature is increased. The optimum temperature for maximum aromatic saturation depends on LHSV, hydrogen partial pressure, and catalyst type but typically lies in the range of 670–730 °F.

Mono-aromatic rings are much more difficult to saturate than the di- and tri-aromatic rings because the saturation of the last aromatic ring requires the most energy. This means that as aromatic saturation proceeds, there is little progress in total aromatics reduction until most, if not all, of the di- and tri-aromatics have been saturated. The complete saturation of aromatics requires the application of noble metal catalysts in a sulfur- and H_2S-free environment and is generally not possible in conventional hydrotreating with base metal sulfide catalysts.

Metals and Nonmetal Removal

Most metallic contaminants are present as organometallic compounds. Once deposited, these metals contribute to catalyst deactivation; unlike coke, they cannot be removed by regeneration. In naphtha hydrotreating, the most commonly occurring contaminants are arsenic from certain crude sources, alkali metals (e.g., Ca, Na), mercury from certain condensates, and silica from polydimethylsiloxane-based antifoam agents used in visbreakers, delayed cokers, and deepwater drilling for crude oil. Gas oil streams may contain traces of nickel and vanadium in the heavier fractions. These too are deposited on the catalyst and contribute to deactivation. Atmospheric residua can contain metals, almost exclusively Ni and V, in the 20–500 ppm range. Hydrodemetallation of that type of feedstock is an important goal of processing and special hydrodemetallation catalysts are applied for that purpose. Hydrodemetallation of nickel and vanadium occurs before any substantial hydrodesulfurization and conversion of the feedstock take place:

$$\text{R-Me} + H_2S \rightarrow \text{R-}H_2 + \text{MeS}$$

Arsenic trapping catalysts, necessary for trapping organo-arsine contaminants such as triethylarsine, are typically NiS based. These trapping catalysts rely on arsenic binding with NiS to form nickel arsenides. Higher operating temperatures lead to greater arsenic pickup. In the case where arsenic and silica are both present, it is advantageous to utilize a moderate concentration of Ni, as in 10–15 wt%, so that the trapping catalyst will still have sufficient surface area to trap silica.

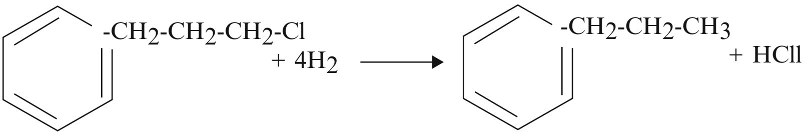
Alkali metals can originate from various crudes, from mis-operation of the crude desalter, and from various operations which utilize caustic soda. Alkali metals adsorb to the acid sites of the catalyst support, reducing activity. Their presence may also be indicated by a rapid increase in pressure drop, especially in the layers above the primary hydrotreating catalyst(s). During catalyst regeneration, the presence of alkali metals tends to sinter the catalyst surface, resulting in surface area loss beyond what is typically observed.

Mercury contaminants can generally be classified as hydrocarbon soluble, water soluble, and asphaltenic. These can be found, in various proportions, within those crudes extracted near tectonic plate boundaries. Elemental mercury and alkyl-mercury compounds will exit a crude column with the product streams according to their relative volatility, from the LPG through to the heavy diesel. Water-soluble mercury would be found in the heels of crude storage vessels and in the aqueous drawoff from desalters. Asphaltenic mercury can be found in the atmospheric resid and vacuum resid refinery streams. Asphaltenic mercury can be converted to the lighter, hydrocarbon-soluble forms of mercury through hydroprocessing, which can be problematic for an equipment that processes finished product streams, since elemental mercury will form amalgams with Cu-containing alloys and with equipment constructed at least in part of aluminum, leading to embrittlement failures. In general, mercury is not substantially trapped by typical hydrotreating catalysts, so installation of a posttreat bed of mercury-trapping adsorbent may be needed to prolong downstream equipment life and to otherwise satisfy market requirements (Hadden et al. 2010).

Silica guard catalysts, loaded above the primary HDS catalysts in naphtha hydrotreaters, are designed with high surface area. These catalysts are often designed with a modest hydrogenation function via the NiMoS active phase. The heat release of hydrogenation in this reactor drives the silica capacity higher than an equivalent silica guard support without a NiMoS active phase. The adsorption mechanism is directed by the available surface area and the operating temperature, such that higher temperatures and surface areas result in greater silica capacities. Silica adsorption can be tracked by proxy via the regular monitoring of the hydrodenitrogenation performance, rather than the hydrodesulfurization performance. Several products of polydimethylsiloxane decomposition have been identified. It has been proposed that the decomposition products' silanol groups react with the alumina support hydroxyl groups (Chainet 2012).

Halide Removal

Organic halides, such as chlorides or bromides, can be present in petroleum fractions at trace levels. Under hydrotreating conditions, organic halides are largely converted to the corresponding hydrocarbon and hydrogen halide. The typical reaction is shown below:



With the above to serve as an introduction and overview, a number of important hydrotreating applications are presented below in greater detail.

Distillate Hydrotreating

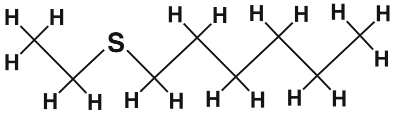
As specifications for diesel fuels became ever more stringent, especially with regard to sulfur but also with regard to aromatics and density, improved hydrotreating technology is needed to satisfy the new specifications. This has led to the development of ever more active catalysts, e.g., Type II hydrotreating catalysts, and an intensification of research and development efforts aimed at improving hydrotreating fundamentals understanding.

Catalytic Chemistry of Diesel Desulfurization

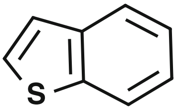
Full-range diesel has a rather broad boiling range, from ~300 °F to ~700 °F, and contains a very broad range of sulfur compounds ranging from lower-molecular-weight alkyl sulfides and benzothiophenes through dibenzothiophene, substituted dibenzothiophenes, and higher-molecular-weight naphthobenzothiophenes. Generally, all sulfur compounds boiling lower than 4-methyldibenzothiophene undergo rapid desulfurization at conditions required for production of 10 wppm sulfur diesel (ULSD).

Examples of typical sulfur compounds found in diesel fuels are presented below, ranging from the easiest sulfur compounds to convert to the most difficult:

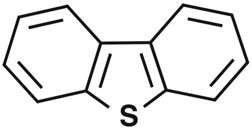
Ethylhexyl sulfide:



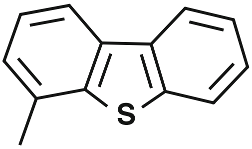
Benzothiophene:



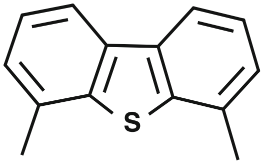
Dibenzothiophene:



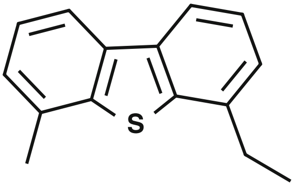
4-methyldibenzothiophene:



4,6-dimethyl dibenzothiophene:



4-ethyl, 6-methyl-dibenzothiophene:



The most difficult sulfur compounds to desulfurize are the substituted dibenzothiophenes, especially those where the substituent is adjacent to the sulfur atom, in the 4- position or in the 4- and 6- positions for the case of double substitution. These compounds, such as 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene and similar structures, present the most difficult compounds to desulfurize.

Analytical Characterization

Approximately 10 years ago saw the introduction of a powerful new analytical technique applied to the characterization of petroleum fractions, comprehensive gas chromatography (GC), or "two-dimensional" GC, commonly referred to as GCxGC. While the description of the method may be found elsewhere, the results offer much greater insights into the chemical composition of petroleum fractions than was possible previously. A comprehensive GC 3D representation of the hydrocarbon structures present in a distillate is shown in Fig. 6.

The paraffinic structures appear as spikes along the x-axis with increasing molecular weight.

Single-ring aromatics appear as families of spikes angling at a 45° angle to the right, again with increasing molecular weight as one progresses to the right from one family to the next, e.g., from C_3 benzenes to C_4 benzenes. The larger spikes, beyond the indane "range," are the di-aromatics (naphthalenes) again arranged in "families" of increasing molecular weight. The next, smaller, series of spikes are three-ring aromatics, followed by traces of multi-ring aromatics. All compounds may be identified and quantified to fully characterize the composition of the distillate.

A similar GCxGC analysis focusing on sulfur compounds is shown in Fig. 7.

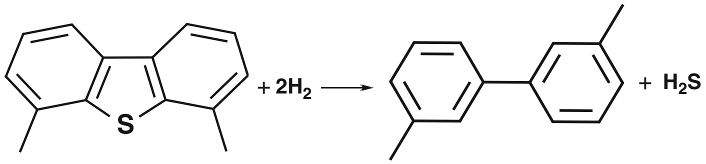
The type of compound is shown, e.g., thiophene, benzothiophene, or dibenzothiophene, as well as the extent of substitution on the ring.

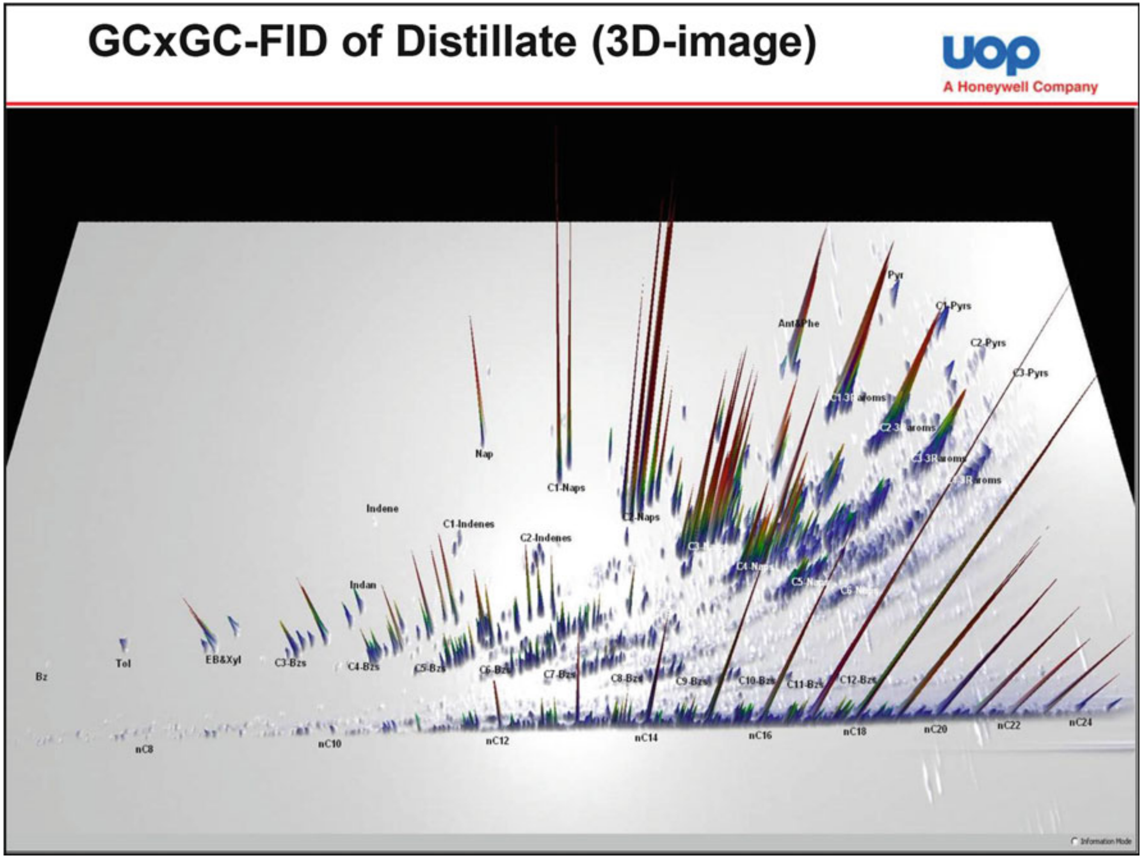
The same can be accomplished for nitrogen species (Fig. 8).

Catalysts and Reactions

Both Co/Mo and Ni/Mo catalysts have been employed in the hydrotreatment of distillate fuels. While, in the early stages of development, the Ni/Mo catalysts were judged to be slightly more active in hydrodesulfurizing diesel fuels to ULSD (<10 wppm Sulfur) specifications, more recent developments have provided Co/Mo catalysts with equivalent activity to ULSD. The observations that Ni/Mo catalysts may be more active for ULSD is in accord with the theory that for the desulfurization of the most difficult sulfur molecules, dimethyldibenzothiophenes with substituent groups in the 4- and 6- positions, such as 4,6-dimethyldibenzothiophene, one of the rings needed to undergo saturation of one of the rings, allowing the sulfur atom to be more accessible due to the greater flexibility of the saturated ring. This pathway for desulfurization was termed the "hydrogenation" pathway and was most pronounced over Ni/Mo catalysts with their higher activity for saturation. The other pathway involved direct abstraction of the sulfur atom, and formation of H_2S was termed the "direct abstraction" route and was the dominant route on Co/Mo catalysts.

The direct abstraction reaction is depicted below:





GCxGC-FID of Distillate (3D-image)

Fig. 6 Comprehensive GC 3D image of hydrocarbon content of distillate

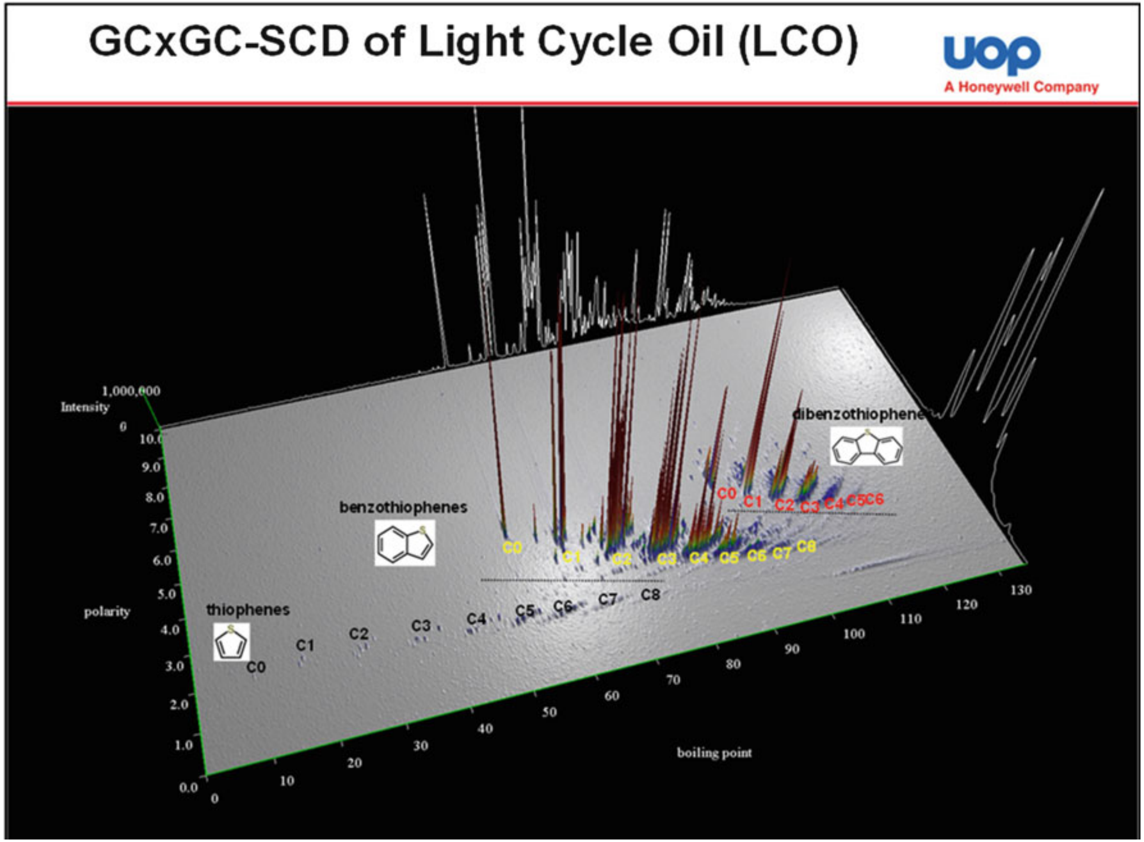


Fig. 7 Comprehensive GC 3D image of sulfur compounds in distillate

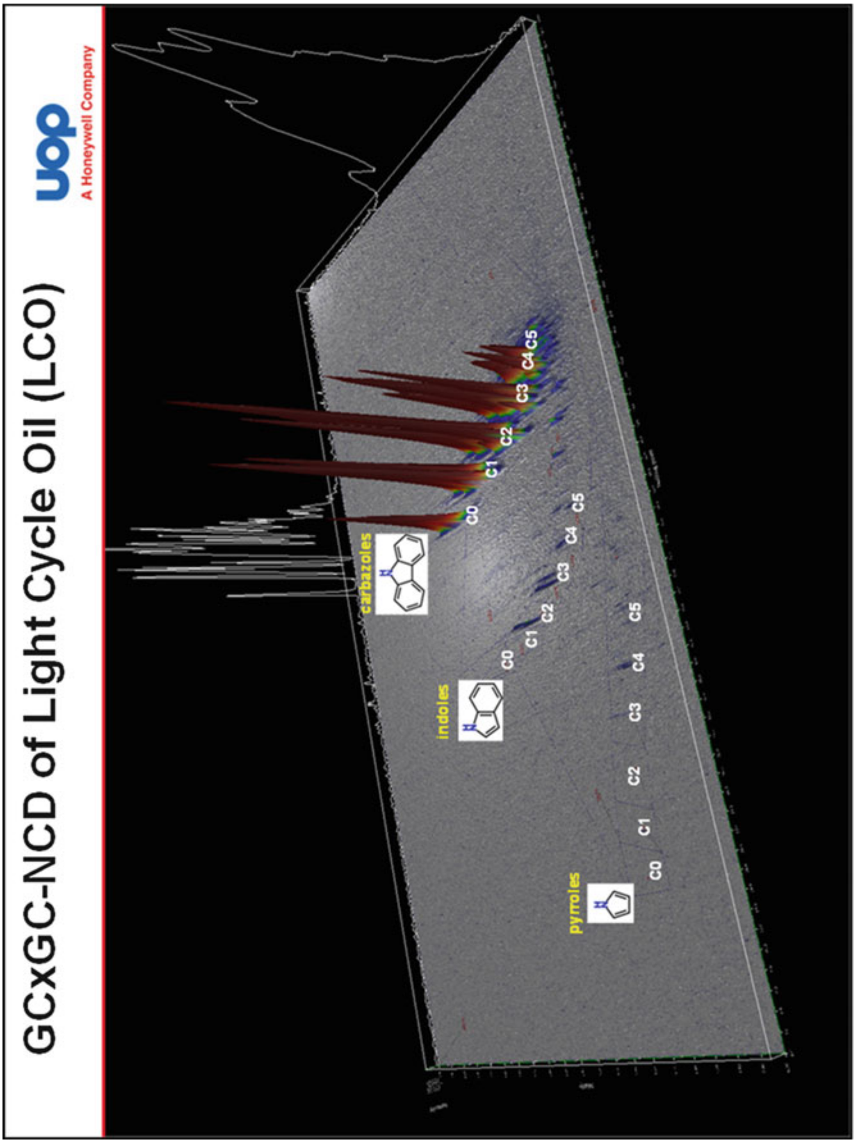
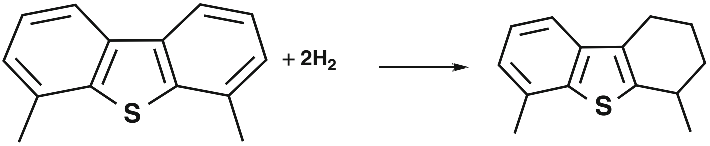
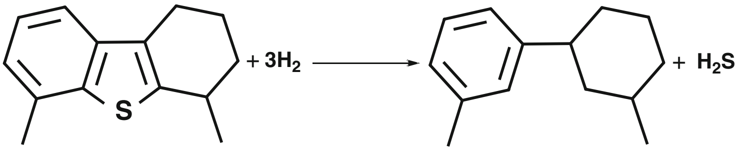


Fig. 8 Comprehensive GC 3D image of nitrogen compounds in distillate

The “hydrogenation” pathway, in simplified form, is



followed by



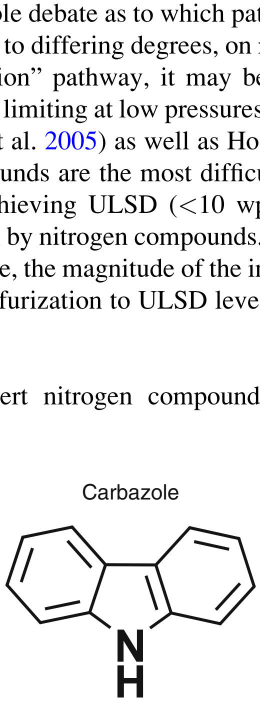
There has been considerable debate as to which pathway is dominant; it is likely that both are active, although to differing degrees, on modern Type II catalysts. For the case of the “hydrogenation” pathway, it may be inferred that the reversible saturation of one ring may be limiting at low pressures. This issue was addressed by Jones and Kokayeff (Jones et al. 2005) as well as Ho (Ho 2003, 2004).

While these sulfur compounds are the most difficult to desulfurize and present the greatest challenge to achieving ULSD (<10 wppm S diesel), an additional complication is the inhibition by nitrogen compounds. While inhibition by nitrogen has been known for some time, the magnitude of the inhibitory effect can only been appreciated when deep desulfurization to ULSD levels is required.

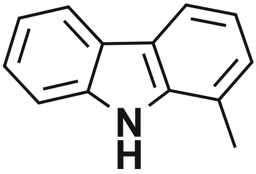
Nitrogen Compounds

The most difficult to convert nitrogen compounds present in diesel are the carbazoles.

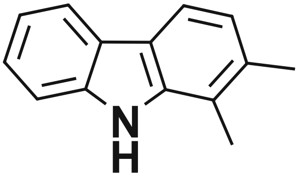
Carbazole



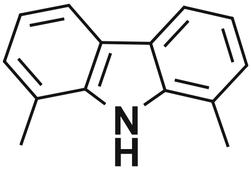
Methyl Carbazole



1,2-Dimethyl Carbazole



1,8-Dimethyl Carbazole

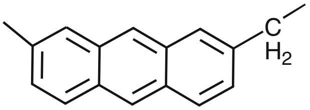


The carbazole compounds boil within the same boiling range as the substituted dibenzothiophenes, ~620–660 °F. At conditions that desulfurize the feed to <10 wppm S, hydrodenitrogenation is very extensive and is essentially complete.

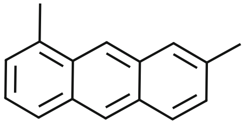
Aromatics

Aromatic compounds are another class of compounds that are of importance in the hydrotreating of distillate fuels. Aromatic compounds may be classified in three main classes – multi-aromatics (3+ condensed rings), di-aromatics, and mono-aromatics.

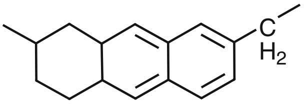
2-Ethyl-7-methylanthracene



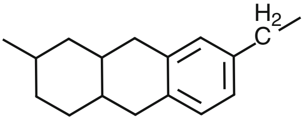
1,7-Dimethylanthracene



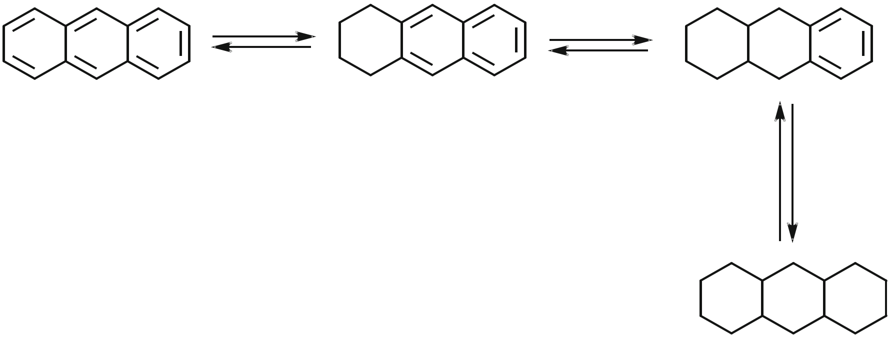
7-Ethyl-2-methyl-1,2,3,4,4a,9a-hexahydroanthracene



7-Ethyl-2-methyl-1,2,3,4,4a,9,9a,10-octahydroanthracene



Saturation reactions of aromatic compounds proceed sequentially



The saturation reactions are exothermic and reversible. These reactions consume hydrogen (not shown) but also improve the quality of the diesel fuel by increasing the cetane number; therefore, they are not necessarily undesirable, and distillate hydrotreater pressures and catalyst choices are sometimes dictated by the desire to achieve a given cetane number. Additionally, there is evidence that aromatics may inhibit the desulfurization of the most difficult, sterically hindered dibenzothiophenes, sulfur species (Jones et al. 2004).

Feedstocks

Feed to a distillate hydrotreating unit may be any blend or combination of straight-run distillate (SRD), coker distillate (LCGO), and light cycle oil (LCO).

Straight-run distillate is, as the name implies, derived from the distillation of crude oil and is the cut obtained crude column, boiling in the range of ~300 °F to ~730 °F. Straight-run distillates are characterized by high API gravities, in the range of 28–32 and sometimes higher and low levels of sulfur (0.5–1.5 wt%), nitrogen (40–100 wppm), and aromatics (usually <20 wt% total).

Coker distillates, while boiling in the same range as straight-run distillates, are derived from coking operations and differ from straight-run distillates in that they contain greater amounts of sulfur (up to 2.5–3.0 wt are possible), higher levels of nitrogen (500–1,500 wppm), and somewhat higher aromatics content. The additional feature that sets them apart is the presence of olefins (typically measured as a bromine number) with a bromine number of 10–30. Due to the olefin content and the higher aromatics content of coker distillates, their processing in a hydrotreater is accompanied by a significant temperature rise due to the exothermic saturation reactions of olefins and aromatics. Finally, the presence of fragments of the Si-based antifoam agent used in cokers will deactivate the hydrotreating catalysts processing the coker streams.

Light cycle oils are characterized by low gravities (API gravities in the range of 12–22) and high levels of aromatics. Aromatics levels in LCOs may be as high as 70 wt% with the di-aromatics being the most prevalent. A typical aromatics distribution of an LCO containing 70 wt% aromatics may be 10 wt% mono-aromatics, 45 wt% di-aromatics, and 15 wt% tri-aromatics. The concentration of sulfur in an LCO may range from ~500 wppm (for an LCO derived from an FCC with an FCC feed pretreater) to ~2 wt% for FCC units processing high-sulfur feeds without a FCC feed pretreater. Nitrogen levels are not usually very high, reaching into several hundred wppm. Processing LCO in a hydrotreater is accompanied by high hydrogen consumption due to the saturation of the aromatic compounds and high heat release and temperature rise due to the exothermic nature of the saturation reactions. Temperature control is important due to the rapid saturation rate of the multi-ring aromatics.

Process Configuration

A simplified process flow diagram of a distillate hydrotreater is shown in Fig. 9.

The feed enters the feed surge drum from which it is pumped through a bank of feed/effluent exchangers, is mixed with recycle gas, is heated to reaction temperature, and enters the reactor. Reactor effluent is passed through a bank of feed/effluent exchangers and a fin fan cooler and then enters the separator. The gas is recovered and sent to an amine scrubber to remove hydrogen sulfide and ammonia and then routed to a recycle gas compressor and recycled to the reactor. The liquid product is then directed to a flash drum, where any light gases are recovered overhead while the hydrocarbon is routed to a stripper to remove any dissolved hydrogen sulfide and ammonia in the product as well as any wild naphtha formed. The stabilized product is then sent to blending or storage. Wash water is added to the reactor effluent just upstream of the air fin cooler to absorb the ammonia produced in order to avoid precipitation of ammonium hydrosulfide salts in the colder sections for the plant.

The process flow diagram shows one quench location between two catalyst beds. The number of beds and quenches will depend on the type of feed being processed with SR distillates requiring only one point while LCGOs and LCOs requiring three or more beds with interbed quenches to control temperature rise.

Process Conditions

Process conditions applied in distillate hydrotreating today are much more severe than they were in the past. This is due primarily to the requirement to produce

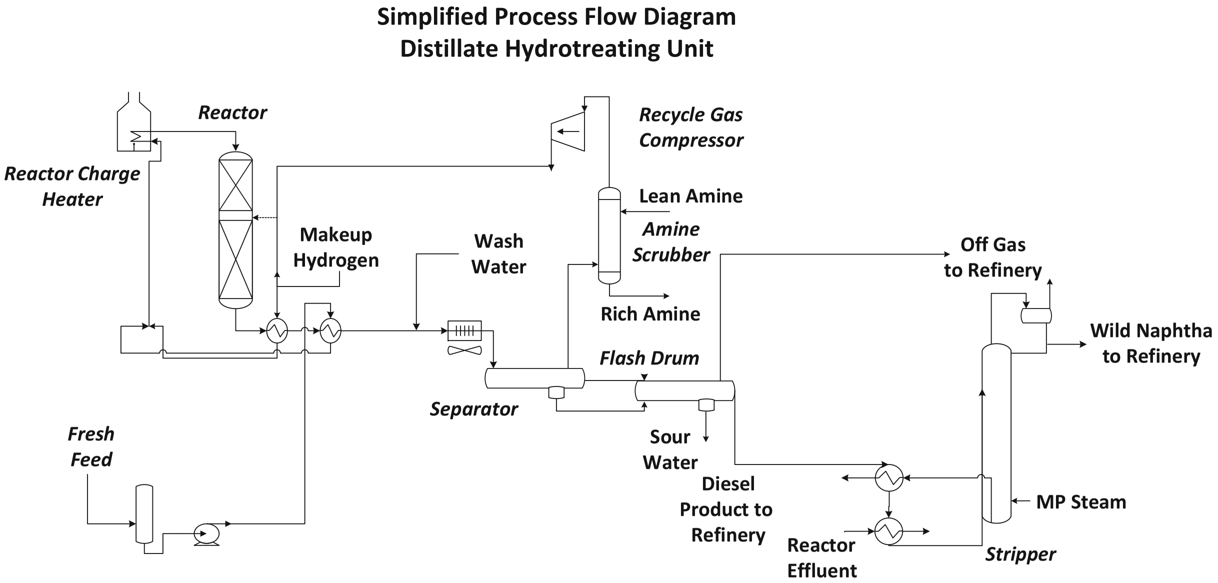


Fig. 9 Simplified process flow diagram of a distillate hydrotreater

Table 1 Distillate hydrotreater typical process conditions

Feed type	SRD (straight run)	LCGO (coker distillate)	LCO (Light cycle oil)
LHSV, h^{-1}	1.5–2.0	1.0–2.0	0.75–1.5
SOR temperature, °F (°C)	630–660 (330–350)	640–680 (340–360)	670–710 (355–375)
Pressure, psig (barg)	600–700 (41–48)	700–800 (48–55)	750–1,000 (50–70)
H_2/Ol, SCF/B (Nm^3/m^3)	1,500 (250)	2,000 (340)	2,000 (340)

ULSD (ultra-low-sulfur diesel, i.e., with a sulfur level <10 wppm). Typical process conditions are shown in Table 1.

The variation in process conditions is due to a number of factors including feedstock characteristics, such as sulfur content and nitrogen content, feedstock type, and process objective: hydrodesulfurization to ULSD levels and/or cetane improvement. Note that conditions to effect significant improvements in cetane are usually sufficient to produce ULSD sulfur specifications.

Naphtha Hydrotreating

Introduction

Naphtha is a general term that refers to the lightest liquid fraction of material in the refinery. A full boiling range naphtha typically has an initial boiling point of 85 °F (30 °C) and a final boiling point ranging from 380 °F to 420 °F (193–215 °C), which roughly corresponds to C5 through C12 material. The back-end cut point of full boiling range naphtha ultimately depends on the individual refinery's configuration and whether the objective is to maximize gasoline, diesel, or petrochemical feedstock production.

Straight-Run Versus Cracked Naphtha

Naphtha can be broadly categorized as either straight-run or cracked naphtha. Stabilized naphtha from the crude column is referred to as straight-run material, since it has not been exposed to any severe thermal or catalytic process conditions and therefore has a negligible olefins content. In contrast, naphtha produced from a carbon rejection process, such as a coking or fluidized catalytic cracking, is considered a cracked stock and will contain a significant olefins content. More specifically, cracked naphtha will contain both monoolefins and diolefins; the reactivity of these olefin species requires specific design considerations.

This section will primarily focus on straight-run and coker naphtha, since these two streams often share the same disposition in the refinery. When producing gasoline, refiners tend to handle FCC naphtha differently, since it has a relatively

Table 2 Properties of naphtha streams

	Straight-run naphtha	Coker naphtha
Sulfur, wppm	500	5,700
Nitrogen, wppm	10	150
Silicon, wppm	0	3–7
Diene, wt%	Nil	3
Olefins, wt%	0	25

higher octane value and therefore it requires selective desulfurization to meet final gasoline product sulfur specifications.

In addition to the difference in olefin content, straight-run naphtha contains less sulfur and nitrogen than its coker naphtha counterpart from the same crude source. Furthermore, coker naphtha also contains silicon due to the use of antifoaming agents in the upstream coking unit, which can negatively affect hydrotreating catalyst as well as catalysts in downstream operating units, such as a naphtha reforming process.

Table 2 provides an example of typical properties of straight-run naphtha compared to that of coker naphtha.

Naphtha Disposition

For refineries that produce gasoline, the inherent octane values of the straight-run and coker naphtha stream are too low to allow blending of the entire stream into the gasoline pool. To ensure that the naphtha stream can be fully utilized for gasoline production, the refiner will send the naphtha stream to a catalytic naphtha reforming unit to increase the stream's octane value, primarily via dehydrogenation of naphthenes to aromatics. Prior to being processed in the reforming unit, the naphtha stream needs to be effectively hydrotreated to minimize the presence of organic sulfur, nitrogen, other trace contaminants, and olefins to avoid poisoning of the precious metals reforming catalyst and fouling its continuous regenerator. The final liquid product from the reforming unit is often referred to as reformate and can be used as a low-sulfur (sulfur-free), high-octane gasoline blend component.

Alternatively, some refiners choose to minimally hydrotreat their naphtha stream and sell the lightly treated naphtha on the market as feedstock for petrochemicals production. In areas with high bitumen crude production, naphtha can also be utilized as a diluent to improve the properties of bitumen crude for transportation.

Processing Objectives and Considerations

Table 3 summarizes the recommended hydrotreated naphtha quality for feed to a naphtha reforming unit.

In order to achieve the reformer feed quality, the below contaminant removal reactions need to take place in the presence of the appropriate grading material and

Table 3 Reformer feed specifications

	Product
Sulfur, wppm	0.5 max
Nitrogen, wppm	0.5 max
Silicon, wppm	Nil
Diene, wt%	Nil
Olefins, wt%	Nil

hydrotreating and under the right set of process conditions. In the era of leaded gasoline, gasoline re-run through the naphtha hydrotreater also required hydrodemetallation to prevent lead and other metals from poisoning the naphtha reforming catalyst.

Desulfurization (HDS for hydrodesulfurization) difficulty depends on the type of sulfur molecule, such as mercaptan, sulfide, thiophenol, thiophene, or benzothiophene sulfur. Relatively, mercaptan sulfur is the easiest type of sulfur to remove, whereas benzothiophene is approximately 15 times harder to remove than mercaptan sulfur. Sulfurs contained in an aromatic structure are removed by initially opening the ring, removing the sulfur molecule, and saturating the resulting olefin molecule.

Denitrogenation (HDN for hydrodenitrogenation) is generally more difficult than desulfurization due to the structure of the nitrogen compound. Nitrogen contained in an aromatic structure is removed via a different mechanism than sulfur contained in an aromatic compound. In denitrogenation, the aromatic ring is first saturated, then the ring is cleaved, and finally the nitrogen molecule is removed. Since aromatic saturation is required to remove aromatic bound nitrogen, the design pressure of the hydrotreating unit is more sensitive to the nitrogen content of the feed rather than the sulfur content of the feed.

Olefin saturation is a relatively rapid reaction that occurs alongside with desulfurization and denitrogenation. There are two main types of olefins to consider when processing cracked naphtha stock: diolefins or dienes (molecules containing two double bonds) and monoolefins (molecules containing a single double bond).

Dienes can potentially polymerize and form gums if introduced to hydrotreating catalyst and hydrogen at the typical temperatures required for hydrodesulfurization and denitrogenation. Gum formation can either occur in feed heat exchangers or at the top of the first reactor catalyst bed, leading to fouling and pressure drop issues, which could ultimately lead to an unplanned unit shutdown and shortened cycle length.

For combined naphtha streams with a significant amount of diene content, the stream can first be treated in a separate diolefin saturation reactor to minimize the risk of gum formation. The diolefin reactor utilizes a relatively low-activity hydrotreating catalyst and operates within a low enough temperature range to ensure the diolefin saturation reaction preferentially occurs instead of the polymerization reaction. After the dienes are stabilized, the naphtha stream can then be heated up and sent to a second reactor loaded with the main hydrotreating catalyst to complete the removal of sulfur and nitrogen.

Once the diene content of a cracked naphtha blend is addressed, the next consideration focuses on the monoolefin molecules. The olefin saturation reactions occur fairly rapidly in the main hydrotreating reactor and result in a substantial amount of heat release. The reaction occurs so readily that at start of run conditions the majority of the olefins are saturated within the first bed of a hydrotreating reactor, resulting in a significant heat rise across the first bed, and smaller temperature rises in the following bed. It is important to manage the heat released due to olefin saturation in order to prevent coking, catalyst sintering, or uneven catalyst utilization across the different catalyst beds. This can be achieved by recycling some of the olefin-free reactor product with the fresh feed in order to dilute the olefins available for saturation. Ultimately, the proper management of olefin heat release is required to achieve the desired catalyst cycle length in the main hydrotreating reactor.

Potential for Recombination with Cracked Stock

Due to presence of olefins in coker naphtha material, the potential for mercaptan recombination exists. The below equation describes the equilibrium between mercaptans and olefin and H_2S present in the reactor. It is desirable to favor the left-hand side of the equation so that the sulfur content from the feed is present in the off-gas from the unit instead of the liquid product. This can be done by installing a relatively small posttreat reactor that operates at a lower condition than the main hydrotreating reactor, which favors the left-hand side of the equation and reduces the amount of mercaptan sulfur than can be found in the hydrotreated naphtha material:

$$\mathrm{R = R' + H_2S \leftrightarrow R\text{-}R'\text{-}SH}$$

Typical Operating Conditions

Table 4 compares the general range of operating conditions for the main hydrotreating reactor for both a straight-run naphtha hydrotreating unit and a coker naphtha hydrotreating unit.

Table 4 Naphtha hydrotreater operating conditions

	SR naphtha only	SR and coker naphtha
Pressure, psig (barg)	300–500 (21–35)	500–800 (35–50)
Main HT reactor LHSV, h^{-1}	4–12	2–8
Gas-to-oil ratio, scf/bbl (Nm^3/m^3)	250–400 (40–75)	900–3,000 (150–500)

Pressure

Hydrotreating feeds with a significant amount of coker naphtha material typically contain higher amounts of nitrogen, which requires the hydrotreating reactor to operate at higher pressures to ensure the appropriate denitrogenation reactions take place to meet the 0.5 wppm nitrogen specification for reformer feed.

LHSV

In addition to higher sulfur and nitrogen contaminant levels in coker naphtha feed blends, the presence of Si also requires the addition of trapping material, which lowers the liquid hourly space velocity (LHSV) in the hydrotreating unit. Liquid hourly space velocity is the liquid feed rate divided by the catalyst volume and is expressed in units of inverse time. LHSV is inversely proportional to the liquid residence time in the catalyst. The amount of Si trap required depends on the concentration of Si in the feed blend, the trapping capacity of the hydrotreating catalyst or guard material, and the desired cycle length:

$$\text{LHSV}\ [1/\text{h}] = \frac{\text{Charge rate}\ \left(\text{ft}^3/\text{h or m}^3/\text{h}\right)}{\text{Volume catalyst}\ \left(\text{ft}^3\text{or m}^3\right)}$$

Gas-to-Oil Ratio

A minimum H_2 partial pressure in the reactor is required to ensure reasonable rates of reactions and additionally to prevent possible coking of the catalyst. As summarized in the table above, higher levels of contaminants require higher levels of gas-to-oil ratio in the hydrotreating unit.

The gas-to-oil ratio is calculated as follows:

$$\text{Gas to oil ratio [SCFB]} = \frac{\text{Total gas to reactors (SCFH or Nm}^3/\text{h)}}{\text{Raw oil charge (BPH or m}^3/\text{h)}}$$

Diene Reactor

A diene reactor typically operates with a LHSV varying from 3 to 6 h^{-1} and a gas-to-oil ratio ranging from 250 to 1,000 scf/bbl (40–170 Nm^3/m^3).

Posttreat Reactor

The posttreat reactor LHSV can range from 12 to 18 h^{-1}. Since the total reactor effluent is sent to the posttreat reactor prior to any gas-liquid separation, treat gas is primarily introduced as a quench to ensure the posttreat reactor operates at a low enough temperature to favor the formation of H_2S and a saturated hydrocarbon over the formation of a mercaptan. For additional assurance of satisfying naphtha reforming and paraffin isomerization feed sulfur requirements, a sulfur guard can be applied to treat the stabilized product. NiS-based adsorbents are typically applied in sulfur guard bed services.

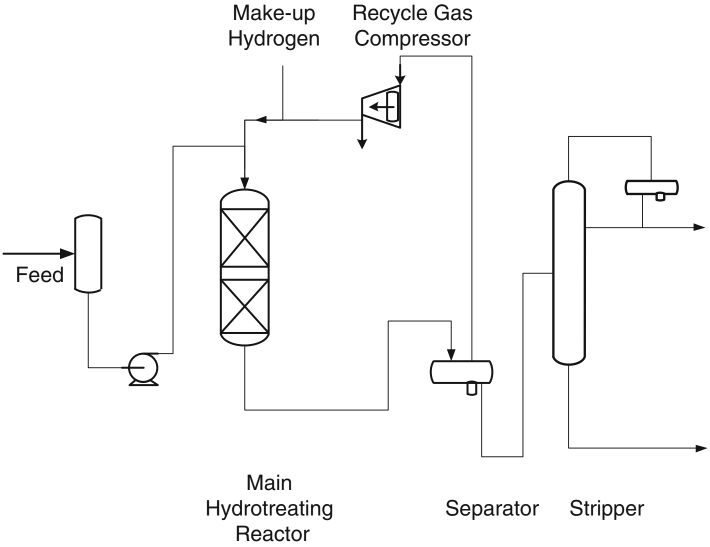


Fig. 10 Simplified process flow diagram of a naphtha hydrotreater

Process Configuration

Figure 10 provides a simplified flow diagram of a straight-run naphtha hydrotreating unit. Typically a recycle gas scrubber is not required when hydrotreating straight-run naphtha alone. The stabilized product from the bottom of the stripper unit can either be sent directly to the reforming unit as feed or be split into light and heavy naphtha portions in a downstream naphtha splitter.

Figure 11 presents a simplified flow diagram of a typical coker naphtha hydrotreating unit. Additional pieces of equipment are required to address the higher levels of sulfur and nitrogen contaminant as well as the presence of olefins in coker naphtha material. As discussed earlier, the coker naphtha hydrotreating unit will also contain a diene reactor and a posttreat reactor. Another differentiating feature in the coker naphtha flow scheme is the recycle of treated product with fresh feed to manage the exotherm in the main hydrotreating reactor. Lastly, a recycle gas scrubber will typically be specified to remove H_2S and NH_3 from the recycle gas stream to minimize inhibition of catalyst activity in the main hydrotreating reactor.

Desulfurization of FCC Gasoline

Introduction

While hydrotreating of most other feedstocks is characterized by a desire for the most active catalyst to effect a given conversion (whether of sulfur, nitrogen, or aromatics), the case of desulfurization of FCC gasoline is unique in that it is

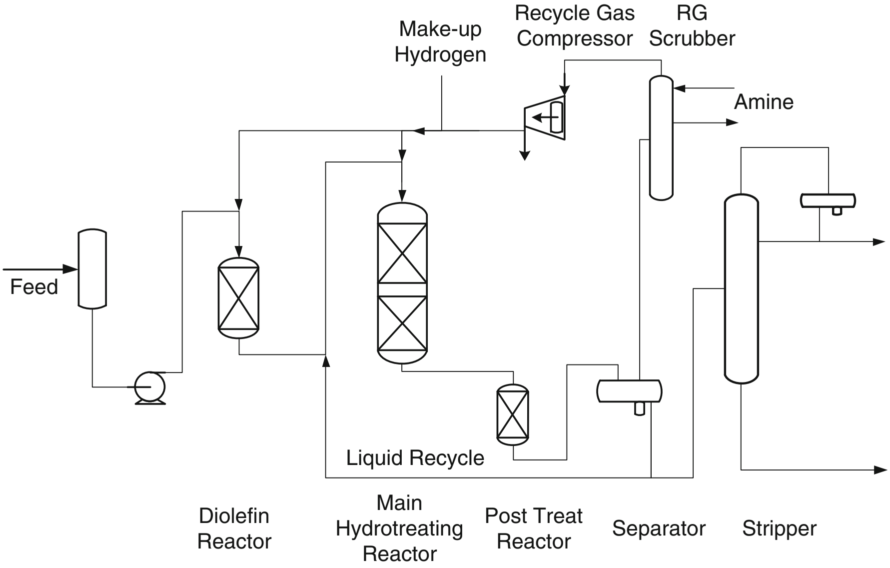


Fig. 11 Simplified process flow diagram of a coker naphtha hydrotreater

characterized by selectivity rather than activity considerations. Specifically, it is desired to reduce the sulfur level to the required specification while minimizing the saturation of olefins and subsequent octane loss.

Composition of FCC Gasoline

FCC gasoline is composed of n-paraffins, i-paraffins, n-olefins, i-olefins, cyclic olefins, naphthenes, and aromatics. The desirable, high-octane, components are olefins and aromatics and, to a lesser extent, i-paraffins.

Sulfur compounds present in FCC gasoline include mercaptans, sulfides, and thiophenes as well as benzothiophenes. While these compounds do have differences in reactivity, i.e., some undergo desulfurization more easily than others, the differences in reactivity are not nearly as pronounced as observed for sulfur compounds present in distillates. The most difficult sulfur compounds to desulfurize in FCC gasoline are thiophenes with substituent groups in the 2- position, e.g., 2-thiophene, 2-ethylthiophene. 2,5-dimethyl thiophene, and 2-ethyl-5-methyl thiophene. While these compounds may be more difficult to desulfurize than the sulfides and mercaptans, the greatest complicating factor in the desulfurization of FCC gasoline is recombination, i.e., the formation of mercaptans from the olefins present in the feed and the H_2S formed during desulfurization.

Recombination

Recombination is the name applied to the reaction of olefins with H_2S to form mercaptans:

$$R = R' + H_2S \leftrightarrow \text{R-R}'\text{-SH}$$

Recombination is a reversible reaction that approaches equilibrium at conditions used to effect desulfurization. It is an exothermic reaction and becomes less favorable with increasing temperature. To fully appreciate the complications caused by this reaction consider the following expression for the equilibrium between the species involved, olefins, H_2S, and mercaptans:

$$K = \frac{P_{RSH}}{P_0 P_{H_2S}}$$

This may be rewritten as

$$W_{RSH} = f * K W_o P_{H_2S}$$

where W_{RSH} is the weight fraction (in wppm) of mercaptan in the liquid hydrocarbon, W_o is the weight fraction of olefins in the liquid hydrocarbon, P_{H2S} is the partial pressure of H_2S, K is the equilibrium constant, and f is a conversion factor.

The amount of recombinant mercaptan remaining in the liquid hydrocarbon is dependent upon the concentration of olefins present and the partial pressure of H_2S. One may simplify this a bit further for clarity as follows:

$$W_{RSH} = f * K W_o W_{FS}$$

where W_{FS} is the sulfur content of the feed, in wppm.

What can be gleaned from this is that the amount of recombinant mercaptan that will remain in the gasoline is dependent on the weight fraction of olefins and the sulfur content of the feed, where it was assumed that all the sulfur content originally present in the feed is converted to H_2S. The higher the olefin content of the product (it is desired to preserve olefins) and the higher the sulfur content of the feed, the higher the recombinant mercaptan sulfur that will remain in the gasoline, thus placing a limit on the extent of “desulfurization” that is possible to achieve.

An additional complication arising from recombination is the loss of olefins by the desulfurization of the mercaptans:

$$R = R' + H_2S \leftrightarrow \text{R-R}'\text{-SH}$$

$$\text{R-R}'\text{-SH} + H_2 \rightarrow \text{R-R}' + H_2S$$

Thus, while the formation of recombinant mercaptans is a reversible, equilibrium-dominated reaction, there is also the “drainage” reaction, the desulfurization of the mercaptan, which, in combination, provides an alternate path for olefin loss in addition to the conventional olefin saturation reaction. Complications presented by the recombination reaction in FCC gasoline desulfurization are covered by Leonard and Kokayeff (Leonard et al. 2006).

Process Considerations

The three main process licensors of hydrotreating technology for processing FCC gasoline are ExxonMobil (SCANfining™ Process), IFPEN/Axens (Prime-G+™ process), and Honeywell UOP (SelectFining™ Process). While all three process licensors offer a number of different flow schemes based on feed characteristics, e.g., sulfur level, and product targets, these technologies have much in common.

Saturation of Diolefins

Besides olefins, FCC gasoline contains diolefins which may cause fouling of heat exchanger surfaces as well as pressure drop in the hydrotreating reactor and catalyst deactivation by deposition of coke. The removal of diolefins is accomplished in a similar manner as is done for coker naphtha hydrotreaters, i.e., by processing the feed at mild conditions over a hydrotreating catalyst. This simple procedure effects the saturation of diolefins to monoolefins. In the Axens Prime-G+™ process, this step contains a catalyst that is also active for the reaction of mercaptans with olefins to form thioethers:

$$R_1 = R_2 + RSH \leftrightarrow R_1\text{-}R_2\text{-}SR$$

The thioether boils at a much higher temperature than the mercaptan, thus allowing for the conversion of low-boiling, low-molecular-weight mercaptans to be converted to much higher-boiling sulfur compounds. This allows for the separation of the light cracked naphtha (LCN) which is sulfur-free and contains C_5 and C_6 olefins from the sulfur-rich, higher-boiling portion of the feed, which needs to be processed. The benefit is that the removal of these olefins preserves them from undergoing saturation in the hydrotreating reactor and also allows for a lower olefin content of the stream that is hydrotreated, thus allowing for the attainment of lower sulfur levels while minimizing octane loss due to olefin saturation.

Desulfurization

A common feature to all the process licensors is the selective desulfurization reaction of the FCC gasoline carried out over a catalyst specifically designed to effect desulfurization with minimal saturation of olefins. In all cases, the feed to the selective desulfurization reactor has been processed in a DIOS (diolefin saturation reactor) to saturate the diolefins. In some cases, the effluent of the DIOS may be split into two in a splitter with the splitter overhead (LCN) either being sulfur-free (Prime-G+™) or being subjected to a mercaptan extraction process (e.g., Merox or Exomer) and the splitter botts then routed to the selective desulfurization reactor.

Reactions occurring in the selective desulfurization reactor include:

Desulfurization

$$\text{R-S-R}' + 2\text{H}_2 \rightarrow \text{RH} + \text{R}'\text{H} + \text{H}_2\text{S}$$

Olefin saturation

$$\text{R} = \text{R}' + 2\text{H}_2 \rightarrow \text{RH-R}'\text{H}$$

Recombination

$$\text{R} = \text{R}' + \text{H}_2\text{S} \leftrightarrow \text{R-R}'\text{-SH}$$

Olefin drainage

$$\text{R} = \text{R}' + \text{H}_2\text{S} \leftrightarrow \text{R-R}'\text{-SH}$$

$$\text{R-R}'\text{-SH} + \text{H}_2 \rightarrow \text{R-R}' + \text{H}_2\text{S}$$

While all these reactions are exothermic, the catalysts are so selective that desulfurization takes place to a much greater degree than olefin saturation, and hence the temperature rise can be kept to manageable levels.

Process Configurations

The simplest process configuration consists of a DIOS followed by a selective desulfurization reactor and a product stripper to remove H_2S (Fig. 12).

Such a simple process configuration would be satisfactory when feed sulfur levels are low, typically less than ~300 wppm. In such cases, it is possible to achieve very low product sulfur levels, <10 wppm, with minimal saturation of olefins and good octane retention.

A more complex process configuration would be required when the feed sulfur content is higher than ~300 wppm. In this case, the feed is first routed to a DIOS reactor to saturate the diolefins with the effluent of the DIOS entering a splitter with the LCN sent overhead and the bottoms routed to a selective desulfurization reactor. The splitter overhead may be subjected to a process such as UOP's Merox Process™ to extract the light mercaptans (Fig. 13).

A modification of the above process is Axens Prime-G+™, wherein the thioetherification function inherent in the diolefin saturation/selective hydrogenation catalyst, or SHU™, is also applied. The light mercaptans are converted to higher-boiling sulfides by reaction with olefins. The sulfides thus formed boil at a much higher

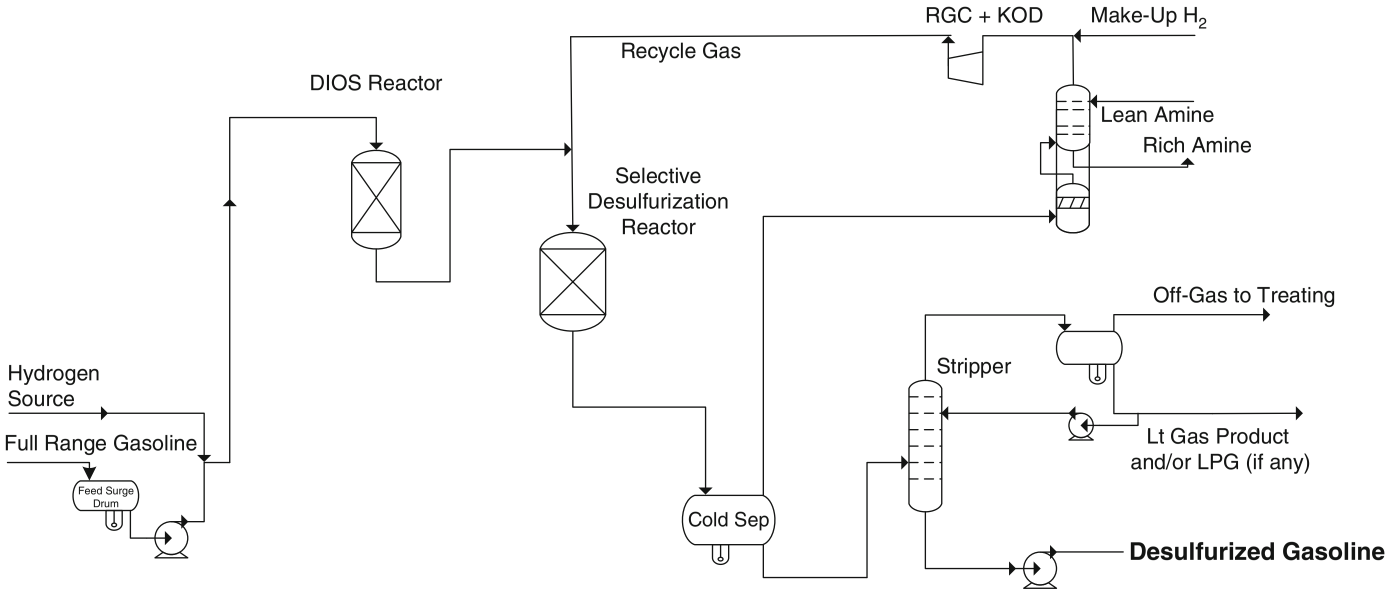


Fig. 12 Simplified process flow diagram of an FCC gasoline desulfurization unit – single stage

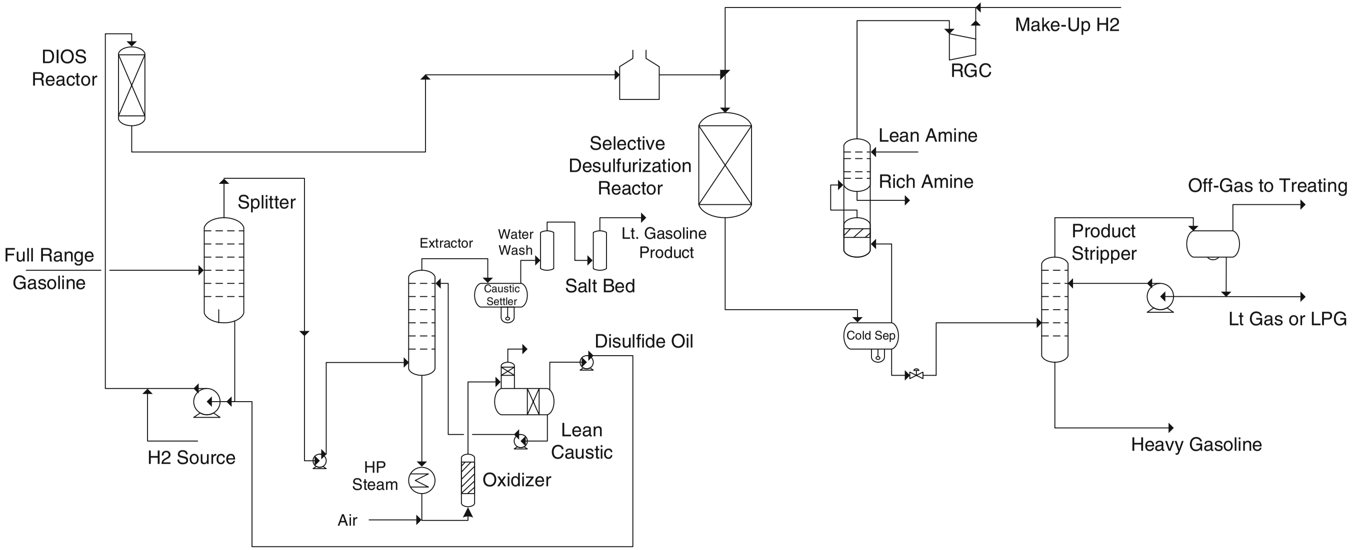


Fig. 13 Simplified process flow diagram of an FCC gasoline desulfurization unit – single stage with extractive Merox Process™

temperature and appear in the splitter bottoms and are subsequently desulfurized in the selective desulfurization reactor(s). The effluent from the SHU™ reactor is routed to a splitter which separates the light cracked naphtha (LCN) as an overhead product which is essentially sulfur-free. The splitter bottoms is routed to the selective desulfurization reactors HDS-1 and HDS-2 (Fig. 14). The second desulfurization reactor operates at a higher temperature. Decomposition of the remaining sulfur compounds, due to the higher temperature, limits the remaining recombinant mercaptans to meet the desired sulfur specification.

At high feed sulfur levels, the amount of H_2S produced is so high, and the formation of mercaptans is so extensive that low product sulfur levels cannot be achieved without separation of the H_2S between two stages of desulfurization. This type of flow scheme is represented below by two-stage SelectFining (see Fig. 15). The FCC gasoline enters the DIOS reactor to saturate diolefins. The effluent of the DIOS reactor is mixed with recycle gas, heated to reaction temperature, and routed to the first selective desulfurization reactor. The effluent of the first desulfurization reactor is cooled, stripped of H_2S, mixed with recycle gas, heated to reaction temperature, and routed to the second selective desulfurization reactor. Finally, the effluent of the second selective desulfurization reactor is stripped of H_2S and routed to product blending/storage.

Process Conditions

Typical process conditions are shown in Table 5.

FCC Feed Pretreating

Hydrotreating the feed to an FCC is usually practiced to remove sulfur and limit SOx emissions but also impacts the FCC in other ways. Hydrotreating the feed to the FCC results in hydrogen addition to the feed due to saturation of aromatics, thus rendering the resulting molecules easier to crack in the FCC and increasing conversion and gasoline yield. An additional benefit is the reduction in the sulfur content of the FCC gasoline, thus reducing the severity required of the FCC gasoline posttreater and consequently limiting olefin saturation and octane loss.

FCC feedstocks are vacuum gas oils boiling in the range of ~650–1,100 °F. Sulfur levels may vary widely from ~0.5 to 3 wt%. Nitrogen levels may vary from 500 to 3,000 wppm. Additionally, depending on the end point, metals (Ni and V) may also be present. While decreasing the sulfur content of the FCC feed has beneficial effects, reducing the nitrogen content and adding hydrogen will increase conversion and gasoline yield.

Feedstock Characteristics

Generally the chemical nature of the FCC feed is similar to that of distillates but of higher molecular weight.

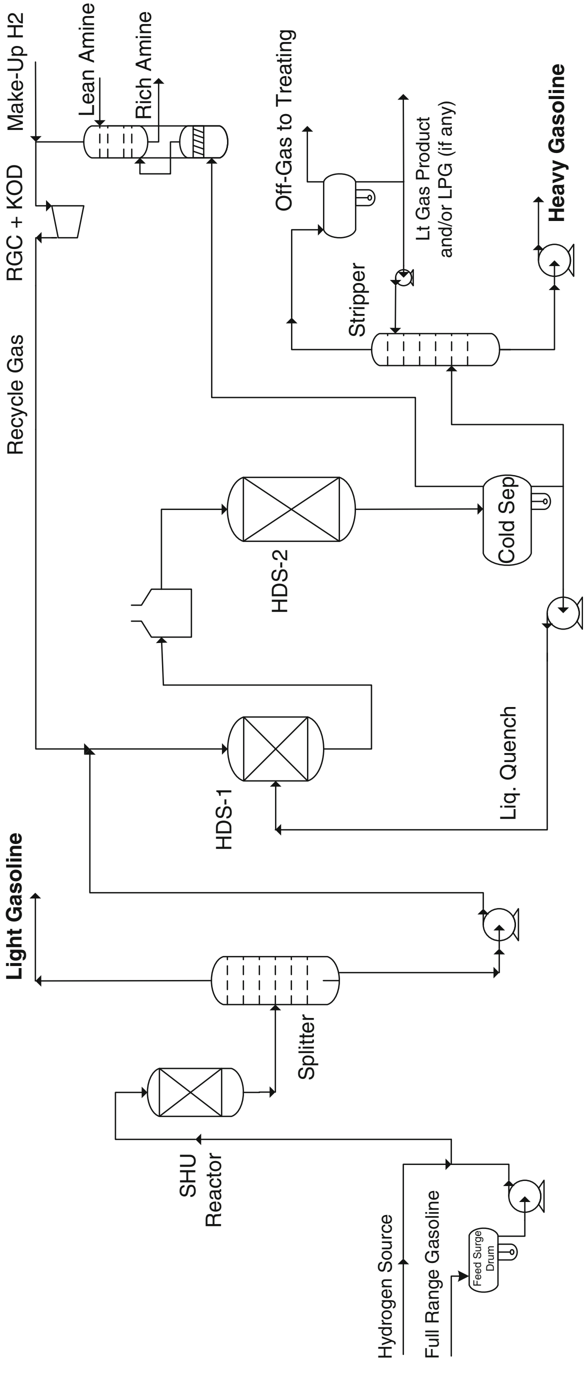


Fig. 14 Simplified process flow diagram for FCC gasoline desulfurization

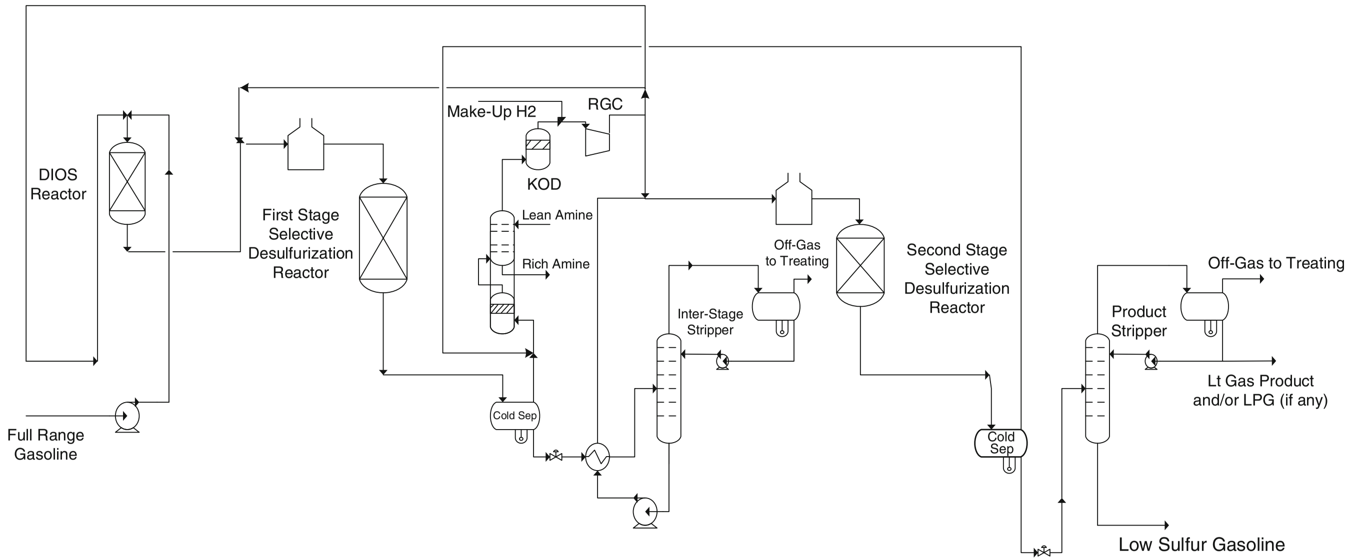


Fig. 15 Simplified process flow diagram of a two-stage SelectFining process unit

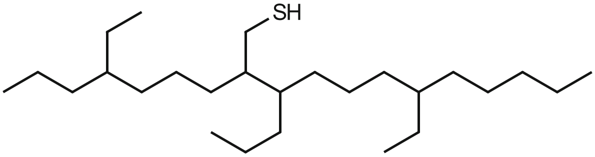
Table 5 FCC gasoline desulfurization process conditions

	LHSV, h^{-1}	Pressure, psig (barg)	Temperature, °F (°C)	H_2/oil, SCF/B (Nm^3/m^3)
DIOS/ SHU™	3–12	200–400 (14–28)	200–400 (90–200)	50–1,000 (8–170)
Selective HDS, first stage	1–3	200–400 (14–28)	475–600 (250–315)	1,500–4,500 (250–760)
Selective HDS, second stage	1–3	200–400 (14–28)	475–600 (250–315)	1,500–4,500 (250–315)

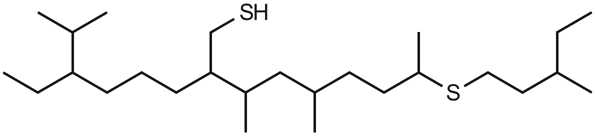
Sulfur Compounds

Sulfur compounds, even in structures without rings, are more complex higher in molecular weight and may contain more than one sulfur atom:

7-Ethyl-2-(4-ethylheptyl)-3-propyldodecanethiol

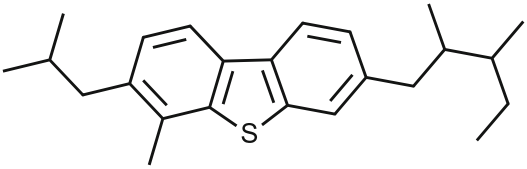


2-(4-Ethyl-5-methylhexyl)-3,5-dimethyl-8-(3-methylpentylthio)nonanethiol



Similarly, structures containing rings are also larger, more complex, and higher in molecular weight:

7-(2,3-Dimethylpentyl)-2-isobutyl-1-methyl-9-thiafluorene



Analytical Characterization

As described in the section on distillate hydrotreating, comprehensive GC has become a very valuable tool in the characterization of the composition of vacuum gas oils. A comprehensive GC 3D image of the hydrocarbon composition of a VGO

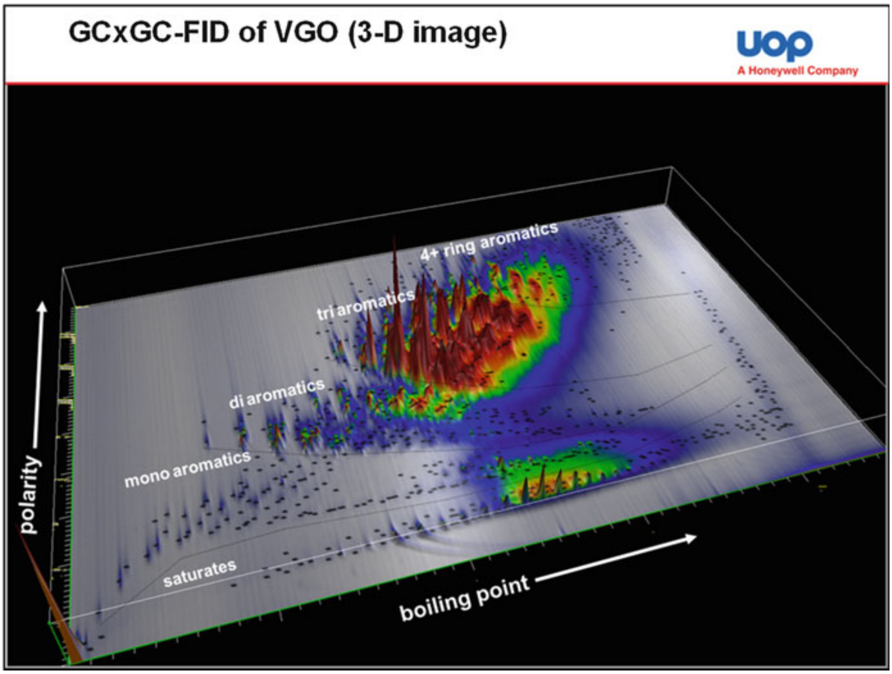


Fig. 16 Comprehensive GC 3D image of hydrocarbon compounds in a VGO

is shown in Fig. 16. The saturates all appear along the x-axis with increasing boiling point. Aromatic compounds appear as "families," mono-aromatic, di-aromatic, tri-aromatic, and 4+ ring aromatic structures, of peaks according to the extent of substitution of the ring.

A similar 3D representation of the sulfur species present in a VGO appears in Fig. 17. The sulfur compounds appear as families of thiophenic structures with increasing numbers of both aromatic rings (polarity) and substitution (boiling point).

The characterization of the VGO by these methods allows for much more accurate determinations of reactivity and the application of the optimal catalysts and process conditions to effect the desired conversion.

Catalysts and Reactions

Both Co/Mo and Ni/Mo catalysts have been applied in the hydrotreatment of FCC feed. Co/Mo catalysts are sufficiently active for desulfurization at lower pressures, while Ni/Mo catalysts are more active for denitrogenation and saturation of aromatic rings at higher pressures, both of which increase the activity of the FCC catalysts and increase gasoline yield. Tri-metallic catalysts that provide average activities for all functions (hydrodesulfurization, hydrodenitrogenation, and aromatics saturation) have also been successfully applied.

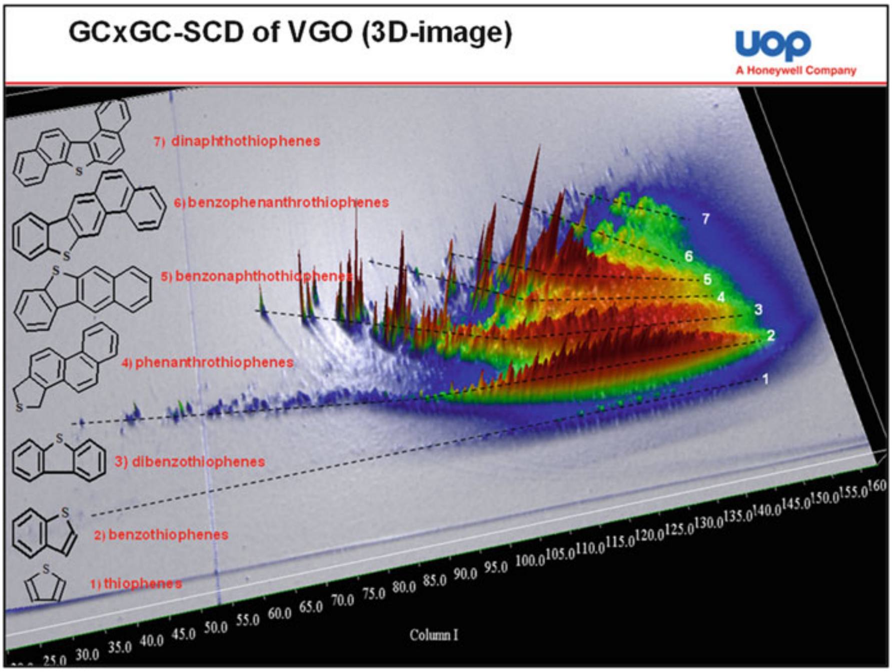


Fig. 17 Comprehensive GC image of sulfur compounds in a VGO

Hydrodesulfurization, hydrodenitrogenation, and saturation reactions are similar to those occurring in distillate hydrotreating except the reacting species are of higher molecular weight.

Feedstocks

Feedstocks to an FCC feed pretreating unit may include vacuum gas oils (VGO) as well as heavy coker gas oil (HCGO). Sulfur contents may range from 0.5 to 3 wt% and nitrogen from 500 to 3,000 wppm. The higher values, especially for nitrogen, are found in HCGO. HCGO additionally contains olefins with bromine numbers ranging up to ~20. The olefinic nature of the HCGO feed requires consideration of catalyst bed distribution and temperature management due to the highly exothermic nature of the very rapid olefin saturation reactions.

Process Configuration

A simplified process flow diagram of a typical FCC feed pretreater is shown in Fig. 18. The feed is pumped from the feed surge drum and mixed with recycle gas, and the mixture is then heated in a bank of feed/effluent exchangers and then passes to the reactor charge heater where it is heated to reaction temperature and then enters the reactor. The reactor is shown with three beds of catalyst with recycle gas being routed to the quench zones to reduce the temperature of the effluent of each bed to the desired inlet temperature of the next catalyst bed. The number of catalyst beds is dependent on

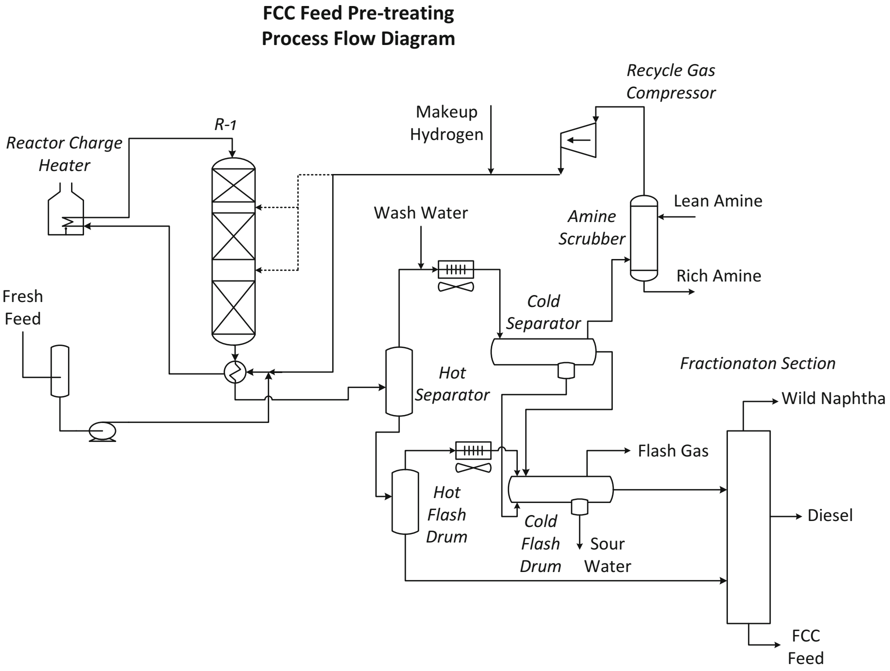


Fig. 18 Simplified process flow diagram of an FCC feed pretreater

the heat release and allowable temperature rise in each bed. Reactor effluent is first cooled against the combined feed or individual fresh feed and recycle gas streams in the feed/effluent exchangers and is then passed to a series of separators to recover the liquid hydrotreated hydrocarbon and the recycle gas. The recycle gas is scrubbed free of H_2S in an amine scrubber and then compressed and routed back to the reactor. Water is added to the hot separator vapors to dissolve the NH_3 and prevent the formation of ammonium hydrosulfide salts in the cold sections of the plant. The hydrocarbon liquid from the separator system is routed to a fractionation section to recover a wild naphtha stream, a diesel stream and the hydrotreated FCC feed.

Process Conditions

Process conditions applied in FCC feed pretreating have been getting more severe with the necessity to reduce SOx emissions from the FCC regenerator to ever lower levels. While desulfurization of the FCC feed to sulfur levels of 2,000 wppm has been acceptable in the past, the trend has progressed past 1,000 wppm sulfur to <500 wppm sulfur and recently to lower levels in efforts to minimize or eliminate the posttreatment of FCC gasoline. Typical process conditions are shown in Table 6. The more severe (lower LHSV, higher pressure and temperature, etc.) conditions are applied to blends containing HCGO, DAO, or both. Typically the FCC pretreating unit is designed to operate with a cycle that matches the FCC turnaround cycle, which typically is 4–5 years.

Table 6 FCC feed pretreating process conditions

LHSV, h^{-1}	0.7–2.0
Temperature, °F (°C)	670–730 (355–390)
Pressure, psig (barg)	800–1,600 (55–110)
H_2/oil, SCF/B (Nm^3/m^3)	1,500–4,000 (250–675)

Hydrocracker Pretreat

Introduction

Hydrotreating and hydrocracking share many common elements. Both processes catalytically upgrade the feedstock by adding hydrogen under moderate to high operating pressures and elevated reactor temperatures. However, a key differentiator is that hydrocracking catalysts have a stronger acid function compared to that of hydrotreating catalysts, which allows the hydrocracking catalysts to facilitate deeper cracking reactions as well as naphthenic ring-opening reactions.

A hydrocracking unit requires the use of both hydrotreating and hydrocracking catalysts to obtain the desired product qualities in the naphtha, jet, and diesel products as well as the desired operating cycle length. This section briefly touches upon the hydrotreating reactor section in the context of a hydrocracking unit.

Feedstock Types

A hydrocracking unit can be designed to handle a wide range of feedstock types. Ultimately, unit design is constrained by the economic return of processing the most severe feedstock in comparison to the associated capital expenditure and operating expense.

Vacuum gas oil (VGO) and heavy coker gas oil (HCGO) are more commonplace feedstocks for a hydrocracking unit, but as the product quality specifications for clean fuel become more stringent and the demand for transportation fuel continues to increase in lockstep with the ever-growing global population, refiners have increasingly found interest in processing feeds such as light cycle oil (LCO) from the FCC and DAO (deasphalted oil) from solvent deasphalting (SDA) units to produce high-quality fuel, such as diesel.

All four of these feedstock types will have an appreciable amount of organic sulfur (1–3 wt%) and nitrogen (500–3,500 wppm) that will need to be nearly completely removed in the hydrotreating section to protect the downstream hydrocracking catalyst from these poisons.

Light cycle oil is a highly aromatic diesel boiling range stream produced in the FCC unit. Due to the high concentration of two- and three-ring aromatics, LCO has a low cetane value, which makes it a poor blend stock for the refinery's diesel pool. Conventional hydrotreating pressure is frequently inadequate to completely remove the native sulfur species in LCO to meet ULSD specifications. Therefore, processing the LCO in a hydrocracking unit becomes an attractive alternative. The difficult sulfur species in LCO can be more effectively removed in the high-pressure hydrotreating section of the hydrocracking unit. Furthermore, the LCO quality is further improved by the higher operating pressure of the hydrocracking unit, since additional aromatic saturation can take place to improve the cetane qualities of the stream.

Deasphalted oil is another feedstock that some refiners find economical to send to a hydrocracking unit. Processing DAO in a hydrocracking unit requires additional catalyst system considerations to account for the higher metal content (Ni and V) as well as the potential for the presence of very heavy molecules as condensed-ring aromatics. DAO is created in a solvent deasphalting unit that separates on the basis of molecular type rather than boiling point. Therefore, for moderate to heavy lifts, increasing extent of extraction, in the SDA unit the heaviest molecules in the DAO are not adequately characterized by boiling point due to the limitations of the current distillation test methods. The higher metal content in DAO is addressed by specifying an adequate amount of metal trapping material in the hydrotreating section of the hydrocracking unit. Due to the presence of very heavy molecules, the potential for a higher deactivation rate should also be considered when selecting the design operating pressure and sizing both the hydrotreating and hydrocracking catalyst beds.

Optimization Between the Hydrotreating and Hydrocracking Function

In a typical hydrocracking flow scheme, the hydrotreating section effluent is directly routed to the inlet of the hydrocracking section without any removal of the H_2S and NH_3 that are formed from the hydrotreating reactions. Ultimately, the catalyst loading for the hydrotreating section depends on the concentration of contaminants, organic sulfur and nitrogen, the fresh feed, and the permissible level of these contaminants entering the hydrocracking section. There is some degree of flexibility in the level of contaminants permitted to enter the hydrocracking section, particularly organic nitrogen, from the hydrotreating section. The permissible concentration will depend on the relative reactor volumes available for loading hydrotreating versus hydrocracking catalyst, the target conversion rate, and the desired product quality from the hydrocracking unit.

Residual Oil Hydrodesulfurization

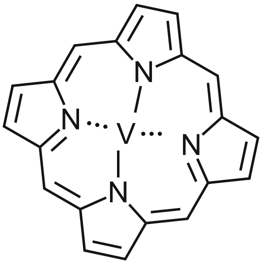
Residual oil, as the name implies, is the material remaining after distillation. Atmospheric residue (AR) is the bottoms of the atmospheric column and generally has the boiling range of ~650 °F+. Vacuum gas oil is contained within AR. Vacuum residue (VR) is the bottoms of the vacuum column. With the vacuum gas oil (VGO) removed, the boiling range of the vacuum residue is ~1,050 °F+.

One of the defining characteristics of the residual oils is the presence of metals, primarily Ni and V, although smaller amounts of other metals may also be present. Ni and V are typically present in concentrations ranging from ~25 to ~1,000 wppm. Sulfur concentrations are also quite high, sometimes exceeding 3 wt%. A further defining feature of the residual oils is their high Conradson carbon residue (CCR), frequently exceeding 20 %. Additionally, the presence of condensed-ring aromatics and asphaltenes necessitates the application of high pressures and specialized catalysts to achieve reasonable cycles, typically 12–18 months.

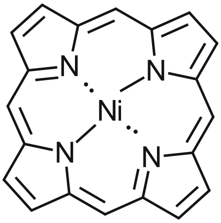
Catalysts and Reactions

The main feature that differentiates residual oil hydrotreaters from hydrotreaters in other applications, e.g., distillate and FCC feed pretreaters, is the presence of high concentrations of metals and the necessity of removing these prior to the main hydrotreating reactors. This is accomplished by the use of specialized catalysts having larger pore diameters to accommodate the metals containing molecules (typically, but not always present in porphyrin structures; see figure below). The large pore diameters are required to allow the metal-containing molecules to penetrate to the center of the catalyst pellet rather than depositing at the pore mouth and plugging the pore, rendering it inactive despite having a "fresh" and active interior.

Vanadyl porphyrin



Nickel porphyrin



Sulfur and nitrogen atoms are also generally located in condensed-ring aromatic structures making residual oils much more difficult to process.

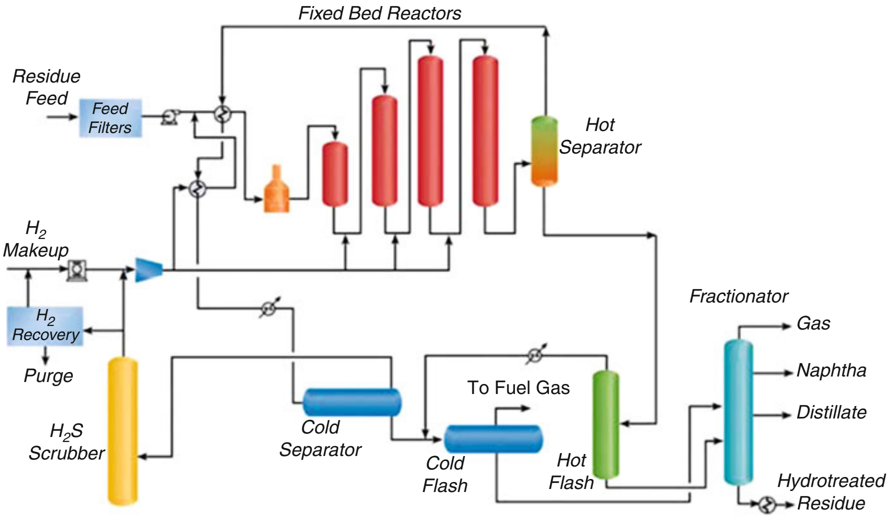


Fig. 19 Simplified process flow diagram of a residual oil hydrotreater

Process Configuration

As mentioned above, the key feature of hydroprocessing residual oils is the necessity to provide guard reactors containing large pore catalysts for the removal of metals. The guard reactors may or may not be arranged in a swing reactor system where one reactor may be taken off-line for catalyst removal and replacement while the spare reactor is placed into service. A typical process configuration of a resid hydroprocessing unit is depicted in Fig. 19. The first two reactors in fig. 19 are the "guard" reactors filled with hydrodemetallation catalysts while the remaining two are hydrodesulfurization reactors.

Process Conditions

Process conditions depend on a number of factors including, feed type (AR or VR), degree of desulfurization, metals levels, carbon residue, and required cycle length. Typical process conditions are presented in Table 7.

Catalysts

Hydrotreating catalysts, in general, are high-surface-area materials consisting of an active component and a promoter, which are uniformly dispersed on a support. The catalyst support is normally gamma alumina (γ-Al_2O_3), doped sometimes with small amounts of silica, phosphorus, fluoride, and/or boron and prepared in such

Table 7 Typical process conditions for a residual oil hydrotreater

LHSV, h^{-1}	0.2–0.7
Temperature, °F (°C)	670–730 (355–390)
Pressure, psig (barg)	1,800–2,500 (125–170)
H_2/oil, SCF/B (Nm^3/m^3)	3,000–5,000 (500–850)

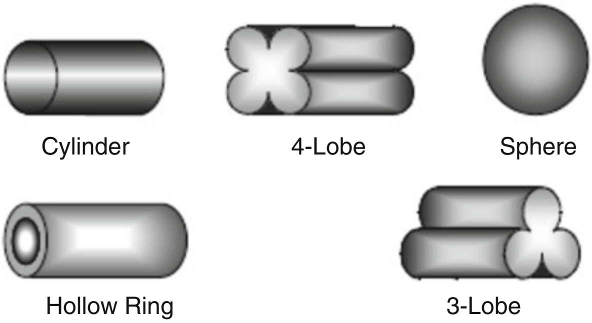


Fig. 20 Hydrotreating catalyst shapes

a way so as to offer a high surface area upon which to disperse the active metals and an appropriate pore structure, so that pore plugging with coke and/or metals is sufficiently mitigated to achieve the desired operating cycle. The active component is normally molybdenum sulfide, although tungsten-containing catalysts are also used (though seldom, and that generally for special applications such as lube oil processing). Regarding molybdenum catalysts, both cobalt (CoMo) and nickel (NiMo) are used as promoters. The promoter has the effect of substantially increasing (approximately 100-fold) the activity of the active metal sulfide. The acidity of the support (which itself may be increased with dopants, beyond the nascent acidity) can be increased to boost the catalyst activity for hydrocracking and isomerization reactions. The commercially available catalysts have varying amounts of promoters and active components, depending on the desired applications, but in general they can contain up to about 25 wt% promoter and up to 25 wt% active component as oxides. Hydrotreating catalysts come in different sizes and shapes and vary depending on the manufacturer (Fig. 20):

Cylindrical	1/32″–1/4″
Trilobe	1/20″–1/10″
Quadrilobe	1/20″–1/10″
Spheres	1/16″–1/4″
Hollow rings	Up to 1/4″

Other shapes include nodular beads and wagon wheels. In general, the size and shape of the catalyst pills is a compromise between the desire to minimize pore diffusion effects in the catalyst particles (requiring small sizes) and pressure drop across the reactor (requiring large particle sizes). The physical characteristics of catalysts also vary from manufacturer to manufacturer and the intended use of the catalyst but in general are as follows:

Surface area	100–250 m^2/g (typ.)
Pore volume	0.5–1.0 cc/g
Median pore diameter	65–150 Å
Compacted bulk density	35–55 lb_m/ft^3
Crushing strength	4–20 lb_f/in^2
Average length (except spheres)	1/8–3/8 in.

Cobalt-Molybdenum Catalysts

CoMo catalysts have been designed primarily for desulfurization with minimum hydrogen addition; nevertheless, modest denitrogenation and demetallation is also achieved. These catalysts can treat feedstocks of widely varying properties. CoMo catalysts have the lowest hydrogenation activity; therefore, they have the lowest hydrogen consumption per mole of sulfur removed. They also have the lowest sensitivity of H_2 consumption to changes in operating pressure. CoMo catalysts have sufficient desulfurization performance at low operating pressures (<600 psig, or <~40 barg). These catalysts also have the lowest denitrogenation performance due to low hydrogenation activity. Because CoMo catalysts exhibit the highest sulfur removal per unit of hydrogen consumed, they are best suited for desulfurization at lower pressures and when hydrogen is in short supply.

Nickel-Molybdenum Catalysts

NiMo catalysts have been designed for hydrodesulfurization but particularly for hydrogenation and hydrodenitrogenation. Metal removal can also be achieved. These catalysts can treat feedstocks of widely varying properties. NiMo catalysts have higher denitrogenation activities than CoMo and are therefore used for cracked stocks or other applications where denitrogenation and/or saturation is as important as desulfurization. The higher hydrogenation activity of NiMo catalysts allows them to be used as a topping layer to saturate olefins and other gum precursors to mitigate catalyst bed fouling, leading to pressure drop accumulation and poor liquid flow distribution through the catalyst bed. The performance of NiMo catalysts is very good at high pressures. NiMo catalysts show a greater response in denitrogenation and desulfurization performance to changes in H_2 partial pressure than CoMo. High-pressure operations, such as FCC and hydrocracking feed pretreatment, therefore favor the use of NiMo catalysts. NiMo catalyst use is also favored for naphtha hydrotreaters upstream of catalytic reforming units as the modern reforming catalysts are very sensitive to the nitrogen content of the feedstock.

Other Catalysts

Other catalysts that have been used in hydrotreating are supported NiCoMo (still in use for hydrotreating) and NiW (very rarely in use for hydrotreating). NiCoMo catalysts attempt to combine the benefits of CoMo and NiMo at intermediate pressures, achieving sufficient hydrodesulfurization (primarily) at the minimum required hydrogen consumption. NiW catalysts are more widely practiced in hydrocracking applications than hydrotreating applications. Historically, sulfided NiW exhibits hydrocracking activity surpassing that of both CoMo and NiMo. Increasing the activity of the support material with promoters, amorphous silica alumina, or zeolite can further enhance the hydrocracking activity.

Type I vs. Type II Hydrotreating Catalysts

The designations "Type I" and "Type II," as originally applied by Topsøe et al. refer to the nature of the bonding between the active phase (e.g., CoMoS, NiMoS) and the support, the extent of stacking of the active phase as dispersed MoS_2 nanosheets, and the coordination of the promoter metal at the edges of the nanosheets. The promoted active phase along the edges, as Co(Ni)-Mo-S structures, is believed to be responsible for the relatively greater hydrotreating activity of Type II catalysts. Catalysts of the former type consist predominantly of an active phase that is more strongly bound to the support, as in Mo-O-Al where the support is γ-alumina, with relatively shorter stacks of MoS_2 nanosheets, and wherein a relatively smaller portion of the promoter metal is coordinated into the MoS_2 nanosheets' edges. Catalysts of the latter type consist predominantly of an active phase that is more weakly bound to the support via dipole-dipole (van der Waals) interactions, with relatively taller stacks of MoS_2 nanosheets, and wherein a relatively greater portion of the promoter metal is coordinated into the MoS_2 nanosheets' edges. The active phase is, in general, fully sulfidable (Topsøe et al. 1996; Hensen et al. 2002; Topsøe and Clausen 1984). This description may require some revision, especially as regards the necessity for taller stacks of MoS_2 nanosheets.

Unsupported or Bulk Transition Metal Sulfide (TMS) Catalysts

The quantum improvement in hydrotreating catalyst performance can be observed in the activity of unsupported TMS catalysts. Unsupported catalysts appear to represent a hearkening back to the very early history of hydrotreating, when most hydrotreating catalysts were unsupported (Čejka 2003). In principle, today's unsupported catalysts are comprised only of active phase, representing a much higher population density of active phase per unit volume than Type I and Type II supported catalysts, without the limitation of active phase-support interactions.

Such catalysts are comprised almost entirely of metals, as in NiMoW. Their HDS and HDN hydrotreating activities (RVAs) can exceed those of the contemporary Type II supported catalyst by 50–100 %. It is for this reason that unsupported catalysts are typically loaded in addition to supported catalysts, since the hydrogen consumption and heat release of a full reload with an unsupported catalyst could exceed process design allowances. The active phase appears to take many forms. One might observe active phase structures similar to those seen on Type II supported catalysts as well some others. In general, these catalysts are prepared via precipitation of the oxidic precursor followed by the sulfidation of the precipitate or based on the direct precipitation of the (mixed) sulfide (Chianelli et al. 2009).

Measuring Catalyst Performance

Catalyst performance is measured by several criteria shown below, which are more or less self-explanatory:

- Initial activity, which is measured by the temperature required to obtain desired product at the start of the run. During the cycle, the catalyst activity can be calculated as shown below:

  $$D_s = D_S^0 e^{At}$$

  where
  D_s = desulfurization activity
  D_S^0 = initial desulfurization activity
  A = deactivation rate, °F/bpp
  t = catalyst life, bpp
- Stability, which is measured by the rate of temperature increase required to maintain product quality
- Product quality, which is a measure of the ability of the catalyst to produce products with the desired use specifications, such as pour point, smoke point, or cetane number

Catalyst Manufacture

Hydrotreating catalysts contain metals dispersed on a support. That support is γ-lumina which is arrived at by synthesis. Several raw materials can be used to produce the γ-alumina:

- Gibbsite (α-alumina trihydrate)
- Bayerite (β-alumina trihydrate)
- Boehmite and pseudoboehmite (γ-AlO(OH))

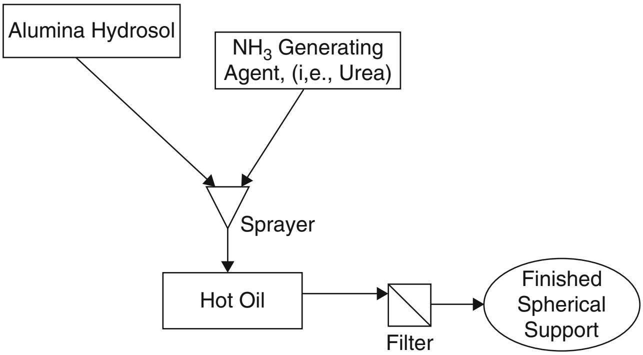


Fig. 21 Oil dropping (spherical support preparation)

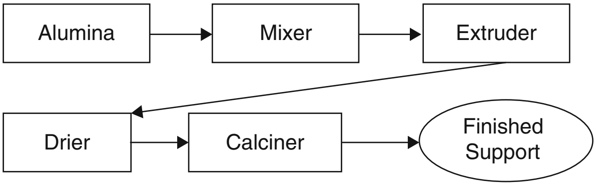


Fig. 22 Support preparation by extrusion

Hydrotreating catalysts are typically manufactured by several methods:

- Dry (incipient wetness) or wet impregnation
- Co-mulling
- Hot soaking/dip impregnation

Forming of the Support

Figure 21 shows the preparation of a spherical support by the oil dropping method. Figure 22 shows support preparation by extrusion. In the typical case where pseudoboehmite is used to prepare the catalyst support, the powder is blended with an acid solution, either organic or inorganic, and mixed and/or mulled until reaching a colloidal state, suitable for extrusion. The process of converting the powder to an extrudable colloid using an acid solution is referred to as peptization. The colloidal "dough" is then extruded through fixed dies in the desired shape and size, before being dried and converted to γ-alumina in a high-temperature calcination step (usually 900–1,300 °F). Many factors influence the final pore volume distribution, surface area distribution, and the mechanical strength: the raw pseudoboehmite itself, the type and concentration of the acid solution, the presence of burn-out agents and extrusion aids, the type of blending and its intensity, the extrusion flux and die plate pressure, the drying, and the calcination (duration, temperature, application of steam). More recently, syntheses utilizing surfactants are being developed in the case of γ-alumina supports, to more directly tailor pore structure and increase surface area (Eijsbouts et al. 2007).

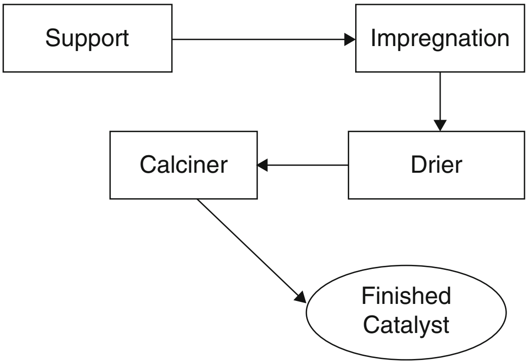


Fig. 23 Dry (incipient wetness) and wet impregnation

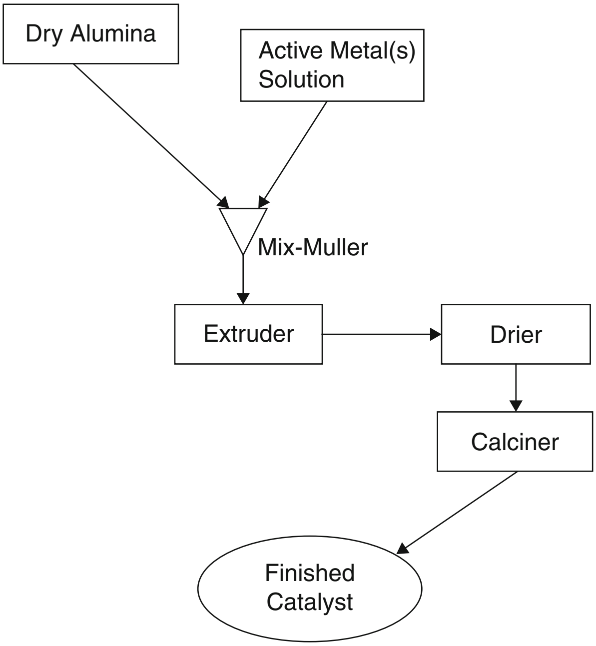


Fig. 24 Co-mulling

Support Impregnation

The support, either spherical or extruded, is then finished with an impregnation as shown in Fig. 23. Figure 24 depicts hydrotreating catalyst manufacture by co-mulling. Figure 25 shows the schematic of catalyst manufacturing by hot soaking. Impregnation solutions are prepared after a measurement of the pore volume of the support, typically via Hg intrusion. An appropriate volume of impregnation solution is then prepared to fill the available pore volume, usually with a slight percentage excess. The species to be deposited on the catalyst support are introduced into the impregnation solution as precursors, such as nickel nitrate (hydroxycarbonate), cobalt nitrate (carbonate), ammonium heptamolybdate,

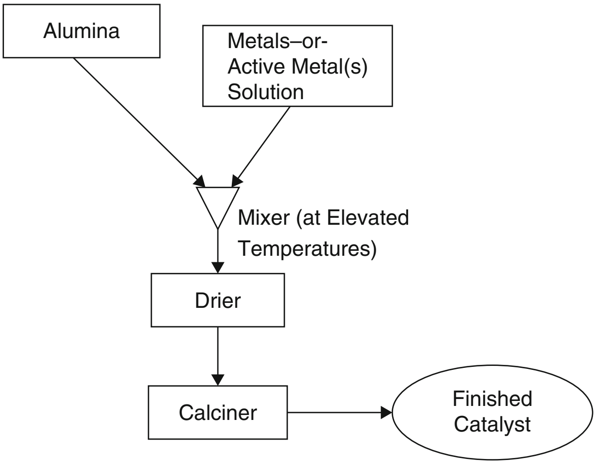


Fig. 25 Hot soaking

molybdenum trioxide, and ammonium metatungstate. The volumes of support and impregnation solution are then mixed, excess water is removed by drying if necessary, and the catalyst is heat-treated to convert the metal precursors to metal oxides. In the case of Type II hydrotreating catalysts, it is typical to include at least one additive to the impregnation solution. EDTA and NTA are common examples of chelating agent additives. It is also typical that the heat treatment is not carried out at temperatures which would completely remove the additive. The purpose of the additive or additives is to facilitate formation of the Type II active phase when the catalyst's metal oxides are converted to metal sulfides during activation/sulfidation. This may occur via multiple pathways: stabilize the impregnation solution especially in the case of high metal loadings, improve the dispersion of the active phase during the course of impregnation (buffering effect), bind with those support species which would otherwise bond with the active phase, act as an inert support upon which the active phase may deposit, and adjust the sulfidation rate of one or more of the metal oxides (an effect of chelation) during the activation to facilitate greater coordination of the promoter to active phase nanosheet edges (Frizi et al. 2008; Breysse et al. 2008).

Catalyst Loading and Activation

Catalyst Loading

There are two methods of catalyst loading: sock loading and dense loading. Pouring catalyst into a hopper mounted on top of the reactor and then allowing it to flow through a canvas sock into the reactor is sock loading. Dense loading or dense bed packing is done with the aid of a mechanical device. Dense loading techniques were first introduced in the mid-1970s. Catalysts loaded by sock loading will have a higher void fraction than catalysts that were dense loaded, typically 10–15 % lower loaded density. Dense bed loading/packing and the resulting higher pressure drop provides a more even distribution of liquid in a trickle-flow reactor, which is the prevalent flow regime in the hydrotreating of diesel-range streams and heavier. Dense loading of at least the primary hydrotreating catalyst bed(s) is usually preferred in order to maximize the reaction rate per unit reactor volume throughout the catalyst life cycle. Dense loading delivers catalysts into a reactor at a controlled rate, varied according to the rising bed height, so that the catalysts are oriented similarly throughout the dense bed. This uniform orientation helps facilitate a uniform vapor/liquid flow distribution and catalyst utilization. Catalyst particle orientation is especially critical with respect to shaped, extruded catalysts in trickle-flow reactors. Of all the factors influencing catalyst utilization, catalyst loading has generally proven to be the most important factor. Another advantage of dense loading is that it allows loading more catalyst in the reactor because of the reduced void fraction in the catalyst bed. Thus, the catalyst life can be extended, or else the unit can be operated at more severe conditions (lower product sulfur level, increased feed rate) than if the catalyst had been sock loaded. Except for the hydrotreaters that have reactor pressure drop limitations mainly due to operation at higher-than-design throughputs, most hydrotreaters are dense loaded. Ex situ presulfurized catalysts (see catalyst activation) are self-heating materials. Thus, they should be loaded in an inert atmosphere though some loading contractors do load them under air atmosphere.

Catalyst Activation

Hydrotreating catalysts have to be activated in order to be catalytically useful. The activation of the catalyst is performed by conversion of metal oxides to metal sulfides and is commonly called sulfiding, though several other names are used to describe the same thing. Other names that are used to describe catalyst activation techniques are pre-sulfiding or pre-sulfurizing. The metals on the catalysts are in an oxide form at the completion of the manufacturing process. More often than not, this is typically accomplished in situ; however, more refiners have started to use catalyst which had the sulfiding compound loaded onto the catalyst outside the unit (ex situ pre-sulfidation). It is likely that more and more refiners will opt to receive the catalyst at the refinery site in pre-sulfided state to accelerate the start-up of the unit and because it is more environmentally friendly (eliminates the VOC and odors evolved when the sulfiding compound is introduced into the unit).

In situ sulfiding can be accomplished either in vapor or liquid phase. In vapor phase sulfiding, the activation of the catalyst is accomplished by injecting a chemical which decomposes easily to H_2S, such as dimethyldisulfide (DMDS) or dimethylsulfide (DMS). The usage of H_2S/H_2 was common up until the end of the last century, but now it is only rarely used because of environmental and safety concerns. Liquid phase sulfiding can be accomplished with or without organo-sulfur compounds added to the feedstocks. In the latter case, the feedstock is generally a straight-run gas oil that contains sulfur compounds in ranges from a few thousand to 20,000 parts per million. The H_2S necessary for the activation of the catalyst is generated by the decomposition of the sulfur compounds. This method is in very little use today, but it was “state of the art” in the 1960s and early 1970s. The preferred sulfiding procedure in the industry is liquid phase with a sulfur-containing component added to the feed (generally a form of DMDS or a polysulfide). It results in savings of time when compared to either vapor phase or liquid phase without these agents. In addition to the time savings, liquid phase sulfiding is desirable because the liquid phase provides a heat sink for the exothermic sulfiding reactions which helps prevent high catalyst temperatures and temperature excursions which could otherwise result in sintering and metals reduction. The active phase in Type II hydrotreating catalysts, orders of magnitude more active than Type I at start of run, is especially susceptible to such damage during the sulfiding process. Another advantage of liquid phase over gas phase sulfiding is that by having all the catalyst particles wet from the very beginning, there is very little chance of catalyst bed channeling which can occur if the catalyst particles are allowed to dry out. The in situ sulfiding occurs at temperatures between 450 °F and 650 °F (230–345 °C) regardless of the method used. Some catalyst manufacturers recommend that the sulfiding be conducted at full operating pressure, while others prefer it be done at pressures lower than the normal operating pressure. It is also very typically recommended that cracked feedstocks should be introduced very gradually, over a period of 3–7 days. Cracked feedstocks are composed of relatively more olefins and aromatics, and so introducing these during the start of run period would lead to excessive heat release, leading to catalyst damage via sintering of the active phase.

In the case of ex situ presulfurization of the catalyst, sulfur compounds are loaded onto the catalyst. The activation occurs when the catalyst, which has been loaded in the reactor, is heated up in the presence of hydrogen and the sulfur compounds decompose to H_2S. During this period, the H2S scrubber is off-line so that the H2S can accumulate in the recycle gas circuit.

Catalyst Deactivation, Regeneration, and Rejuvenation

Catalyst deactivation is the gradual loss of the catalyst's ability to produce the desired specification product unless reactor temperatures are increased (or feed rate is decreased). The catalyst activity determination is shown under the "Catalysts" section of this chapter. Typically, as the run progresses, the catalyst loses activity. Catalysts will lose activity in several ways described below.

Coke Deposition

Coke is the term used to describe the formation of hydrogen-deficient carbonaceous materials, most particularly on the catalyst surface. Coke is generally formed by thermal condensation, catalytic dehydrogenation, and polymerization reactions. A schematic of this is shown below:

$$\text{Hydrocarbons} \underset{(2)}{\overset{(1)}{\rightleftarrows}} \text{Coke precursors} \overset{(3)}{\rightarrow} \text{Coke}$$

Where:

1. Dehydrogenation
2. Hydrogenation
3. Condensation/polymerization

The coke level rapidly rises to an equilibrium level during the early part of a catalyst cycle. This initial coke is often referred to as “soft” coke. During the rest of the cycle, the total amount of coke remains almost constant; however further structural changes occur to produce what is often referred to as “hard” coke. Thus, the observed catalyst deactivation during a cycle is primarily the result of structural changes to the coke rather than an actual marked increase in the total amount of coke. Short-term recovery of catalyst activity has been observed on a number of occasions after a period of hot hydrogen stripping. This fits with the expectation that soft coke should be able to be partially stripped or washed from the catalyst.

As can be seen from the reaction schematic, the route to coke precursor formation is dehydrogenation. Hydrogen-deficient feedstocks (i.e., cracked stocks) therefore result in faster coke deactivation. High temperatures favor faster coke deactivation because the laydown of coke on a catalyst is a time-temperature phenomenon in that the longer the exposure and/or the higher the temperature the catalyst is subjected to, the more severe the deactivating effect. Coke is not a permanent poison. Catalyst, which has been deactivated by coke deposition, can be, relatively easily, restored to close to original condition by regeneration. Low hydrogen partial pressures also favor coke formation. In general, the heavier feedstock will produce higher levels of coke on the catalyst. In general, the maximum coke laydown is about 20 wt%.

Metals Deposition

Deposition of metals is not reversible, even with catalyst regeneration. The metals may come into the system via additives, such as silicon compounds used in coke drums to reduce foaming, or feedstock contaminants such as Pb, Fe, As, P, Na, Ca, and Mg, or organometallic compounds in the feed primarily containing Ni and V. The deposition of Ni and V takes place at the pore entrances or near the outer surface of the catalyst, creating a “rind” layer – effectively choking off access to the interior part of the catalyst, where most of the surface area resides.

Catalyst Support Sintering

This is another reason for loss of catalyst activity and it also is irreversible. This is also a result of high temperatures and particularly in connection with high water partial pressures. In this case the catalyst support material can lose surface area from a collapse of pores or from an increase in the diameter of pores, with the pore volume remaining approximately constant.

Catalyst Regeneration

The activity decline due to coke laydown can be recovered by burning the coke off in a controlled atmosphere. The regeneration can be accomplished in any of three ways: in situ with steam/air, in situ with nitrogen/air, or ex situ. The majority of commercial catalyst regenerations, at least in the industrialized world, are performed ex situ, by specialized contractors, because of environmental considerations as well as because it results in a superior regenerated catalyst. Prior to regeneration, the spent catalyst must be de-oiled; this activity can be done in situ at the refinery or ex situ at the service provider's facility. De-oiling is needed to prevent the formation of sulfates during the regeneration. The formation of sulfates will lead to disappointing catalyst performance and shorter cycle length. During regeneration/combustion, coke is converted to CO_2 and H_2O. In the absence of excess oxygen, CO may also form. Hydrotreating catalysts contain sulfur, as metal sulfides. In the regeneration process, the metal sulfides are converted into the corresponding metal oxides and the sulfur is emitted as SO_2. In general, sulfur dioxide emission starts at lower temperature than CO_2 emission. Regeneration service providers rely on several forms of equipment. One vendor uses a continuous rotolouver, which is a cylindrical drum rotating slowly on a horizontal axis and enclosing a series of overlapping louvers. The spent catalyst passes slowly through the rotolouver, where it encounters a countercurrent of hot air. Another uses a belt furnace. The catalyst is conveyed with the stainless steel belt through a stationary furnace. A third vendor makes use of an ebullated bed furnace/reactor to perform the catalyst regeneration. Regardless of the process, the spent catalyst is submitted to de-oiling prior to regeneration, which eliminates as much hydrocarbon as possible and which removes as much sulfur as possible, preventing the formation of sulfates which could deposit on the catalyst and not be removed during regeneration. Sulfates are deleterious to catalyst performance. While the in situ regeneration results in about 90 % catalyst activity recovery, ex situ catalyst regeneration can result in 95–97 % catalyst activity recovery. Following regeneration, Type II hydrotreating catalysts require a rejuvenation step, wherein the active phase is re-dispersed as it was when fresh.

Design and Operation of Hydrotreating Reactors

Design and Construction of Hydrotreating Reactors

Hydrotreating reactors are downflow, fixed-bed catalytic reactors, generally operating in trickle-flow regime. Because hydrotreating occurs at moderately high pressure and relatively high temperature and in the presence of hydrogen and hydrogen sulfide, the reactors are vessels with relatively thick wall. The reactors are usually cylindrical vessels, and while those used for naphtha hydrotreating as well as many of the older vintage reactors are made from lower alloys, most of those designed in the last 10 years are typically constructed of 1¼ Cr–½ Mo or 2¼ Cr–1 Mo base metal with a lining of stabilized austenitic stainless steel for added corrosion protection. This choice of alloys gives the high strength of the base metal and the excellent corrosion resistance of the inner lining. There are several items concerning the selection of materials that must be taken into consideration during the operation of the unit. Concerning the use of austenitic stainless steels in hydrotreating units, the possibility exists for corrosion cracking to occur if proper procedures are not followed. Corrosion cracking in a hydrotreating unit can occur through chloride attack or polythionic acid attack. Chloride attack can be prevented by minimizing the amount of chloride in the process material that will come in contact with the austenitic stainless steel during normal operations. In addition, during start-up and shutdown operations, precautions should be taken to limit the chloride content in any flushing, purging, or neutralizing agents used in the system.

Polythionic acids occur as the result of the action of water and oxygen on the iron sulfide scale that forms on all items made of austenitic stainless steel. Once formed these acids can attack the austenitic steel and cause intergranular corrosion and cracking. To prevent polythionic acid attack, it is necessary to maintain the temperature above the dew point of water in those areas containing stainless steel. Under normal operating conditions, the system is essentially free of oxygen. However, when the system is depressurized and the equipment is opened to air, it becomes necessary to maintain a nitrogen purge to prevent air from entering. In cases where adequate temperatures or purges cannot be maintained, a protective neutralizing environment should be established. Generally, a 5 % soda solution is used to neutralize the austenitic stainless steel.

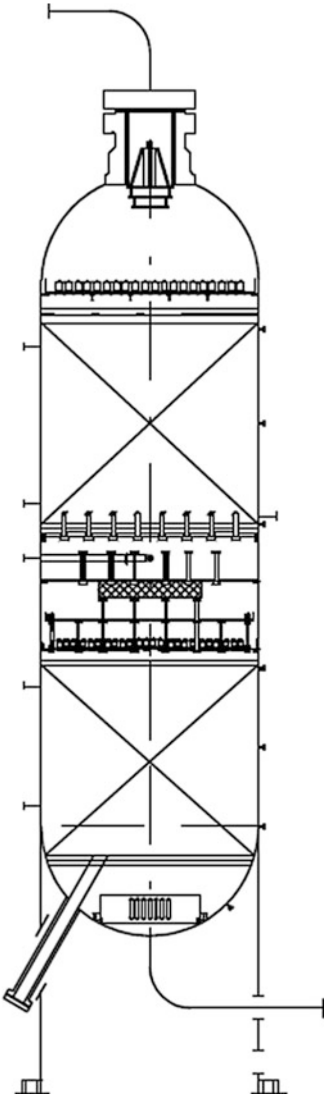
Figure 26 shows a hydrotreating reactor with two beds of catalyst and one interbed quench zone pictured, but the number of beds can vary for different designs. As already indicated, most naphtha hydrotreaters only have one catalyst bed. Many reactors processing cracked feedstocks will have several beds to facilitate temperature control by cooling with hydrogen quench between the catalyst beds. For example, a reactor design could require three catalyst beds and two interbed quench zones.

The reactor vessel is designed to allow maximum utilization of catalyst. Creating equal flow distribution, providing maximum liquid/vapor mixing, and providing multiple beds with quench zones for efficient catalyst usage achieve this. The internals of the reactor found in a reactor are the following (though not all reactors necessarily have all of them):

- Inlet diffuser
- Top vapor/liquid distribution tray
- Quench section (present only when there are multiple catalyst beds)
- Catalyst support grid (present only when there are multiple catalyst beds)
- Outlet collector

The size of hydrotreating reactors varies widely depending on the design conditions and is dependent on the desired mass velocity and acceptable

Fig. 26 Two-bed hydrotreating reactor with interbed quench



pressure drops. Since heat release is a common feature for all hydrotreaters, reactor temperature control has to be exercised. Generally, the maximum allowable ΔT is 75 °F (42 °C). If that temperature is not expected to be exceeded, the reactor will contain only a single bed, and temperature control will be exercised by changing the reactor inlet temperature. If the overall maximum reactor temperature rise is expected to exceed 75 °F (42 °C), a multiple-bed reactor should be installed with cold hydrogen quench inserted in the quench section for temperature control.

Hydrotreater Reactor Operation

During operation, the hydrotreating catalyst gradually loses some of its activity. In order to maintain the desired quality of the products at the design feed rate, the average bed temperature is gradually increased. The temperature increase in many cases is very small, less than 2 °F/month (1 °C/month). When the average bed temperature reaches a value close to the design maximum, the catalyst has to be replaced or reactivated. Because the required temperature increase per unit time is relatively small, the reactor can be operated with the same catalyst for several years before regeneration or replacement of the deactivated catalyst becomes necessary. Quite often, catalyst regeneration or replacement is dictated by a high reactor pressure drop, due to catalyst fouling.

In hydrotreating, the key catalytic properties are initial activity, stability, and product quality. The temperature required to obtain the desired product at the start of the run measures the initial activity. Catalyst stability is a measure of change of reaction rate over time. The product quality is a measure of the ability of the process to yield products with the desired use specification such as pour point, smoke point, or octane. Table 8 shows some of the important product quality measurements and the chemical basis for these measurements.

Hydrotreating Process Variables

The proper operation of the unit will depend on the careful selection and control of the processing conditions. By careful monitoring of these process variables, the unit can operate to its full potential.

Reactor Temperature

Reactor temperature should be minimized while maintaining desired product quality. Increasing reactor temperature will accelerate the rate of coke formation and reduce the length of the operating cycle. The required temperature is dependent upon feed rate and quality and processing objectives. The reactor inlet temperature is most easily and commonly controlled by the operator to adjust for obtaining the desired product quality. The reactor outlet temperature is a function of the feed quality and cannot be easily varied except by changing the reactor inlet temperature or the temperature profile across the beds by the use of quench. The inlet temperature must always be controlled at the minimum required to achieve the desired product properties. Temperatures above this minimum will only lead to higher rates of coke formation and reduced processing periods. The weight average bed temperature (WABT) is the kinetic parameter typically used to compare the relative catalyst activity. The WABT can be calculated as shown in Fig. 27.

If the reactor only has inlet and outlet thermometry (as is the case in perhaps as many as two-thirds of hydrotreaters), the WABT represents the average of inlet and outlet temperatures. The rate of increase in this temperature is referred to as the deactivation rate expressed as °F per barrel of feed per pound of catalyst (°C per m^3

Table 8 Chemical basis for product quality

Quality measurement	Chemical basis
High smoke point	Low concentration of aromatics
Low pour point	Low concentration of *n*-paraffins
Low freeze point	Low concentration of *n*-paraffins
Low cloud point	Low concentration of *n*-paraffins
Low CFPP	Low concentration of *n*-paraffins

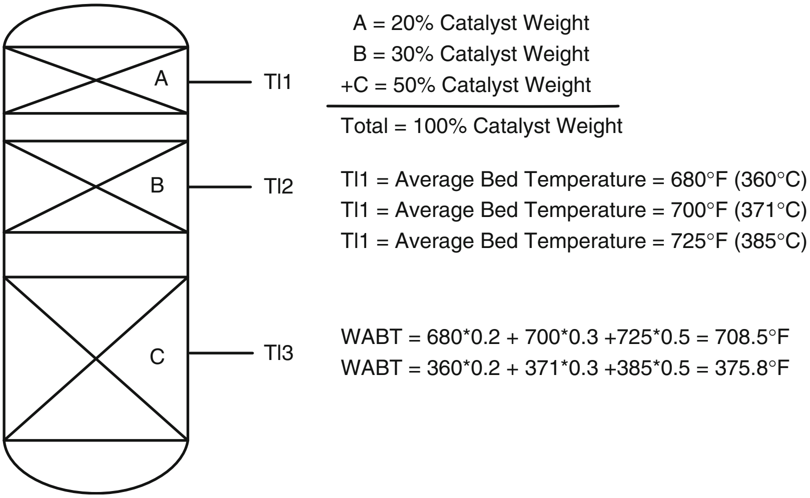


Fig. 27 Weighted average bed temperature (WABT)

of feed per kilogram of catalyst) or simply as °F per day (°C per day). During the course of an operating cycle, the temperature required to obtain the desired product quality will increase as a result of catalyst deactivation. The maximum catalyst operating temperature determines the temperature cycle and cycle length of the catalyst.

The metallurgical design temperature of the reactor(s) will determine the maximum allowable catalyst operating value. The axial and radial temperature rise across the reactor(s) must be monitored continuously in order to assure that the design limitation of the unit is not exceeded. This can be especially important when changing feedstocks since olefin saturation results in considerably higher heats of reaction. Units are typically designed for a maximum reactor bed temperature rise <60 °F (33 °C).

Feed Quality and Rate

The amount of catalyst loaded into the reactors as well as other design parameters are based on the quantity and quality of feedstock the unit is designed to process. While minor changes in feed type and charge rate can be tolerated, wide variations should be avoided since they will tend to reduce the useful life of the catalyst. An increase in the charge rate will require higher reactor temperature to achieve a constant desulfurization (or denitrogenation) as well as higher recycle gas rate to maintain a constant ratio of H_2 to hydrocarbon. The increased reactor temperatures will lead to a faster rate of coke formation that will reduce the cycle length. A reduced feed rate may lead to bad flow distribution through the catalyst, such that higher temperatures will be required to obtain good product quality. A feed's distillation range and API gravity best indicate the type of feed being processed. An increase in the end point of the feed will make sulfur and nitrogen removal more difficult, thus requiring higher reactor temperatures which, in turn, accelerate coke formation. Coke deposition is also accelerated by the fact that heavier feed contains more of the precursors that favor coke formation. In addition to the above, high boiling fractions also contain increased quantities of metals which lead not only to higher reactor pressure drop but to rapid catalyst deactivation as well. A reduction in the API gravity of the feed for the same boiling range is an indication of higher unsaturates content. This type of feed will result in increased hydrogen consumption and higher temperature rise across the catalyst bed. It also contains more of the materials that easily condense to form coke in the reactor and associated equipment.

Hydrogen Partial Pressure

The hydrogen partial pressure is calculated by multiplying the H_2 purity of the recycle gas times the pressure of the product separator. The hydrogen partial pressure required for the operation of a unit is chosen based on the degree of sulfur (or nitrogen, or aromatic saturation) removal that must be achieved and is generally an economic optimum that balances capital cost and operating costs against catalyst life. Hydrogen partial pressure is also a critical design parameter for achieving the desired degree of feed saturation. Figures 28 and 29 illustrate the effect of hydrogen partial pressure on the quality of the products. A reduction of the operating pressure below the design level will have a negative effect on the activity of the catalyst and will accelerate catalyst deactivation due to coke formation.

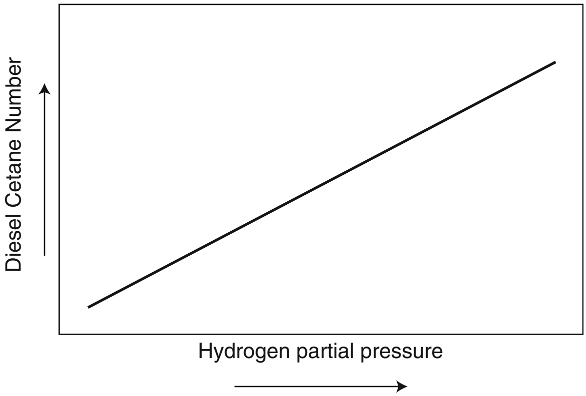


Fig. 28 Effect of pressure on aromatics saturation

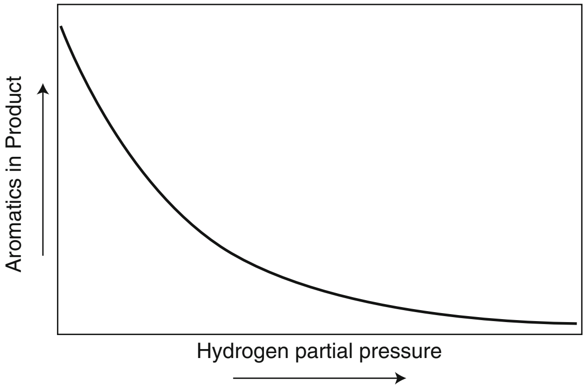


Fig. 29 Effect of pressure on distillate quality

Gas-to-Oil Ratio

This is an important variable for the satisfactory performance of a hydrotreater. If the unit is operated at lower than design ratios, more rapid catalyst deactivation will result. The circulating gas also provides the heat sink for the removal of the heat of reaction. Though various hydrotreating unit designers and catalyst manufacturers use different values, it is generally accepted that the minimum gas-to-oil ratio should be at least three to four times the amount of hydrogen consumption, although this may be lower for distillate and naphtha hydrotreating operations.

Liquid Hourly Space Velocity

The design quantity of catalyst per unit of feed will depend upon feedstock properties, operating conditions, and product quality required. A simplified kinetic expression based on sulfur and/or nitrogen removal determines the design liquid hourly space velocity for most feedstocks and processing objectives. This initial value may be modified due to other considerations such as unit size, extended catalyst cycle life, abnormal levels of feed metals, and requirements of other processing units in the refinery flow scheme. A unit design is based on operation to achieve optimum performance. One criterion is liquid mass flux across the catalyst bed. At reduced throughput, unit operation may become difficult due to hydraulic considerations. Also, liquid distribution in the reactor may become unequal as preferential flow paths are established. For these reasons, the unit should not be operated below the minimum turndown capacity for extended periods. Unit turndown will vary for each design and is typically 50–70 % of design capacity. Operation at too high of space velocity (compared to original design) is not advisable because of increased catalyst deactivation rates as well as increased system pressure drop.

Recycle Gas Purity

The effective completion of the hydrogenation reactions occurring over the catalyst requires that a certain quantity of hydrogen be present at a minimum hydrogen partial pressure. As noted previously, both the quantity (gas-to-oil ratio) and partial pressure are dependent upon the hydrogen content, i.e., purity, of the recycle gas.

Practical considerations, such as the cost of compression, catalyst life, etc., limit the purity of the recycle gas to a minimum value usually in the range of 70–80 mol%. Lower hydrogen purities are detrimental to the performance of the unit since higher temperatures must be used to achieve the desired product quality. The purity of the recycle gas is determined by the following factors:

- The purity of the makeup gas and introduction of light ends into the reactor circuit
- Vapor/liquid equilibrium at the separator that forms the recycle gas
- The amounts of light hydrocarbons and H_2S that are allowed to accumulate in the recycle gas

In most instances, the makeup gas H_2 purity cannot be easily manipulated since it is fixed by the operation of the reformer or the hydrogen manufacturing plant. The light hydrocarbons present in the recycle gas enter the system with the makeup gas in addition to those being formed in the reactor and must be vented from the high-pressure separator to prevent their accumulation in the recycle gas. The amount of hydrogen required is determined by:

(a) Chemical hydrogen consumption – the hydrogen consumed during the hydrotreating reactions.
(b) Solution losses – the hydrogen that is removed from the reactor circuit dissolved in the liquid hydrocarbon leaving the high-pressure separator.
(c) Mechanical losses – the hydrogen lost through the makeup and recycle gas compressors' packing vents and seals. This value may be roughly estimated at 3–5 % of the combined chemical consumption plus solution losses.
(d) Venting losses – the hydrogen lost in the purge stream from the high-pressure separator to maintain recycle gas purity.

The H_2S formed in the reactors can reach equilibrium values as high as 5 mol% in the recycle gas. This concentration of H_2S has an inhibiting effect on the activity of the catalyst. Therefore, in many cases it is desirable to remove the H_2S from the recycle gas. The removal of H_2S is performed in a scrubber where the recycle gas is contacted with an amine (generally MEA, DEA, or MDEA) solution. In this manner, the H_2S content of the recycle gas can be reduced to the parts per million range.

Another method to increase hydrogen purity is membrane separation. This system removes the hydrogen from the vent gas and recycles it back with the makeup hydrogen.

Feed Contaminants and Catalyst Poisons

Temporary

Process variables influence catalyst life by affecting the rate of carbon deposition on the catalyst. There is a moderate accumulation of carbon on the catalyst during the initial days of operation. The rate of increase will be reduced to very low levels under normal processing conditions. A carbon level of 5 wt% may be tolerated without a significant decrease in desulfurization. However, denitrogenation activity would be reduced.

The sulfur and nitrogen found in the feed could be considered contaminants to the extent that they produce hydrogen sulfide and ammonia which can react to form ammonium bisulfide. The water injected into the reactor effluent dissolves the ammonium bisulfide and prevents exchanger fouling. Organic nitrogen in the feed, if present in amounts higher than expected, will require higher reactor temperatures for processing and will lead to a reduction in catalyst life.

If the water injection should be stopped for any period of time, the H_2S and NH_3 may accumulate in the recycle gas and result in a sudden loss in catalyst activity. The activity will return to normal once wash water is reestablished. Catalyst bed temperatures should not be increased to compensate for the temporary activity loss.

Small amounts of molecular nitrogen, CO, and CO_2 that enter the system with the makeup gas are not harmful to the catalyst, but must be vented to prevent accumulation in the recycle gas. Excessive amounts of CO and CO_2 may have an adverse effect on catalyst performance, as they may be methanated by the catalyst taking up active sites and liberating heat. This will raise the outlet temperature and reduce the apparent catalyst activity. The unit should never be pressured up with high $CO + CO_2$ containing makeup gas as a temperature runaway may result.

Permanent

Permanent loss of catalyst activity is usually caused by the gradual accumulation of inorganic species picked up from the feed, makeup hydrogen, or effluent wash water. Examples include arsenic, lead, calcium, sodium, silicon, and phosphorus. Low concentrations of these elements (and other alkaline metals) can cause deactivation over time as they are deposited on the catalyst.

Organic metal compounds are decomposed and typically deposit in the upper section of the catalyst bed as a metal sulfide. The graded catalyst bed, if used, may contain demetallation catalysts that have a high metal retention capacity. Some of these catalysts may retain as much as 100 wt% of the fresh catalyst weight as metals from the feed. These demetallation catalysts typically have a lower activity for desulfurization and denitrogenation.

Hydrotreating catalysts exhibit a moderate tolerance for metals such as arsenic and lead. Total metal content of 2–3 wt% of the hydrotreating catalyst have been observed. However, product analysis frequency should be increased to monitor breakthrough when calculations show the metal level on the hydrotreating catalyst exceeds 0.5 wt%. Metals cannot be removed by catalyst regeneration. Catalyst replacement should be considered when metal loading of 1–2 wt% is exceeded on the hydrotreating catalyst.

Apparent catalyst deactivation may be caused by the accumulation of deposits on top of the catalyst bed. Solid material, such as corrosion products and coke, will lead to rapid fouling of the catalyst bed if allowed to enter the reactor. This problem is remedied by skimming a portion of the catalyst, screening, and reloading.

Feed filtering is a first defense and is quite effective in removing solid material and as such results in longer operating cycles due to the lower rate of reactor pressure drop buildup. The use of feed filtering will depend on the type of feed processed and its source. A second line of defense is the use of specially shaped particle or reticulated media loaded above the active hydrotreating catalysts to remove fines that pass through the feed filter or are formed in situ in the reactor circuit.

Hydrotreating Technology Suppliers and Catalyst Manufacturers

Technology Suppliers

Historically many companies have offered to supply hydrotreating unit technology. Most types of hydrotreating processes are offered through licensing arrangements and some are non-licensed technologies. Today, CB&I/Chevron Lummus Global (CLG), Axens/IFP Energies Nouvelles, Shell Global Solutions/KBR, Haldor Topsøe, DuPont, and Honeywell UOP are the main providers of technology for the various types of hydrotreating units.

Catalyst Manufacturers

Through the years, there have been many manufacturers of hydrotreating catalysts. Some suppliers have consolidated with others. Other manufacturers have absorbed some, some have changed names, and some have discontinued hydrotreating catalyst manufacturing. Some suppliers simply sell catalyst they have re-branded with their name. The following is a list of the current major suppliers of hydrotreating catalysts: Advanced Refining Technologies (ART), Albemarle, Axens/IFP Energies Nouvelles, Criterion Catalysts and Technologies (CRI)/Shell Global Solutions, Haldor Topsøe AS, Orient Catalyst Co. Ltd., Clariant International Ltd./ Süd-Chemie Inc., and Honeywell UOP.

References

P.E.M. Berthelot, Methode universelle pour réduire et saturer d'hydrogéne les composés organiques. Bull. Soc. Chim. **11**(278), 278–286 (1869)

M. Breysse, C. Geantet, P. Afanasiev, J. Blanchard, M. Vrinat, Catal. Today **130**, 3–13 (2008)

J. Čejka, Appl. Catal. Gen. **254**, 327–338 (2003)

F. Chainet, Ph.D. Thesis, Spéciation du silicium dans les charges d'hydrotraitement, 2012

R.R. Chianelli, G. Berhault, B. Torres, Unsupported transition metal sulfide catalysts: 100 years of science and application. Catal. Today **147**(3–4), 275 (2009)

A.I. Dugulan, *High Pressure Sulfidation of Hydrotreating Catalysts – Genesis and Properties of the Active Phase*, Delft University Press (IOS Press, 2008)

S. Eijsbouts, S. Mayo, K. Fujita, Unsupported transition metal sulfide catalysts: from fundamentals to industrial application. Appl. Catal. Gen. **322**, 58 (2007). Active Phases for Hydrotreating Catalysis

N. Frizi, P. Blanchard, E. Payen, P. Baranek, C. Lancelot, M. Rebeilleau, C. Dupuy, J.P. Dath, Catal. Today **130**, 32–40 (2008)

R. Hadden, T. Moss, Dealing with mercury in refinery processes, PTQ Q3 (2010)

E.J.M. Hensen, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, Catal. Lett. **84**(1), 59 (2002)

T. Ho, Inhibiting effects in hydrodesulfurization of 4,6-diethyldibenzothiophene. J. Catal. **219**, 442–451 (2003)

T. Ho, Deep HDS of diesel fuel: chemistry and catalysis. Catal. Today **98**, 3–18 (2004)

V.N. Ipatieff, Russkoe Fiziko-Kimischeskoe Obshchestvo, **33**, 143–154, 496–506, 532–545, 632–643 (1900–1902)

L. Jones, P. Kokayeff, Distillate hydrotreating to ULSD – the impact of aromatics, in *Paper 90a, AIChE 2004 Spring National Meeting*, 27 Apr 2004

L. Jones, P. Kokayeff, Equilibrium limitations in distillate hydrotreating, in *Paper 61d, AIChE 2005 Spring National Meeting*, 10 Apr 2005

L. Leonard, P. Kokayeff, Recombination – a complicating issue in FCC naphtha desulfurization, in *Paper 177c, AIChE 2006 Spring National Meeting*, 26 Apr 2006

M. Pier, Z. Elektrochem. **53**, 297 (1949)

P. Sabatier, J.B. Senderens, Action du nickel sur l'éthyléne. Compt. Rend **124**, 1358 (1897)

A.N. Stranges, Friedrich Bergius and the rise of the German synthetic fuel industry. Isis (Hist. Sci. Soc.) **75**(4), 643–667 (1984)

H. Topsøe, B.S. Clausen, Importance of Co-Mo-S type structures in hydrodesulfurization. Catal. Rev. Sci. Eng. **26**(3), 395 (1984)

H. Topsøe, B. Clausen, F.E. Massoth, *Catalysis: science and technology*, vol. 11 (Springer, Berlin, 1996)

O. Weisser, S. Landa, *Sulfide catalysts: their properties and applications* (Pergamon, Oxford, 1973)

W.R.K. Wu, H.H. Storch, Hydrogenation of coal and tar. Bur. Min. Bull. **633**, (1968)

TransportPolicy.Net, *Nationwide Diesel and Gasoline Sulfur Limits* (International Council on Clean Transportation, 2014), www.TransportPolicy.Net

Alkylation in Petroleum Processing

Douglas A. Nafis, Kurt A. Detrick, and Robert L. Mehlberg

Contents

D.A. Nafis (✉) • K.A. Detrick • R.L. Mehlberg
UOP, A Honeywell Company, Des Plaines, IL, USA
e-mail: doug.nafis@honeywell.com; kurt.detrick@honeywell.com;
robert.mehlberg@honeywell.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_5

Abstract

Motor fuel alkylation in the petroleum refining industry refers to the acid-catalyzed conversion of C_3-C_5 olefins with isobutane into highly branched C5-C12 isoparaffins collectively called alkylate, a valuable gasoline blending component. Alkylation reactions are catalyzed by liquid and solid acids. HF alkylation and sulfuric acid alkylation are the most widely practiced commercial motor fuel alkylation processes and are the focus of this section. In recent years, considerable development effort has gone into solid acid catalysts and processes that mitigate the hazards associated with HF and H2SO4. Several of these processes have been offered commercially, but have not caught on because of high recycle isobutane requirements and high capital costs associated with catalyst regeneration. A new wave of ionic liquid catalysts is currently nearing commercialization.

Keywords

Alkylation • Motor fuel alkylation • Hydrofluoric acid (HF) alkylation • Sulfuric acid alkylation • Solid catalyst alkylation • Ionic liquid alkylation

Introduction

Motor fuel alkylation in the petroleum refining industry refers to the acid-catalyzed conversion of C_3–C_5 olefins with isobutane into highly branched C_5–C_{12} isoparaffins collectively called alkylate, a valuable gasoline blending component. A major constituent of alkylate is 2,2,4-trimethylpentane which is defined on the octane scale by a value of 100.

Alkylation reactions are catalyzed by liquid and solid acids, including H_2SO_4, $AlCl_3$-HCl, HF, HF-BF_3, H_2SO_4-HSO_3F (fluorosulfuric acid), trifluoromethanesulfonic acid, chlorided Pt-alumina, BF_3 on alumina, zeolites, and ion-exchange resins. However, the catalysts and associated processes commercialized during World War II for aviation gasoline, HF alkylation and sulfuric acid alkylation, are the focus of this section as these remain the primary commercially practiced motor fuel alkylation processes.

In recent years, considerable development effort has gone into catalysts and processes that mitigate the hazards associated with HF and H_2SO_4. Several solid catalyst processes (UOP Alkylene^{TM}, CB&I/Albemarle/Neste Oy AlkyClean^{TM}, and Exelus ExSact^{TM} processes) have been offered commercially, but have not caught on because of high recycle isobutane requirements and high capital costs associated with catalyst regeneration. A new wave of alkylation processes based on ionic liquid catalysts is currently nearing commercialization.

History

From 1932 to 1936, alkylation was independently discovered by Universal Oil Products (Ipatieff and Grosse 1935) (now UOP a Honeywell Company), Shell, the Anglo-Iranian Oil Company (now BP), and Texaco whose first publications issue in that order.

Herman Pines told the story of UOP's discovery of the alkylation of ethylene by pentanes in 1932 (Pines 1982). At that time, leading universities taught that isoparaffins were inert except at high temperatures and pressures. After finding anomalies in an olefin assay based upon H_2SO_4 extraction, Pines and his mentor Vladimir Ipatieff hypothesized that paraffins may not be inert to acids. Despite the ridicule, they tested that hypothesis by bubbling ethylene into chilled pentanes over $AlCl_3$ and found that all the ethylene was converted into saturated hydrocarbons. Over the next few years, they tested $AlCl_3$-HCl, H_2SO_4, HF, and HF-BF_3 as alkylation catalysts.

Alkylate derived from butenes and isobutane was found to have excellent aviation gasoline properties. It was the highest octane fuel component then known, with high motor octane and excellent lead response. All of these properties are derived from the highly branched paraffins that form its composition.

Humble Oil (now ExxonMobil) built the first commercial H_2SO_4 alkylation unit in 1938 at Baytown, Texas (Hooper 1986). Alkylation for aviation gasoline grew rapidly with the Allies' war effort. In 1939, six petroleum companies formed a consortium to pool their alkylation technology and develop both sulfuric acid and HF acid processes for 100 octane aviation fuel. As a result of this effort, the first commercial HF alkylation unit started up in 1942 at Phillips Petroleum's Borger, Texas refinery, broadening the feedstock to include propylene and pentene along with butenes (Phillips 1946). During the war, a total of 60 alkylation units were built for the Allies' war effort. Half were built with sulfuric acid as the catalyst and half with hydrofluoric acid. Following World War II, most alkylation operations were discontinued although a few refiners continued to use the process for the production of aviation and premium automobile gasolines.

In the mid-1950s, the use of higher-performance automotive engines required the refining industry to increase both gasoline production and quality. The development of catalytic reforming, such as the UOP Platforming™ process, provided refiners with an important refining tool for the production of high-octane gasolines. However, the motor fuel produced in such operations, called reformate, is highly aromatic with a higher sensitivity (the spread between research and motor octane) and a lower lead response than alkylate. Many refiners expanded their alkylation operations and use of propylene, and even some pentenes in the alky unit feed in addition to butenes became more widespread.

With the phaseout of leaded gasoline and the advent of environmental gasolines, the lead response of alkylate is no longer valued, but the importance of alkylate and its production have both grown because of its other properties. Its high unleaded motor octane, low volatility, low sulfur, and nearly zero olefins and aromatics make alkylate critical to the production of quality environmental gasolines. Alkylate typically makes up about 15 % of the gasoline blending pool but can reach as much as 60 % of the low-sulfur reformulated premium pool. Following the phase-out of MTBE from gasoline in 2004 and mandates established in the Energy Policy Act of 2005 and Energy Independence and Security Act of 2007, ethanol is blended into most US gasoline at average levels of about 10 vol%. The low RVP of alkylate is important for offsetting the high vapor pressure of the added ethanol while maintaining high octane.

Licensors of commercially proven H_2SO_4 alkylation processes are ExxonMobil and DuPont^{TM} STRATCO^{R}. Following its acquisition of the Conoco Phillips HF Alkylation technology in 2007, UOP LLC is now the sole licensor of motor fuel HF Alkylation.

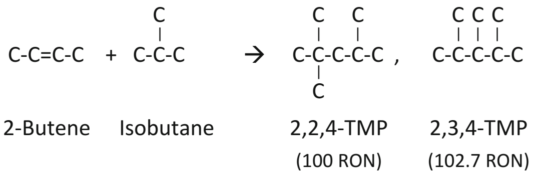
Process Chemistry

The reactions taking place in the alkylation reactor are many and relatively complex, proceeding by a *t*-butyl carbenium ion chain mechanism (Jernigan et al. 1965). The principal overall reactions are described below.

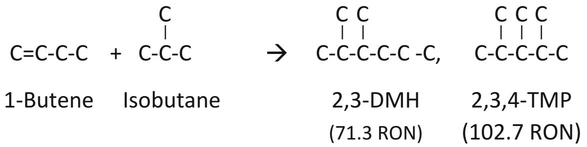
Primary Alkylation Reactions

Most of the alkylate product is made by primary alkylation reactions. In these reactions, one mole of olefin reacts with one mole of isobutane to form an isoparaffin exactly four carbon numbers heavier. Sample primary alkylation reactions, showing only the carbon framework and one or two of the principal product isomers, are shown for each of the principal feed olefins in Eqs. 1, 2, 3, 4, and 5. It should be noted that the isomers shown are not necessarily the expected primary product but are the ones most commonly observed. For example, the reaction of 2-butene and isobutane in Eq. 1 might be expected to give 2,2,3-trimethylpentane as the primary product, but due to isomerization and methyl transfer reactions described below, the 2,2,4-TMP and 2,3,4-TMP isomers are more commonly observed. Isomer distributions also vary somewhat for different catalysts.

Alkylation of 2-Butene

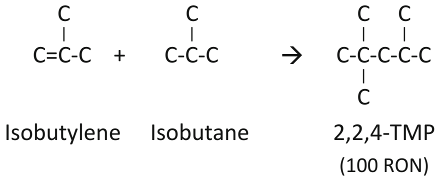

$$\mathrm{C{-}C{=}C{-}C} + \mathrm{C{-}\overset{C}{C}{-}C} \rightarrow \mathrm{C{-}\underset{C}{\overset{C}{C}}{-}C{-}\overset{C}{C}{-}C},\quad \mathrm{C{-}\overset{C}{C}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \tag{1}$$

Alkylation of 1-Butene



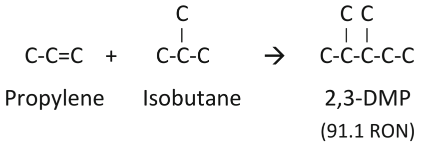
(2)

Alkylation of Isobutylene (i-Butene)



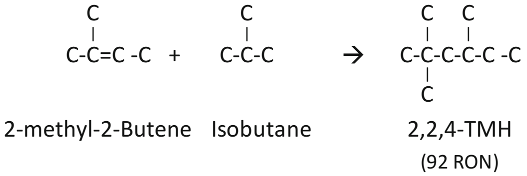
(3)

Alkylation of Propylene



(4)

Alkylation of Amylenes



(5)

Complex Alkylation Reactions

The balance of the alkylate and small amounts of undesirable by-product conjunct polymer is formed by more complex reactions of the ionic intermediates. Some of these reactions are given by Eqs. 6, 7, 8, 9, and 10. For brevity, only a few key steps and no structures are shown.

Hydride Transfer (Propylene Example)

$$\begin{array}{l}
C_3H_6 + H^+ \rightarrow C_3H_7^+ \\
\text{(formation of propenium ion)} \\
C_3H_7^+ + iC_4H_{10} \rightarrow iC_4H_9^+ + C_3H_8 \\
\text{(Hydride transfer from isobutane to propenium ion)} \\
iC_4H_9^+ \rightarrow iC_4H_8 + H^+ \\
iC_4H_8 + iC_4H_{10} \rightarrow C_8H_{18} \\
\text{(Alkylation)} \\
\hline
C_3H_6 + 2iC_4H_{10} \rightarrow C_3H_8 + C_8H_{18} \\
\text{(Overall: Propylene + 2 Isobutane} \rightarrow \text{propane + 224-TMP)}
\end{array} \qquad (6)$$

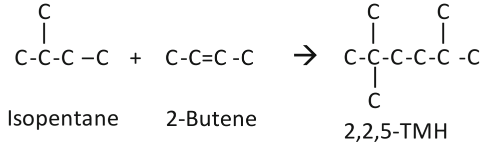
Polymerization (Isobutylene Example)

$$\begin{array}{l}
iC_4H_8 + iC_4H_9^+ \rightarrow iC_8H_{17}^+ \\
iC_4H_8 + iC_8H_{17}^+ \rightarrow iC_{12}H_{25}^+ \\
iC_{12}H_{25}^+ + iC_4H_{10} \rightarrow iC_{12}H_{26} + iC_4H_9^+ \\
\hline
2iC_4H_8 + iC_4H_{10} \rightarrow iC_{12}H_{26} \\
\text{(Overall: 2 Isobutylene + Isobutane} \rightarrow \text{Pentamethylheptane)}
\end{array} \qquad (7)$$

Cracking (Cracking of Heavy Ends from Isobutylene)

$$\begin{array}{l}
2iC_4H_8 + iC_4H_9^+ \rightarrow iC_{12}H_{25}^+ \\
iC_{12}H_{25}^+ \rightarrow iC_7H_{14} + iC_5H_{11}^+ \\
\qquad \text{(Cracking)} \\
iC_5H_{11}^+ + iC_4H_{10} \rightarrow iC_5H_{12} + iC_4H_9^+ \\
\qquad \text{(Hydride Transfer)} \\
iC_4H_9^+ + iC_7H_{14} \rightarrow iC_{11}H_{23}^+ \\
\qquad \text{(Alkylation)} \\
iC_{11}H_{23}^+ + iC_4H_{10} \rightarrow iC_{11}H_{24} + iC_4H_9^+ \\
\qquad \text{(Hydride Transfer)} \\
\hline
2iC_4H_8 + 2iC_4H_{10} \rightarrow iC_5H_{12} + iC_{11}H_{24} \\
\text{(Overall: 2 Isobutylene + 2 Isobutane} \rightarrow \text{Isopentane + Isoundecane)}
\end{array} \qquad (8)$$

Competition (Isopentane Alkylation)



$$\text{C-C(C)-C-C} + \text{C-C=C-C} \rightarrow \text{C-C(C)(C)-C-C-C(C)-C} \qquad (9)$$

Conjunct Polymerization

$$\begin{array}{c} 17\mathrm{iC_4H_8} + \mathrm{H^+} \rightarrow\rightarrow\rightarrow \quad \mathrm{C_{20}H_{33}}^+ + 4\mathrm{C_{12}H_{26}} \\ (\text{Isobutylene} \rightarrow \text{Conjunct Polymer ion (in acid phase)} + \text{Heavy alkylate}) \end{array} \tag{10}$$

Isomerization

In addition to the listed reactions, the acids catalyze isomerization of olefins or their esters before alkylation as well as isomerization of the alkylate products. Most of the product isomerizations are methyl shifts of ionic intermediates:

- Reaction selectivities – the selectivities of these reactions depend upon the feedstock, catalyst, and reaction conditions.
- Isobutylene and isopentanes are very reactive and are prone to polymerization to heavy alkylate (Eq. 7) and to conjunct polymer (Eq. 10), especially when catalyzed by H_2SO_4.
- Propylene is less reactive and tends to make more conjunct polymer, especially for the H_2SO_4 catalyst.
- 1-Butene yields somewhat less 2,2,4-TMP than 2-butene in HF, but there is little difference in the product from these olefins in H_2SO_4. To maximize octane, many refiners have added selective hydrogenation units (such as UOP-Hüls selective hydrotreating process) upstream of the HF alkylation unit to saturate diolefins reducing the amount of conjunct polymer formed as well as isomerizing most of the 1-butene to 2-butene. Alkylate from both linear butenes is predominantly trimethylpentane with either catalyst.
- HF enhances hydride transfer reactions (Eq. 6) much more than H_2SO_4. For propylene, these hydride transfer reactions increase alkylate yield and octane but also increase the yield of propane. For butenes, these reactions do not affect the yield significantly but they can increase octane. For pentenes, the hydride transfer reactions increase alkylate yield and octane, but they produce isopentane, which increases alkylate RVP.
- H_2SO_4 produces more heavy ends (Eq. 7) and more conjunct polymer (Eq. 10), especially from iso-olefins and propylene. Conjunct polymer is also called “red oil” because of its color, “acid soluble oil,” or simply “polymer.” For all olefins, it produces lower yields and higher end points and consumes less isobutane.
- Increasing reactor temperature increases cracking and conjunct polymer formation at the expense of primary alkylation. This lowers the product octane and increases RVP and acid consumption.
- Increasing isobutane concentration increases primary alkylation and hydride transfer reactions while reducing polymer formation, cracking, and competitive reactions, resulting in increased yield and octane and reduced acid consumption.

HF Alkylation

Process Flow Description

Figure 1 illustrates how an alkylation unit fits into the refinery in a typical FCC-alkylation arrangement. The location of the butane isomerization unit (e.g., UOP Butamer™ process) is also indicated as many refiners have this configuration.

Figure 2 is a simplified process flow diagram for the UOP AlkyPlus™ process for propylene and butene alkylation.

Following the war years, UOP and Phillips licensed the process widely and made key improvements to reduce cost and maintenance requirements. Forced HF catalyst circulation was used in all early units. A Phillips design alternative demonstrated that the density difference between LPG and acid phases could operate to eliminate the acid circulation pump, its seal, and many associated flanges. Numerous gravity-circulated units were licensed as the scheme allowed the reactor, cooler, and settler to be constructed as a single pressure vessel. After UOP acquired the ConocoPhillips alkylation technology, an improved design called the AlkyPlus process was developed to exploit the best commercial features of each heritage technology. The resulting process has demonstrably lower third-party risk when compared to either of the parent technologies.

Feed Pretreatment

In the UOP HF alkylation process, olefin-rich feeds from the FCC gas plant are typically de-ethanized, treated with amine and caustic extraction (UOP Merox™ process) to remove H_2S and mercaptans, and dried. Some refiners have also added MTBE or selective hydrogenation process (SHP) units upstream of the alky unit, and ORU (oxygenate removal units) to remove acetone, ethers, and alcohols.

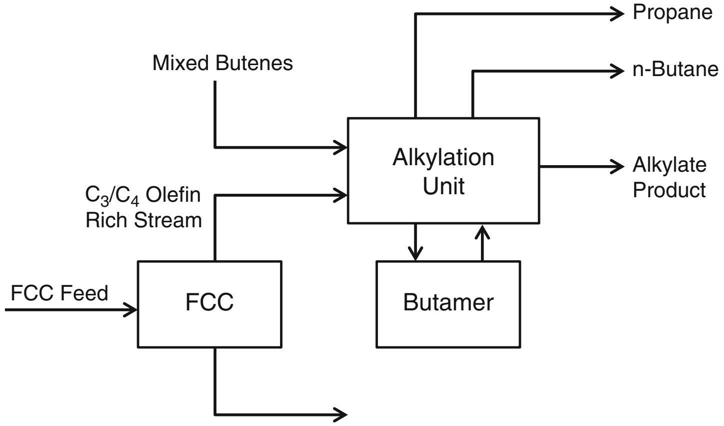


Fig. 1 Typical alkylation unit location in refinery

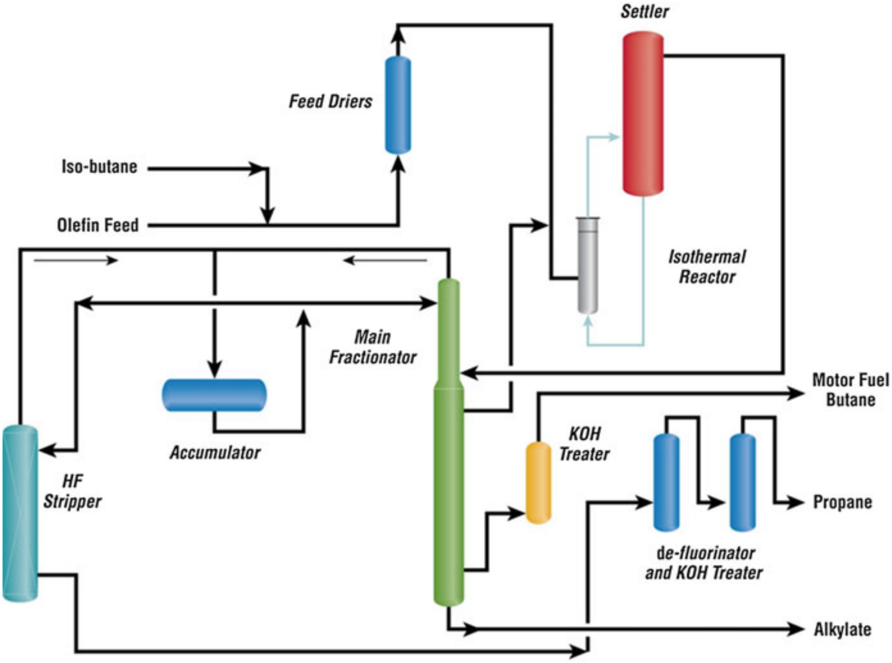


Fig. 2 UOP AlkyPlus^{TM} Process

Reaction

After pretreatment, the olefin feeds are combined with a large excess of recycle isobutane and injected into the circulating HF acid catalyst inside the water-cooled reactor. The molar ratio of isobutane to olefin is typically in the range of 6–14. Cooling water flows through the reactor tubes to remove the highly exothermic heat of reaction and to maintain reaction conditions at 80–100 °F. The alkylation reaction is very fast with 100 % olefin conversion. The excess isobutane, alkylate product, nonreactive hydrocarbons (propane, n-butane), and the acid catalyst pass on to the settler vessel. The dense acid phase separates from the hydrocarbons rapidly by gravity and is then pumped or circulated based on gravity differences back to the reactor. The hydrocarbons containing dissolved HF flow from the settler to the isostripper.

Fractionation

The fractionation section typically consists of an isostripper, a depropanizer, and an HF stripper. The isostripper is the main tower which strips HF overhead, generates a very large isobutane recycle stream, and produces n-butane and alkylate product streams. Alkylate is drawn off the bottom of the tower, cooled in exchangers, and sent to product storage. The next product draw up the tower is the n-butane side draw and above that is a large isobutane recycle draw. On most UOP units, the isobutane draw is located below the feed tray to minimize HF in the isobutane recycle.

The isostripper overhead vapor is a propane-enriched isobutane stream that contains HF, and this stream is condensed and separated in a settling drum. The heavier HF phase is returned to the reactor section. The hydrocarbon phase is charged to the depropanizer.

The depropanizer and its associated HF stripper produce a propane product stream and recover the isobutane and HF to be recycled to the reactor. The depropanizer bottom stream is returned to the reactors as part of the recycle isobutane. The depropanizer overhead contains propane product and HF. The overhead vapor is condensed and the two liquid phases are separated in the overhead receiver. The heavier acid phase is returned to the reactor section, and the acid-saturated hydrocarbon phase is fed to the HF stripper column where the HF is stripped overhead and joins the depropanizer overhead vapor where the HF can be recovered. The HF stripper bottoms is an acid-free propane product which is treated with hot alumina to remove organic fluorides, cooled, and treated over a bed of granular KOH to remove traces of HF and water.

Acid Regeneration

A key advantage of HF alkylation over sulfuric alkylation is the ability to recover the acid from the by-product polymer, water, and other contaminants. A small stream of circulating acid is stripped with superheated isobutane in a small Monel tower called the acid regenerator or acid rerun tower. The regenerator overhead is HF and isobutane that are recycled to the reactor; the regenerator bottom is polymer and the HF-water azeotrope, which are neutralized with aqueous NaOH or KOH. The neutralized polymer has good fuel value. The amount of polymer produced is generally only 1–2 barrels per 1,000 barrels of alkylate product.

KOH Regeneration

Chemical costs and chemical waste products can be reduced by regenerating the KOH used to treat products and all relief and vent gasses. This KOH regeneration is accomplished using lime. As the lime is mixed into the KOH, regeneration of the KOH takes place by the following reaction:

$$2\mathrm{KF} + \mathrm{Ca(OH)_2} \rightarrow 2\mathrm{KOH} + \mathrm{CaF_2}.$$

The calcium fluoride forms a precipitate and can be separated from the regenerated KOH.

Process Variables in HF Alkylation

Key process variables are reactor temperature, isobutane to olefin ratio, acid strength, and acid-to-hydrocarbon ratio.

- Reaction temperature is one of the more important process variables as it has a significant influence on the octane number of the product. Almost all HF alkylation reactors are operated below 110 °F. At higher temperatures, a decrease in alkylate octane number will occur. Above 120 °F polymerization and cracking side reactions become excessive, reducing alkylate quality, and in many cases, acid regeneration capacity of the HF alkylation unit would not be able to maintain proper control of the acid strength.
- Isobutane to olefin ratio is also an important variable in the reactor. As the isobutane to olefin ratio is increased, octane increases and the polymer production decreases. Therefore, the flow of isobutane recycle is usually kept at a practical maximum at all times, up to the capacity of the isostripper. Possible reasons to reduce the recycle ratio are for the conservation of fractionation energy or for a reduction in the hydride transfer reaction.
- Acid strength is usually kept between 85 and 95 mass% HF. The fresh acid is supplied by acid manufacturers at 99.97+ wt% HF. This purity is too high for the optimum performance of the alkylation process. The water content of the acid is typically controlled between 0.5 and 1.5 wt%. Water levels below 0.5 wt% cause a reduction in octane. Levels above 1.5 % lead to higher corrosion rates on the carbon steel piping and vessels. The optimum acid strength is set by a balance between the performance of the unit feed treating systems for sulfur and water removal and acid regeneration operation. In some cases, oxygenate removal or diene removal systems are also used on the feed where there are known to be high oxygenates (such as downstream of an MTBE unit) or high diolefins (from severe FCC conditions). The action of the acid on reactions is a complex phenomenon and is dependent on the type as well as the amount of diluents.
- The acid-to-hydrocarbon volume ratio used in the HF alkylation process is generally 1:1 or higher. At some point, below 0.8:1.0, excess polymerization occurs. In the most extreme cases, alkylate production could stop.
- Pressure does not have an effect on the process as long as it is kept high enough to prevent the vaporization of hydrocarbon and acid in the reactor section.

HF Feed Contaminants

As with many refining processes, the control of contaminants coming into the unit with the normal feedstocks is critical for the long and dependable operation of the HF alkylation unit. Above the recommended maximum levels of feedstock contaminants, acid consumption, acid regeneration requirements, and in some cases unit corrosion and product quality are all measurably affected. Generally all contaminants are kept as low as possible within the capabilities of the feed treating systems. The major feed contaminants normally found in alkylation feeds are water or oxygenates, sulfur compounds, nitrogen compounds, noncondensables, and diolefins.

HF Alkylation Maintenance

Because HF is highly corrosive to most materials, careful control of metallurgy and proper maintenance of equipment is required. Carbon steel is the primary material used for vessels and piping, and it can be used only because of a corrosion barrier layer of iron fluoride that forms on carbon steel surfaces exposed to HF. The iron fluoride layer is tenacious and serves as a barrier against further carbon steel corrosion as long as the iron fluoride layer remains undisturbed. Under certain conditions, such as mechanical wear or elevated water content in the HF acid, this iron fluoride scale can soften or break off leading to both fouling and corrosion issues. In severe cases, this can lead to unscheduled shutdowns as well as potential safety issues. Most refiners aggressively monitor their equipment's remaining corrosion allowance and use regularly scheduled valve and flange replacement to avoid problems. For maintenance during a turnaround, many refiners choose to dissolve all the iron fluoride scale by using a chemical cleaning process.

There are other areas within an HF alkylation unit where conditions are too severe for carbon steel. Alloy 400 (Monel) is the primary metallurgy for such areas because it has good resistance to acid with high water content, especially at higher temperatures. Temperature is an important variable for the corrosion rate of both carbon steel and for alloy 400. Alloy 400 is used for moving parts or where machined surfaces are mated together because the use of carbon steel would cause cementing of the parts together by the iron fluoride scale that is formed on the steel surfaces.

HF Safety and Volatility Suppression

Through the American Petroleum Institute, the industry developed a comprehensive document for the safe operation of HF alkylation units entitled "Recommended Practice for Safe Operation of Hydrofluoric Acid Alkylation Units," API Recommended Practice 751, first published in June 1992 and most recently revised (4th edition) in May 2013.

A consortium of refiners and HF manufacturers led by Amoco developed HF dispersion models and water spray mitigation with extensive, large-scale testing to design release control systems. Together, cosolvents and water spray mitigation can reduce downwind HF concentrations by over 95 % should a release occur.

UOP offers the ReVAP^{TM} and Alkad^{TM} processes, which introduce an additive to the catalyst that significantly reduces catalyst volatility. The ReVAP process was jointly developed by Mobil Oil and Phillips Petroleum, while Alkad was jointly developed by Texaco and UOP. Introduction of the additive, also referred to as

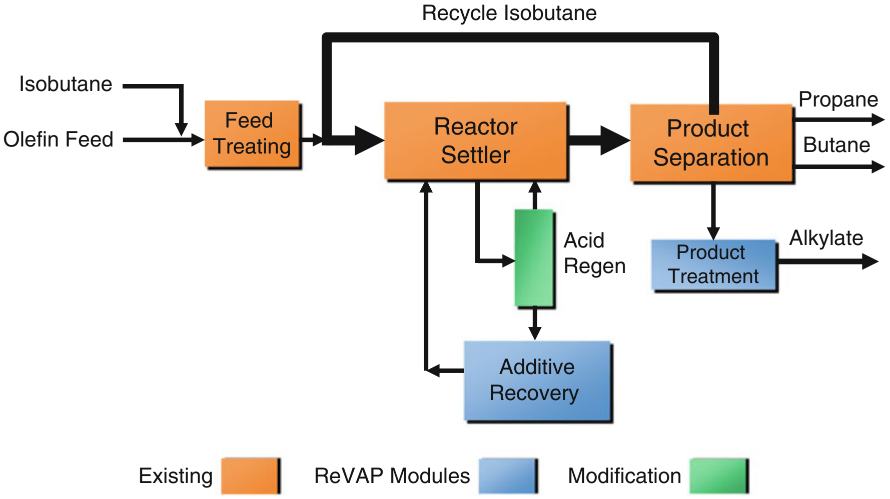


Fig. 3 ReVAP integration with HF Alky Unit

modified HF, provides a passive means of leak mitigation, which requires no action by operator personnel or equipment to be effective. Each system is compatible with existing HF alkylation units. An overview of the ReVAP process is shown in Fig. 3.

Sulfuric Acid Alkylation

Today, there are two main processes for sulfuric acid alkylation – the cascade process licensed by ExxonMobil and the DuPont^{TM} STRATCO^{R} effluent refrigerated process.

Cascade Alkylation Process

Figure 4 shows a typical process flow scheme for the cascade alkylation process.

The FCC olefins are chilled and coalesced to remove water and injected through sparger rings to three to six agitated reaction zones in a large horizontal reactor/settler vessel. Recycle isobutane from the deisobutanizer and the refrigeration system and recycle acid from the settler are fed to a pre-flash zone and "cascade" from one zone through specially designed weirs from which the process name derives. Typical isobutane olefin ratios are 8:1–12:1 for the process. The first zone in the cascade reactor has the lowest operating temperature and the highest isobutane concentration and produces the highest octane alkylate. As additional olefin is injected in subsequent zones, the temperature increases and isobutane concentration decreases and successively lower octanes are produced. Because isobutane and H_2SO_4 are highly immiscible, each zone requires a mixer with high power input to

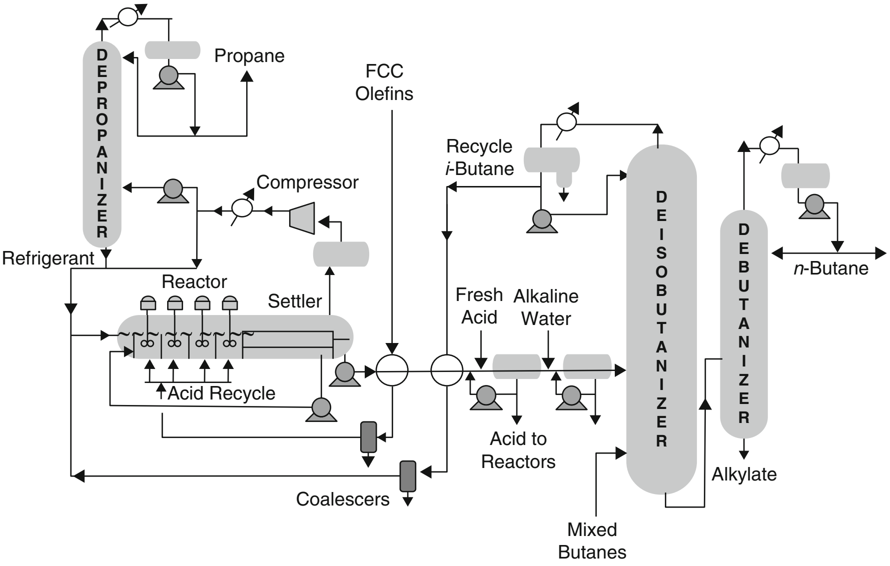


Fig. 4 Cascade auto-refrigerated alkylation process

produce a tight emulsion. After the final reaction zone, the emulsion is allowed to settle. The settler acid phase is pumped back to the lead zone, and the hydrocarbon phase effluent is pumped to effluent treating.

The heat of reaction is removed by "auto-refrigeration" at reaction temperatures of 35–65 °F. While refrigeration is often viewed as costly, in this process, it conserves the heat of reaction and recovers 4–5 mol of isobutane recycle per mole of olefin alkylated and concentrates propane, which reduces the size and cost of the deisobutanizer (DIB) and depropanizer. Isobutane and propane vaporized from the reactor are compressed, condensed with cooling water, and recycled as "refrigerant" to the reactors. A fraction of the refrigerant is charged to the depropanizer to remove propane contained in the feeds from the unit.

Effluent Refrigerated Alkylation Process

Figure 5 shows a typical process flow scheme for the STRATCO^{R} effluent refrigerated process.

In the STRATCO effluent refrigerated alkylation process, the principal differences from the cascade process are in the reactor and refrigeration design, and the reaction is carried out without vaporization.

Treated feeds and recycle isobutane are first chilled and coalesced to remove water and charged to several STRATCO contactors. Feed and isobutane from the DIB and refrigeration system are emulsified with recycle acid from the settler together by the high-power impeller of the STRATCO contactor. After the reaction

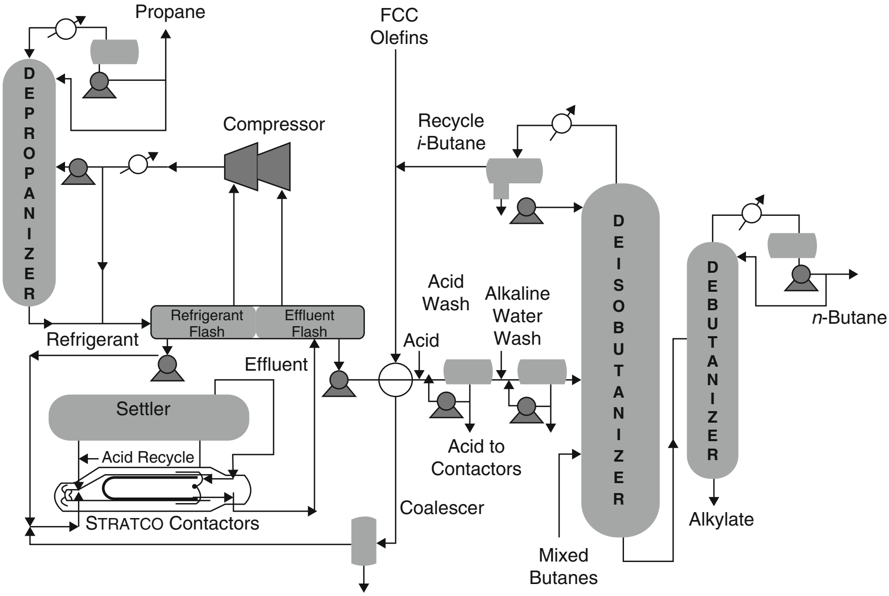


Fig. 5 STRATCO^R effluent refrigerated alkylation process

and chilling, the emulsion passes to the settler located above the contactors for acid separation. The acid phase is recycled by gravity to the contactor impeller. The hydrocarbon phase (effluent) is routed through the tube side of the contactor heat exchanger and allowed to flash to provide refrigeration.

The heat of reaction is removed by chilling the emulsion on the shell side of the contactor heat exchanger by partially vaporizing settler effluent on the tube side. Refrigerant vapor is separated from the effluent liquid in a flash drum, compressed, and condensed. A portion of the condensed refrigerant is routed to a depropanizer. The balance of the refrigeration and depropanizer bottoms is flash cooled and returned to the reactors.

Feed Pretreatment

Feed treatment usually consists of de-ethanizing and Merox treating the FCC olefins. Some refiners have added selective hydrogenation process (SHP) units to saturate dienes and reduce acid consumption. Feeds are generally not dried.

Effluent Treating

The hydrocarbon effluent containing alkylate and excess isobutane is warmed by chilling recycle isobutane and treated to remove traces of entrained acid and ester reaction intermediates. Treating systems include washing with fresh acid and aqueous caustic (as shown). Caustic and water washes, bauxite, and KOH pellets have also been used.

Fractionation

After effluent treating, the balance of reactor isobutane requirement is distilled from the alkylate and n-butane as overhead from the deisobutanizer tower (DIB). Most refiners charge saturated butanes from other units to the DIB for isobutane/n-butane splitting. Normal butane is distilled from the alkylate for the control of product RVP in a debutanizer, and in some cases, an n-butane vapor draw from the DIB. Finally, in a few units, aviation alkylate is produced by removing heavy ends in a rerun column.

Process Variables in H_2SO_4 Alkylation

- Temperature – maximum octanes for butenes and pentenes are obtained at about 35–40 °F and for propylene at about 50 °F. Typically, octane decreases at about 0.04–0.06 RON per 1 °F at higher temperatures.
- Isobutane concentration – reaction selectivity and octane increase with isobutane concentration. Octane typically increases by about 0.1 RON per 1 vol% isobutane in effluent.
- Acid strength – octane is maximized at about 93 wt% acidity. It declines at about 0.2–0.3 RON per 1 % acidity decline below that. The economics of acid cost usually require lower final spending strengths (as low as 88 wt%), so multi-reactor alkylation units typically feed fresh acid to several reactors in parallel operating at 93 % then reuse the 93 % as makeup to other reactors in series.
- Space velocity – octane decreases with the charge rate of olefin. Alkylation reactors are typically designed at 0.15–0.30 LHSV, which is defined as the volume of olefin charged per hour per volume of acid. Operations at much higher throughputs are possible, but low octanes and high acid consumption generally result.
- Acid fraction – octane increases with acid fraction and peaks at about 60 vol% acid in the emulsion.
- Power per unit volume – octane depends upon the mass transfer rate of isobutane from the hydrocarbon phase into the acid phase. According to Sprow (1969), reaction selectivity and octane increase with interfacial area which depends upon the power per unit volume to the 0.25 power.

H_2SO_4 Consumption and Contaminants

Acid consumption is generally expressed as the pounds of acid diluted from 99 % to 90 % by conjunct polymer, water, and other contaminants per gallon or barrel of alkylate. Acid consumption can be as low as 16 lb per barrel alkylate for diene-free, MTBE raffinates run at optimal process conditions. Acid consumption can exceed 40 lb/bbl of alkylate when running high levels of dienes, isobutylene, pentenes, and propylene at high temperatures. The effects of some typical contaminants are summarized below:

- Dienes – butadiene and pentadienes are major contaminants affecting acid consumption. Dienes can account for 10–30 % of the acid consumed. Dienes can dilute 5–20 lb of 99 % acid down to 90 % per lb of diene. Some refiners use diolefin selective hydrogenation units (such as UOP-Hüls SHP) to eliminate this source of acid consumption.
- Water and oxygenates – water can also account for 10–20 % of acid consumption. Wet feeds, wet isobutane recycle, and high reactor temperatures are the main sources of water. Oxygenates including acetone from the FCC and methanol and dimethyl ether from MTBE and TAME units also consume acid. Water and oxygenates dilute 10 lb of 99 % acid to 90 % per lb of contaminant.
- Sulfur and nitrogen compounds dilute about 20 lb of 99 % acid to 90 % per lb of sulfur or nitrogen.
- C_6+ dilutes 2 lb of 99 % acid to 90 % per lb of contaminant. This can be a significant contributor to acid consumption when alkylating pentenes.
- Ethylene dilutes 20 lb of 99 % acid to 90 % per lb of contaminant by forming stable sulfates that stay in the acid.
- Ethane and lighter – while inert, light ends increase compressor discharge pressure for the total condensation. These indirectly increase acid consumption when limited by horsepower by increasing reactor temperature.

H_2SO_4 Regeneration

Sulfuric acid alkylation uses about 100 times as much acid as HF alkylation because H_2SO_4 cannot be stripped from the conjunct polymer, water, and contaminants. Sulfuric acid is typically spent at 88–91 wt% H_2SO_4, below which it is too weak to carry out alkylation.

The spent sulfuric acid is not a waste. It is regenerated by burning the organics (usually along with H_2S) which reduces the H_2SO_4 to SO_2 and water vapor. The SO_2 is then dried with oleum oxidized to SO_3 and finally scrubbed with water to produce oleum and 98.5–99.5 % H_2SO_4.

For sulfuric alkylation, aside from the direct hazards of contacting the acid, there are transportation safety issues around the need to ship and regenerate 20–500 tons of H_2SO_4 daily. Tomitigate transportation risk, several refiners have built dedicated acid plants to regenerate spent acid from the alkylation unit or pipelines to and from an acid manufacturer.

Alkylate Properties

Table 1 illustrates typical alkylate product properties from HF and H_2 SO_4 alkylation units for propylene-butylene and butylene only units. Alkylate is composed of primarily C_7 and C_8 isoparaffins with a relatively narrow boiling range. Motor fuel alkylate has desirable T50 and T90 distillation properties as well as a low end point. RON is typically in the mid- to low 90s and MON is typically only one to two units lower than the RON. High MON is an important property of alkylates. The Reid vapor pressure (RVP) of debutanized alkylate can be as low as about 4 psia. The low RVP and very low sulfur as well as the absence of olefins and aromatics make alkylate a valuable blending component in reformulated gasolines by reducing evaporative, NO_x, and toxic emissions.

In some alkylation units, the feedstock is pretreated in a selective hydrogenation unit to remove the diolefins, which react to form undesirable acid soluble oil. An additional benefit of selective hydrogenation units upstream of an HF alkylation unit is isomerization of the low octane producing 1-butene to the more desirable 2-butene isomers. Such a pretreating unit can raise the octane of HF alkylate product by 1 RON/MON as can be seen in the third column of Table 1.

Table 1 Alkylation product properties/yields

HF alkylation			
Volume yields per vol olefin	FCC propene/ butene	FCC butene only	Butene only with butene isomerization
Isobutane consumed	1.28	1.15	1.15
C5 plus alkylate produced	1.78	1.77	1.77
C5 plus alkylate properties			
Specific gravity	0.693	0.697	0.697
RON-0	93.3	95.5	96.5
MON-0	91.7	93.5	94.5
H_2 SO_4 alkylation			
Volume yields per vol olefin	FCC propene/ butene	FCC butene only	
Isobutane consumed	1.2	1.12	
C5 plus alkylate produced	1.72	1.72	
C5 plus alkylate properties			
Specific gravity	0.693	0.697	
RON-0	92.0	96.0	
MON-0	90.4	94.0	

Recent Developments

Solid Catalyst Alkylation

Researchers have long sought to develop a solid catalyst alkylation (SCA) process that would eliminate the safety and corrosion issues associated with HF or sulfuric acid. Early attempts used supported metal halides, including work by UOP (Kojima and Kocal 1995) and Total (Nascimento et al. 2001) with chlorided alumina; work by Mobil with boron trifluoride supported on silica (Chou et al. 1990a), MCM-25 (Huss and Johnson 1993), or beta zeolite (Chou et al. 1990b); and work by Haldor-Topsoe (Angelis et al. 2001) with triflic acid supported on silica. More recent efforts have focused on wide-pore zeolites.

Zeolites have about an order of magnitude lower acid site concentration per gram than liquid acids and occupy about ten times the volume per gram ($\sim$5 cm^3 vs. 0.5 – 1.0 cm^3/g). This results in significantly larger catalyst volumes required for equivalent reaction. Studies (Nivarthy et al. 1998; Stocker et al. 1994) have shown that stronger Brønsted acid sites are necessary to effectively catalyze hydride transfer, which is the reaction step that has the biggest impact on alkylate product quality and catalyst life. The strength of the acid sites may be modified by dealumination (Corma and Orchilles 2000) and rare earth exchange (Weitkamp 1980).

A key difference between zeolites and liquid acids is their selective and strong chemisorption of olefins. Due to the high polarity of the zeolitic surface, especially in those with a low Si/Al ratio, polar olefin molecules are preferentially adsorbed. Localized higher olefin concentrations in the pores will result in higher relative rates of oligomerization than hydride transfer and is believed to be the main reason why zeolites deactivate so rapidly. Larger molecules are more strongly adsorbed than smaller ones, so once a heavy molecule is formed, it is unlikely to desorb, leading to the formation of coke, which will ultimately block the zeolite pore. The key to running a successful solid catalyst process thus becomes finding a way to regenerate the catalyst and remove the coke in a timely fashion.

Most SCA processes use a combination of “cold” (liquid phase) and “hot” (gas phase) regeneration procedures. This requires the incorporation of a noble metal hydrogenation function in the catalyst. The cold regeneration is essentially a solvent extraction with isobutane saturated with hydrogen. At low temperatures, (<100 °C) most unsaturated species that block the acid sites are hydrogenated and can be more easily desorbed from the catalyst. However, the cold regeneration only partially restores activity, and after a number of cycles, it is necessary to do a high-temperature regeneration with hydrogen. At higher temperatures, there is some hydrocracking of species that are too bulky to leave the pores into smaller species that can diffuse out of the pores, thereby restoring pore volume and access to acid sites.

Several different reactor schemes have been proposed for accomplishing the solid catalyst alkylation process and regeneration. The CB&I/Albemarle/Neste Oy AlkyClean^{TM} process (Gieseman et al. 2006) uses a swing bed strategy. In a typical unit design, there are five identical reactors. At any one point in time, two reactors are in the process mode, two are in the cold regeneration mode, and one is in the hot regeneration mode. Automated valves control the flow of streams in and out of each reactor as each is cycled through the various process steps of reaction, flushing, and regeneration.

In the UOP Alkylene^{TM} process (Roeseler et al. 2002), the catalyst is fluidized and moves through a riser reactor. The catalyst is then disengaged from the product and flows down through a cold regeneration zone to the bottom of the riser, where the cycle starts again. A catalyst slipstream goes to another reactivation vessel for "hot" regeneration. UOP has also introduced a stacked moving bed radial flow reactor scheme (Sadler 2013), in which catalyst flows in a figure eight pattern first down through a series of process stages and next down through a hot regeneration section before completing the cycle. The moving catalyst schemes make more efficient utilization of the catalyst, since there is no duplication of reactor volumes. This is critical because of the relatively low space velocities (large catalyst volumes) used and the expense of the platinum on the catalyst. The continuous process also minimizes isobutane required by swing bed processes for flushing hydrogen out of the pores of the catalyst after the regeneration before the reactor switches back into reaction mode, since any residual hydrogen will saturate the olefin feed and lead to yield losses.

Although the above solid catalyst alkylation processes have been offered to the commercial market, none has achieved commercial success because of the high costs of catalyst, platinum and capital equipment required for regeneration.

Ionic Liquid Alkylation

Since about 2000, there has been much interest in using ionic liquids to replace traditional HF or H_2SO_4 liquid acid catalysts in alkylation. An ionic liquid is essentially a salt that is liquid phase at low temperature ($<100\ ^\circ C$). Typically, the anion and cation are both large, and the cation has a low degree of symmetry. These factors reduce the lattice energy of the crystalline form of the salt and significantly lower its melting point. The field of ionic liquids has been reviewed by several authors, including Seddon (1997) and Welton (1999). Ionic liquid properties can be designed to suit the requirements of a particular process. Melting point, viscosity, density, and hydrophobicity can all be varied by simple changes to the structure of the ions. Their density can be made sufficiently high to facilitate easy separation by gravity settling. In addition, ionic liquids have practically no vapor pressure, so they do not carry the same environmental and safety concerns as HF or H_2SO_4, and can be easily separated by fractionation.

The ionic liquids most commonly used for alkylation have a chloroaluminate anion. The acidity can be controlled by varying the mole fraction of aluminum chloride, $X(AlCl_3)$. For $X(AlCl_3) < 0.5$, the ionic liquid is basic. For $X(AlCl_3) = 0.5$, the ionic liquid is neutral, and for $X(AlCl_3) > 0.5$, the ionic liquid is acidic. The most common acidic form, $Al_2Cl_7^-$, has 2 mol of $AlCl_3$ for each mole of the cation, i.e., $X(AlCl_3) = 0.67$. Higher $AlCl_3$ mol ratios may be possible depending on the cation, but the solubility of the aluminum chloride decreases and solid $AlCl_3$ can precipitate. Acidic ionic liquids, with Hammett acidities of $-H_0 \sim 19$, can have super acidities that are orders of magnitude higher than HF or H_2SO_4 ($-H_0 \sim 12$). The superacid properties of protons in acidic chloroaluminate ionic liquids have been explained by the reaction between dissolved HCl and the acidic species, which releases protons with extremely low solvation and therefore very high reactivity (Wasserscheid and Keim 2000):

$$HCl + Al_2Cl_7^- \rightleftharpoons [H]^+_{nonsolvated} + 2\ AlCl_4^-$$

The cations used in ionic liquids for alkylation are typically quaternary ammonium, quaternary phosphonium, or trialkylsulfonium species (Lacroix et al. 1998; Olivier-Bourbigou et al. 2002). Many authors, including Aschauer et al. (2011), have published results using 1-butyl-3-methyl-imidazolium (BMIM) chloroaluminate ionic liquid. Chevron has numerous patent examples using 1-butyl-pyridinium (BP) chloroaluminate ionic liquids (Elomari et al. 2008; Harris et al. 2009). Researchers at China University of Petroleum (Liu et al. 2014) have developed an alkylation process around a composite ionic liquid consisting of triethylamine hydrochloride chloroaluminate and CuCl. Various additives were tested as modifiers for the Et_3NHCl-$AlCl_3$, and CuCl gave the highest C_8 and TMP selectivities (Huang et al. 2004).

Ionic liquid catalysts are used in the same way as other liquid acid alkylation catalysts. The ionic liquid is intimately mixed with hydrocarbon reactants in the reactor and then separated from the products after reaction, usually by gravity settling. One key difference is the amount of catalyst that must be used. HF and sulfuric acid catalysts are typically operated in the acid continuous mode with the hydrocarbon phase dispersed with an acid-to-hydrocarbon volume ratio >1. For ionic liquid alkylation, the acid-to-hydrocarbon ratio can be as low as 0.1, operating in a hydrocarbon continuous mode with the ionic liquid phase dispersed (Timken et al. 2008). This is important because most ionic liquids are much more expensive than commodity acids such as HF or H_2SO_4.

The efficient mixing of the ionic liquid with the hydrocarbon phase is critical because diffusion is highly mass transfer limited to the acid sites in the viscous ionic liquid. Schilder et al. calculate that a droplet size of <10 μm is necessary to keep the effectiveness factor for olefin conversion above 90 %. The effective reaction rate is nearly proportional to 1/droplet diameter (Schilder et al. 2013). The consequence of creating very small ionic liquid droplets is that their separation from the product becomes increasingly difficult. One of the biggest challenges in commercializing an economic ionic liquid alkylation process will be minimizing entrainment losses of the expensive ionic liquid in the hydrocarbon phase.

Another significant challenge is regenerating the ionic liquid as accumulating conjunct polymer begins to deactivate acid sites. Conjunct polymer is unsaturated oligomeric material, analogous to red oil or acid soluble oil in the liquid acid alkylation processes, that complexes with the acid sites and is very difficult to remove. Elomari et al. describe a number of potential approaches for regeneration (Elomari and Harris 2010).

If these critical issues are addressed, ionic liquid alkylation shows great promise as an alternative to traditional liquid acid alkylation technologies. Chevron, Shell/CUP, and UOP are all actively developing commercial ionic liquid alkylation processes.

References

Anon, *Hydrofluoric Acid Alkylation* (The Phillips Petroleum Company, 1946)

S. Aschauer et al., Liquid-phase isobutane/butene alkylation using promoted Lewis-acidic IL-catalysts. Catal. Lett. **141**(10), 1405–1419 (2011)

T. Chou et al., World Patent WO 90/00534, (1990a)

T. Chou et al., World Patent WO 90/00533, (1990b)

A. Corma, A. Orchilles, Microp. Mesop. Mater. **35–36**, 21 (2000)

A. de Angelis et al., Catal. Today **65**, 363 (2001)

S. Elomari, T. Harris, Chevron USA, U.S. Patent 7,732,363, (2010)

S. Elomari et al., Chevron USA, U.S. Patent 7,432,409, (2008)

J. Gieseman, V. Amico, E. van Broekhoven, *The Alkyclean^{TM} Alkylation Process: New Technology Eliminates Liquid Acids*. Paper AM-06-41 at NPRA 2006 annual meeting, Salt Lake City, 19–21 Mar 2006

T. Harris et al., Chevron USA, U.S. Patent 7,531,707, (2009)

J.H.D. Hooper, Chem. Ind. **20**, 683 (1986)

C.P. Huang et al., Effects of additives on the properties of chloroaluminate ionic liquids catalyst for alkylation of isobutane and butene. Appl. Catal. A Gen. **277**(1–2), 41–43 (2004)

A. Huss Jr., I.D. Johnson, U.S. Patent 5,221,777, (1993)

V.M. Ipatieff, A.V. Grosse, J. Am. Chem. Soc. **37**, 1616 (1935)

E.C. Jernigan, J.E. Gwyn, E.L. Claridge, Chem. Eng. Prog. **61**(11), 94 (1965)

M. Kojima, J. Kocal, U.S. Patent 5,391,527, (1995)

C. Lacroix et al., Akzo, U. S. Patent 5,731,101, (1998)

Z. Liu et al., China University of Petroleum, Beijing, “Reaction performance of isobutane alkylation catalyzed by a composite Ionic liquid at short contact time”. AIChE J. **60**(6), 2244–2253 (2014)

P. Nascimento et al., U.S. Patent 6,225,517, (2001)

G.S. Nivarthy et al., Microp. Mesop. Mater. **22**, 379 (1998)

H. Olivier-Bourbigou et al., IFP, U.S. Patent 7,256,152, (2002)

H. Pines, ChemTech. 150 March (1982)

C.M. Roeseler, D.J. Shields, S.M. Black, C.D. Gosling, *Improved Solid Catalyst Alkylation Technology for Clean Fuels: The Alkylene Process*. Paper at the NPRA annual meeting, San Antonio, 17–19 Mar 2002

C.C. Sadler, U.S. Patent 8,373,014, 2013

L. Schilder et al., Effective and intrinsic kinetics of liquid-phase Isobutane/2-Butene alkylation catalyzed by chloroaluminate Ionic liquids. Ind. Eng. Chem. Res. **52**, 1877–1885 (2013)

K.R.J. Seddon, Chem. Tech. Biotech. **68**, 351–356 (1997)

F.B. Sprow, Ind. Eng. Chem. Process Des. Dev. **8**(2), 254 (1969)

M. Stocker et al., Catal. Lett. **28**, 203 (1994)

H. Timken et al., Chevron USA, Patent 7,432,408, (2008)

P. Wasserscheid, W. Keim, Ionic liquids – new solutions for transition metal catalysis. Angew. Chem. Int. Ed. **39**, 3772–3789 (2000)

J. Weitkamp, Stud. Surf. Sci. Catal. **5**, 65 (1980)

T. Welton, Room temperature Ionic liquids. Solvents for synthesis and catalysis. Chem. Rev. **99**, 2071–2083 (1999)

Olefin Condensation

Robert L. Mehlberg, Peter R. Pujadó, and Dennis J. Ward

Contents

Peter R. Pujadó has retired.
Dennis J. Ward: deceased.

R.L. Mehlberg (✉)
UOP, A Honeywell Company, Des Plaines, IL, USA
e-mail: robert.mehlberg@honeywell.com

P.R. Pujadó
UOP LLC, A Honeywell Company, Kildeer, IL, USA
e-mail: prpujado@gmail.com

D.J. Ward
Ft. Myers, FL, USA
e-mail: djwbridge@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_6

Abstract

Catalytic olefin condensation is the reaction of two or more olefinic compounds to form a heavier olefinic product. Several acid catalyst are used including solid phosphoric acid, organometallic catalysts, silica alumina, zeolites, and sulfonic acid resins. The primary application is to produce high octane gasoline from propene, butenes, or pentenes and more recently to produce distillates. Petrochemical operations include the production of 1-butene, heptenes, nonenes, cumene and ethylbenzene.

Keywords

Dimerization • Oligomerization • Catalytic condensation • InAlk™ • Dimersol™ • PolyNaphtha™ • Alphabutol™ • Polymer gasoline • Codimers • Heptenes • Nonenes • Cumene • Isopropylbenzene • Ethylbenzene • Solid phosphoric acid (SPA) • Organometallic catalysts • Silica alumina • Zeolites • Sulfonic acid resins

Introduction

Catalytic olefin condensation refers in general to the reaction of one molecule of an olefin with one or more molecules of the same olefin or of other olefins to yield heavier olefinic compounds. The term "condensation" reflects the fact that liquid products are obtained from gaseous olefins.

Olefin condensation is in some ways similar to motor fuel alkylation, except that alkylation is the reaction of an olefin with an isoparaffin to yield a paraffinic compound. The key difference of olefin condensation is that the products are olefinic, but may be later hydrogenated in order to meet the requirements and specifications of the end products.

Olefin condensation can be carried out in many ways and over a diversity of catalysts. The common characteristic is that olefin condensation takes place over acid catalysts. These catalysts include solid phosphoric acid (SPA), liquid acids, organometallic catalysts, silica alumina, zeolites, sulfonic acid resins, etc.

Although olefin condensation finds broad application in petroleum refinery refining applications for motor fuels, it is also used in petrochemical applications (often combined with refinery operations) as, for instance, in the production of heptenes, nonenes, and dodecenes and for the production of alkylaromatic derivatives. In fact, some of the same catalysts (e.g., SPA) can also be used for the alkylation of olefins with aromatics as in the production of cumene (isopropylbenzene), ethylbenzene, etc. This review will concentrate on refinery and olefin oligomer applications and will not discuss aromatic alkylation applications.

History

The discovery of acid catalysis, and in particular the development of solid phosphoric acid (SPA) catalysts, is attributed to the pioneering work of Vladimir Ipatieff at what was then called Universal Oil Products and is today known as UOP – a Honeywell company. The first commercial unit for the production of octenes by the dimerization of butenes came on stream in 1935. Introduction of this new gasoline component contributed to the popularization of the automobile that had previously been constrained by the availability of straight-run gasolines from petroleum crude fractionation. In addition, the octenes obtained by butene dimerization had a much higher octane number than naturally occurring straight-run gasolines. Several hundred units were soon built to satisfy the growing demand for gasoline.

The dimerization and oligomerization of olefins over SPA catalysts is known as the catalytic condensation process. This is still the dominant process for the dimerization and oligomerization of olefins. Recent developments include acid zeolite catalysts and, sulfonic acid resin catalysts.

The other type of condensation catalysts most often found in refinery applications for the production of gasoline components is organometallic catalysts developed by the Institut Français du Pétrole (IFP). They are used, in the dimerization of propylene to isohexenes (Dimersol G process), or in the oligomerization of light olefins from cracked gases (Dimersol E) or in the production of heptenes and octenes from propylene and/or butenes (Dimersol X).

Because the production of olefin dimers and oligomers almost invariably produces a blend of isomers and often also a lighter and a heavier fraction, the production of these olefins for petrochemical applications cannot be easily segregated from their application in gasoline and diesel fuel uses. However, it is usually the case that catalysts can be tailored within certain limits so as to yield more branched compounds (higher octane) for gasoline applications and less branched products for petrochemical applications. Because the products from such processes always have some branching, the quality of the products in the diesel range is somewhat poor (low cetane numbers) and their use in diesel applications is not that extensive.

Catalytic Condensation Process

The catalytic condensation process was developed in the early 1930s as a means to convert light gases produced by thermal cracking and thermal reforming into useful products. R. E. Schaad and V. N. Ipatieff discovered that phosphoric acid mixed with kieselguhr (an abundant naturally occurring siliceous diatomite mineral) solidified upon heating. When the solid mass was cooled, broken up, and placed inside a reactor, the propylene and/or butenes condensed into a liquid in the gasoline boiling range. This discovery was scaled up and eventually commercialized (Ipatieff et al. 1938).

Shortly after the introduction of the catalytic condensation process came the catalytic cracking process, initially as a fixed-bed process and later as the fluidized-bed catalytic cracking process, or FCC. These catalytic cracking processes, and in particular FCC, yielded even more olefins than thermal cracking, principally propylene and butenes, which at that time had very little commercial value. Thus, further application of the catalytic condensation process ensued.

Early units operated at about 10 atmospheres, since that was the pressure level of many liquefied petroleum gas (LPG) recovery systems. However, it was soon discovered that, if the reactor was operated at 30 or more atmospheres, catalyst lives could be extended by a factor of 4–6 times, thus began the evolution of higher pressure units. Some units that employed tubular reactors at 60 atmospheres were constructed and were found to be even more successful.

SPA catalyst was also tried for other reactions. In the late 1930s, it was discovered that SPA would catalyze the reaction of olefins with aromatic compounds to yield alkyl aromatics. This discovery was widely used to make cumene (isopropylbenzene) for aviation fuel used in World War II. Cumene has a very high performance number necessary for the aviation gasoline used in internal combustion engines in aircraft. After the war, use of cumene in aviation fuel declined, but cumene found an even more important outlet as feedstock for the production of phenol and acetone. This petrochemical use of cumene continues to dominate this industry, even though in recent years there has been a significant shift from SPA to acid zeolite catalysts for this aromatic alkylation. During World War II, there was also a high demand for ethylbenzene and styrene. Some units were built to produce ethylbenzene by reacting ethylene with benzene over SPA catalyst. The reaction was slow and fairly inefficient, so SPA never gained relevance for this application; most ethylbenzene units at the time made use of aluminum chloride catalysts. Today, practically all existing ethylbenzene capacity makes use of acid zeolite catalysts.

World War II also led to increased demand and production of polyvinyl chloride (PVC). PVC is an excellent plastic material but lacks the flexibility required for many applications. It was discovered, however, that octyl phthalates and the esters of higher alcohols could be used to “plasticize” PVC, that is, to make it more flexible and supple. Octyl to decyl alcohols could be obtained by the “oxo” reaction (hydroformylation reaction) of olefins with carbon monoxide and hydrogen. The corresponding olefins, with one carbon less than the desired alcohols, could be recovered as by-products from the gasoline operation simply by fractionating the desired olefins out of the olefinic gasoline blend obtained by the catalytic condensation process. To this date, this is still the way that these olefins, from heptenes to nonenes, are produced, except that now these olefins are the main products from this operation, and the remaining lighter and heavier fractions are blended back into the gasoline pool.

A further application that derived from World War II was the advent of synthetic detergents to overcome the shortage of soap caused by the diversion of glycerin supplies to the manufacture of explosives. Though not readily biodegradable, one of the earliest and still one of the most active detergent ingredients is dodecylbenzene sulfonate. This was obtained by first alkylating dodecene with benzene according to the technology developed independently by UOP and Standard Oil of California (now Chevron). Dodecene, or propylene tetramer, was readily produced by the oligomerization of propylene over SPA catalyst.

Still, at the apex of its success, the catalytic condensation process was used mostly for the production of gasoline. During World War II, an important component in the aviation fuels used in fighter airplanes of that time was hydrocodimer, described more fully below. This together with cumene, also derived from phosphoric acid catalyst operations, was credited with being a significant factor in Britain's success in the Battle of Britain. The typical refinery product was known as polymer gasoline or "polygasoline" even though in reality it consisted mostly of fairly simple dimers and trimers. At one time there were as many as 300–400 catalytic condensation units producing gasoline alone. Today, production of polymer gasoline is less significant, but the catalytic condensation process is still the preferred route to olefin dimers and oligomers and, despite the inroads made by zeolitic catalysts, is still widely used for the production of cumene. Based on the current demand for SPA catalyst, it may be estimated that about 40 % is for gasoline, 40 % for higher olefins (plasticizer olefins), and the balance 20 % for cumene applications.

Catalytic Condensation Process for Gasoline Production

Figure 1 illustrates a simplified process flow diagram for gasoline production using a tubular reactor.

The tubular reactor system has the catalyst in the tubes, and condensate or boiler feedwater is used to remove the exothermic heat of reaction and to raise steam on the shell side. The reactants are circulated through the catalyst, and the effluent is cooled and passed to a stabilizer column. An LPG (propane–butane) recycle may be maintained to control the concentration of olefins in the feed and the heat release in the system. Usually, the olefin concentration in the feed to the reactor is maintained at not more than about 50 %. The gasoline produced is removed via the bottoms of the stabilizer. Figure 2 illustrates a similar diagram using an adiabatic plug flow reactor.

Adiabatic plug flow reactors do not have provisions for steam generation within the reactor. Instead, an LPG interbed quench is used to control the temperature rise within the reactor with as many as five catalyst beds being arranged within the vessel. The product is sent to a flash drum in which partial condensation occurs, and the liquid is sent to a stabilizer column. The bottom from this column is the final gasoline product. With this type of reactor, the concentration of olefins in the feed is usually limited to about 30 %. From an energy point of view, it is less efficient than a tubular reactor, but it is more economical to build.

For practical purposes, the products made by either system are almost identical.

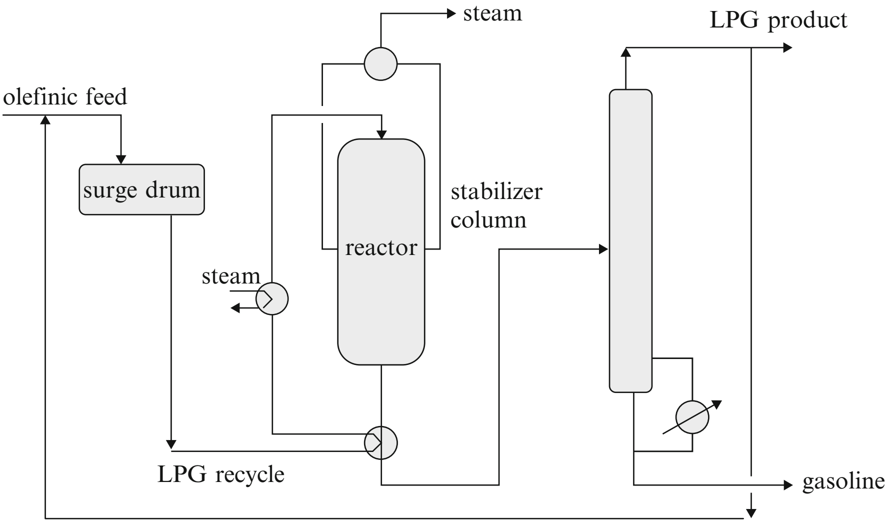


Fig. 1 Catalytic condensation with tubular reactor

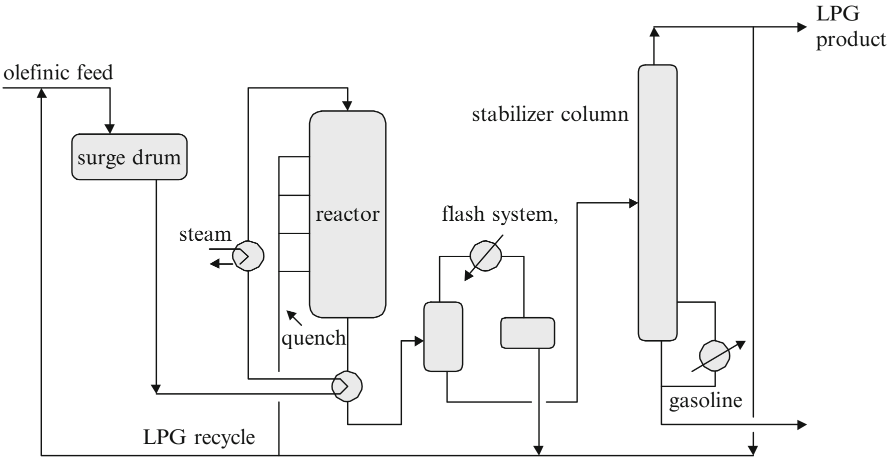


Fig. 2 Catalytic condensation with plug flow reactor and quench

Table 1 illustrates a typical product composition distribution based on a mixed C_3–C_4 feed from an FCC unit expressed as weight percent of the olefins in the charge stock. Feed olefin conversion is about 97 % for propylene and 93 % for butenes, but this may vary somewhat depending on the state of the catalyst, the feed composition, and the operating conditions. Table 2 provides typical distillation properties of depentanized gasoline; actual composition will vary depending on what vapor pressure adjustments are desired to adapt the product to the gasoline

Table 1 Oligomerization reactions

Propylene–butene feed: FCC – C_3–C_4 fraction	
Operation: without polymer recycle	
Wt% yield based on feed olefins	
Unreacted propylene	1.3 (97.3 % conv.)
Unreacted butenes	3.7 (93.1 % conv.)
C_6 olefins	4.4
C_7 olefins	41.3
C_8 olefins	24.0
C_9 olefins	15.8
C_{10} + olefins	9.5

Table 2 Typical polymer gasoline properties

	C_6+ basis		
	C_3 poly	C_3–C_4 poly	C_4 poly
Polymer type: specific gravity	0.739	0.738	0.738
Engler distillation (°*C*)			
IBP	57	93	62
10	114	101	103
30	132	109	113
50	141	119	119
70	151	137	127
90	191	168	181
EP	218	211	216

pool requirements. This means that the end product may also contain some pentenes and butenes if the higher vapor pressure is acceptable for blending into the gasoline pool.

Table 2 also serves to illustrate three different typical operations of these units: (1) polymer gasoline made from propylene only with no attempt made to produce higher olefins beyond the gasoline range, (2) polymer gasoline from a mixed C_3–C_4 feed, and (3) polymer gasoline from a unit operating with butenes only. The specific gravities of all three products are virtually identical.

Although these data are from actual commercial operations, some differences arise from unit to unit. Also, it may be appreciated that the midpoint (50 %) and the end point (100 %) for a propylene feed are higher than for mixed feeds or butene feeds. In actual practice, these end points can be adjusted in order to meet product specifications. Often too the amount of polymer gasoline blended into the pool is small, so that it does not significantly alter the overall properties of the pool; seldom is the product rerun in order to meet more stringent specifications. The butene product in Table 2 is typical of a codimer operation. This type of operation was rare in the past, but because the octane number from this mode of operating is exceptionally high, it has grown considerably since MTBE phaseout for processes like InAlk.

Hydrogenated Versus Non-hydrogenated Polymer Gasolines from the Catalytic Condensation Process

Polymer gasoline is almost totally olefinic and is easily hydrogenated. Historically, except for aviation fuel, it usually has been blended into gasoline without further processing because the relatively high RON of olefins blended synergistically with paraffins. Recently, with restrictions on olefin levels in present gasolines, such as Euro V, and MTBE phaseout, hydrogenation has received increased attention. Polymer gasolines from SPA catalysts are much more highly branched than predicted from thermodynamic equilibrium, it is important to select hydrogenation catalysts and conditions that minimize isomerization for preservation of octane.

Table 3 illustrates typical clear octane numbers of olefinic and hydrogenated products from commercial samples. While the octanes of olefinic C_3 and C_3–C_4 polymer gasolines are adequate for unleaded gasolines, hydrogenation makes them inadequate.

Of much more interest are the RON and MON of hydrogenated butene polymer gasoline, historically called “hydrocodimer,” which are up to 99 and 94, respectively. This ten-number increase in MON is contrary to typical hydrogenation behavior and completely contrary to the negative responses of C_3 polymer. This response was even more striking in the past when lead was added. With the addition of 0.5 g/L TEL, the RON and MON increased to about 111 and 103, respectively. The high MON and excellent lead response of hydrocodimer was important for aviation gasoline during World War II.

Figure 3 illustrates an approximate linear correlation between the propylene content in the feed and the RON of the hydrogenated product. The more propylene, the lower the RON.

Because of the absence of olefins and aromatics, the butene-only product meets or exceeds all current environmental regulations.

Normally, a motor fuel gasoline is a blend of hydrocarbons generated from a number of sources, including: straight-run gasoline (mostly paraffinic with some aromatics, depending on the cut), alkylate (paraffinic), isomerate (paraffinic), reformate (aromatic), FCC gasoline (olefinic and aromatic), polymer gasoline (olefinic or paraffinic), hydrocracked naphtha (paraffinic and aromatic), MTBE, and TAME. The octane numbers of these various components do not blend linearly,

Table 3 Clear octane numbers of hydrogenated polygasolines

	Polymer type		
	C_4 poly		
	C_3 poly	C_3–C_4 poly	(codimer)
Olefinic polygasoline			
RON clear	93	97	99
MON	82	83	84
Hydrogenated polygasoline			
RON clear	49	70	99
MON	59	76	94

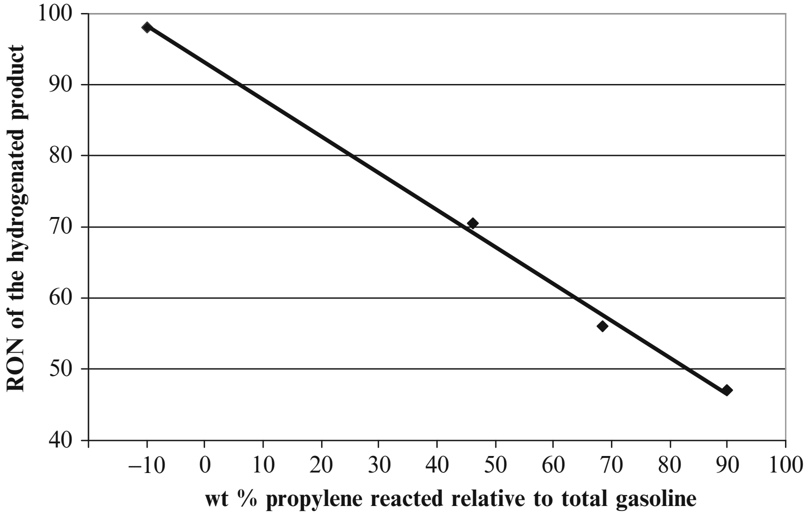


Fig. 3 Effect of propylene content on RON of the hydrogenated polygasoline

Table 4 Blending octanes of polygasolines

	Polymer type		
	C_3 poly	C_3–C_4 poly	C_4 poly
Measured clear octanes			
RON	93	96	98
MON	83	83	83
Blending octanes			
10 vol.% blend			
RON	94	103	126
MON	83	97	99
20 vol.% blend			
RON		103	
MON		92	

Base stock was a mixture of about 60 % FCC gasoline and 40 % reformate with RON/MON of about 93/81

and either a "blending octane" or a blending formula that depends upon the composition is used. Thus, the octane of the blend may be the same, lower, or higher, depending on the synergism among the various components.

Table 4 shows the blending octanes of various polymer gasoline fractions when blended into a base stock of approximately 60 % FCC gasoline and 40 % reformate, having clear octanes of 93 RON and 80.8 MON. Blend stocks consisting of the various polymer gasolines were added at 10 or 20 vol.% levels, and the blending octanes were back calculated from the octanes measured in the resulting mixtures. It must be noted, however, that small errors in the determination of the octane values can lead to significant fluctuations in the estimation of the blending octanes.

Based on these studies and for these particular base stocks, it was determined that propylene-derived polymer gasoline had blending octanes of 94 RON and 83 MON; these values are almost identical to its clear values with no synergism with the base stock. The situation with the propylene–butenes polymer gasoline is quite different. Here, the blend stock had RON and MON of 96 and 83, respectively, but it blended with the base stock at the 10 % level as though the octane numbers of the blend stock were 103 RON and 97 MON, a clear display of synergism with the base stock. Slightly smaller, but still very high blending values are obtained when blended at the 20 vol.% level. Naturally, the blending values decline progressively when the blend stock is added in higher and higher proportions, until they reach the clear measured values on the blend stock at a 100 % blend stock proportion.

The impact of synergism was even higher for the butene-derived polymer gasoline. Here, instead of the measured octanes of 98 RON and 83 MON, blending octanes of 126 and 99 were calculated, displaying a synergism of 28 numbers for RON and 16 numbers for MON.

The above observations are for the olefinic catalytic condensation products. Similar observations can be made with the hydrogenated products. In general, however, the paraffinic product does not exhibit significant synergism with this type of base stock.

A corollary from these observations is that propylene polymer gasoline is fairly poor for most motor fuel applications. Propylene–butene feeds can make reasonably good gasolines, and the gasoline products from the catalytic condensation process based on butenes are excellent.

Selective and Nonselective Gasoline Production with the Catalytic Condensation Process

Most catalytic condensation operations with SPA catalysts on propylene and propylene–butene feeds are conducted in a nonselective mode to maximize light olefin conversion to gasoline. To drive gasoline yield, nonselective units tend to be operated at higher temperatures between 160 °C inlet and 200 °C reactor outlet temperatures. This typically produces a broad olefin distribution with minor amounts of C_6's and primarily C_7–C_{11}'s with significant amounts of C_{12}'s. While this maximizes LPG conversion and gasoline yield, it does not maximize octane, due to partial skeletal rearrangement to less branched, lower octane isomers.

For butenes, however, there are significant octane advantages for selective operations that were first utilized in World War II to maximize aviation fuel octane. Selective operations are generally carried out at lower temperatures, lower space velocity, and with C_4 recycle. Under these conditions, butenes react selectively with each other to form almost exclusively dimers, C_8, and trimers, C_{12}. Most of the dimers are codimers produced by the reaction of one molecule of isobutene with one molecule of *n*-butene. The resulting codimers are high-octane trimethylpentenes or isooctenes.

The typical properties of the codimers and their hydrogenated counterparts called “hydrocodimers” are shown in Table 5. The total codimer product comprises the C_8

Table 5 Properties of codimer products

	Total product (C_8–C_{12})		Dimer product (C_8)	
	Olefinic	Hydrogenated	Olefinic	Hydrogenated
Specific gravity	0.744	0.728	0.737	0.717
Engler distillation (°C)				
IBP	104	104	102	102
10	109	109	107	107
30	113	112	109	109
50	117	117	110	109
70	124	124	111	110
90	174	170	112	111
EP	210	213	134	132
Octane numbers				
RON	99	98	96.8	99
MON	82	93	82.4	93

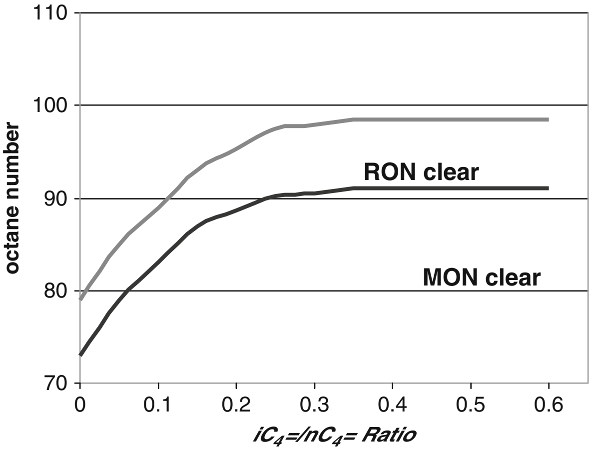


Fig. 4 Octane numbers of 90 % hydrogenated dimer versus iC_4=/nC_4= ratio in feed

and C_{12} fractions and has a very flat boiling range. The total product octanes were 99 RON and 82 MON before and 98 RON and 93 MON after hydrogenation. The C_8 fraction, obtained by fractionation, was 97 RON and 82 MON before and 99 RON and 93 MON after hydrogenation. The −1 to +2 change in RON with saturation of these highly branched olefins is very atypical of olefin saturation. As expected, the specific gravity of the paraffinic products of hydrogenation is slightly lower than the gravity of the olefinic material, but the boiling range remains virtually unchanged.

Figure 4 shows the octane number of the codimer product at 90 % hydrogenation versus the weight ratio of isobutene (iC_4=) reacted relative to *n*-butenes (nC_4=) reacted. The reciprocal of this value is sometimes called the “reaction ratio.” It was learned during World War II that a low reaction ratio (high isobutene fraction) is desirable in order to obtain a high-octane product.

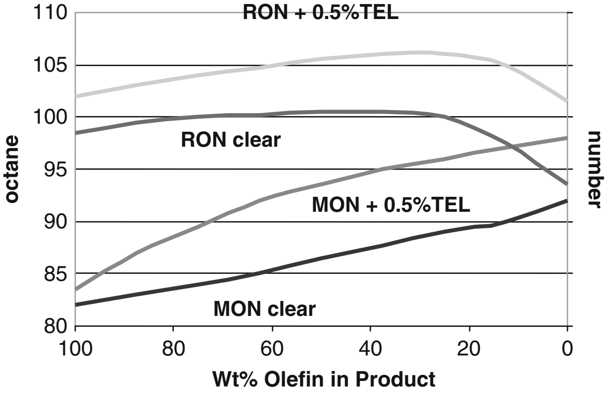


Fig. 5 Octane yields relative to olefin conversion

Figure 4 was based upon 90 % hydrogenation because this is close to a maximum in (R+M)/2 for butene dimers in leaded gasolines. This can be seen in Fig. 5 which shows slight maximum in RON is obtained at about 85–90 % saturation for leaded and 60–70 % saturation for unleaded gasolines. MON continues to increase for both gasolines. This slight maximum is the result of synergistic octane blending of between olefins and paraffins. To simplify control of the degree of hydrogenation, a portion of the polymer gasolines is normally bypassed around the hydrogenation reactor.

Catalytic Olefin Condensation with the InAlk™ Process

UOP has commercialized two selective condensation processes which produce a gasoline nearly identical to alkylate. As discussed elsewhere, alkylate is a high RON and MON, low RVP, paraffin blend stock free of benzene, aromatics, olefins or sulfur, and highly valued for today's environmental gasolines with tight specifications. Alkylate has historically been made by reacting isobutane with butenes or other olefins over sulfuric acid or hydrofluoric acid in the liquid phase or over novel solid heterogenous acid catalysts and ionic liquids now being developed.

These processes produce alkylate *indirectly* by selectively dimerizing butenes over an acid catalyst followed by saturation of the dimers into highly branched paraffins. Either sulfonic acid ion exchange resin or SPA catalysts can be used for the condensation.

Resin-Catalyzed Condensation

The resin InAlk process, shown in Fig. 6, uses a sulfonic acid ion exchange resin catalyst, similar to the catalyst used for MTBE production. This technology is ideally suited to conversion of MTBE plants to indirect alkylate production. The polymerization reactors produce high RON isooctenes rich in

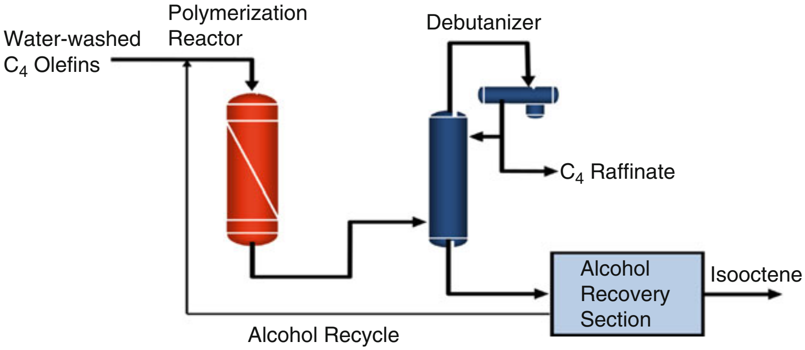


Fig. 6 InAlk process

trimethylpentenes, including diisobutene (DIB). The technology uses a conventional adiabatic fixed-bed reactor.

To minimize production of undesired heavy oligomer products, a C_4 alcohol co-feed is required in the process as a selectivity modifier. The alcohols used are formed in the process by reaction of C_4 olefins with H_2O. The C_4 alcohols are recovered from the oligomer product by water washing and recycled to the reactor section.

Optional saturation of the isooctene product requires the addition of a hydrogenation reactor and a product stripper for the removal of light ends.

Overall isobutene conversions in excess of 95 % are achievable, but *n*-butene conversion is much lower, typically 10–20 %. Higher $nC_4=$ conversion can be achieved with a higher cost unit design, but the resin InAlk process is best suited for applications accepting or desiring fairly low $nC_4=$ conversion. For feeds that require high $nC_4=$ conversion SPA InAlk is generally preferred. Selectivity to the desired diisobutenes or isobutene/*n*-butene codimers is set by the design conditions to meet gasoline T_{90} or other requirements, generally in the 85–90 % $C_8=$ range, with the balance being mostly trimers ($C_{12}=$). The selectivity to heavier compounds (tetramers, etc.) is negligible.

Where possible, it is advantageous to blend olefinic product as there is some octane loss with hydrogenation and since there is a positive blending octane effect when blending olefinic product into a typical gasoline pool. High selectivity to the diisobutene provides an additional positive blending octane effect vs. $C_8=$ oligomers containing less DIB content, making resin InAlk particularly attractive for the high $iC_4=$ feedstock from an isobutane dehydrogenation unit, such as the UOP Oleflex process. An example of olefinic product quality is summarized below.

Feed type	FCC C_4's	Isobutane dehydro C_4's
Oligomer $C_{12}=$, wt%	10.0	10.0
RON	102.6 (neat); blending RON 110.1	103.7 (neat)
MON	85.4 (neat); blending MON 90.1	86.3 (neat)
RVP, psia	2–3	1.8
$^{T}50\,/^{T}90$	224.6/303.4 °F (107.0/150.8 °C)	219/270 °F (103.9/132.2 °C)

SPA-Catalyzed InAlk Process

For the SPA InAlk process shown in Fig. 7, the SPA catalyst is employed at conditions chosen to maximize octane and catalyst life. In InAlk mode operation, SPA catalyst life is significantly increased (2^+ years) relative to the short cycle length typical in traditional catalytic condensation units. The increased catalyst life is the net effect of a reduction of heavy polymer formation on the catalyst in the liquid phase with the solvent helping to remove heavier products from the catalyst surface before they form hard coke and cause excessive catalyst swelling

The InAlk/SPA oligomerization reactors maximize isooctene (DIB and codimers) selectivity by operating at lower temperatures and in the liquid phase with a heavy paraffin solvent co-feed. In the SPA InAlk process, the C_8= selectivity exceeds 90 % in a single pass, another significant improvement over the traditional catalytic condensation process. Figure 7 depicts a typical flow scheme where the entire reactor effluent is hydrogenated, but the saturation section may be moved depending on product specifications for olefin content (i.e., unconverted C_4 olefin and C_8–C_{12} product olefin targets).

Typical hydrogenated C_6+ product quality for a mixed C_4= feed, such as from an FCC unit, is shown below.

RON	97.5–100
MON	92.5–94.5
T-90	333 °F/167 °C

The hydrogenated product neat octane obtained varies in the range shown as a function of the specific C_4 feed composition and the process conditions used. A very high iC_4= content feed, such as from an isobutane dehydrogenation unit (UOP Oleflex process), will have hydrogenated RON/MON even higher than the ranges shown above. The blending octane of the InAlk product is normally higher than the neat octane values reported above for the typical refinery gasoline pool

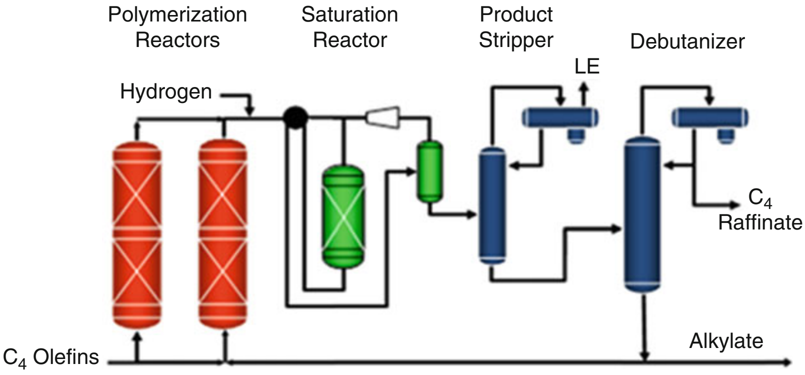


Fig. 7 SPA InAlk process

composition. Olefinic SPA InAlk C_6+ RON values are higher than the values shown above for hydrogenated product.

The InAlk process is flexible with respect to feed olefin type. Though the process is typically applied to a C_4= source feed, operation with a C_5= or mixed C_4–C_5 feeds also achieves similar high product quality.

Catalytic Condensation Process as a Source of Diesel Fuels

The catalytic condensation process can also produce fuels in the diesel boiling range, although because of their relatively high degree of branching, they all have fairly poor cetane characteristics, even after hydrogenation.

Table 6 illustrates a typical range of products in the diesel range obtained by the catalytic condensation process with SPA catalyst followed by hydrogenation. The worst product is the heavy polymer from a C_3–C_4 gasoline operation. The other three materials are products derived from propylene feeds: propylene tetramer (dodecene), heavy polymer from a tetramer operation, and the entire feed to the tetramer rerun distillation column.

A commercial operation for the production of synthetic diesel fuel from propylene was built in South Africa. The commercial results agree reasonably well with Table 6.

It is possible to improve the quality of the diesel range products by operating in the selective mode at lower temperatures and lower per-pass conversions with a higher recycle rate of unconverted material. This approach, however, has not been commercialized.

Zeolitic Distillate

Production of high-quality diesel fuel from C_3 to C_5 olefins over zeolitic catalysts is a very active area of development with some commercial announcements, but no plants are yet in operation.

Table 6 Comparison of hydrogenated polymer products in the diesel range

	Propylene tetramer	Heavy propylene polymer	Tetramer plus heavies	Heavy polymer from C_3–C_4 gasoline
API gravity	54.2	44.4	51.8	49.3
Engler distillation (°C)				
10	184	262	188	154
30	187	266	192	206
50	189	271	198	215
70	193	279	208	229
90	198	300	238	271
EP	213	329	277	304
Cetane numbers	32.8	37.0	36.9	28.7

Petrochemical Operations

Because this chapter is confined to olefin condensation, mostly for motor fuel applications, heptenes and nonenes will be discussed only briefly.

Petrochemical applications of catalytic olefin condensation center on the production of heptenes, nonenes, and dodecene (or propylene tetramer). These were initially recovered by fractionation from polymer gasoline, but modern units are specifically designed and operated to maximize the yield of the desired olefin fractions. The by-products are still blended into the gasoline pool.

Heptenes and nonenes are the main products used for the production of octyl and decyl alcohols via the "oxo" or hydroformylation process. Both these alcohols find end use as esters in plasticizer applications, principally for PVC. Dodecene at one time was a major product for the manufacture of dodecylbenzene sulfonates as active detergent ingredients; however, their relatively poor biodegradability led to the discontinuance of this operation. Dodecenes are still used in the production of tridecyl alcohols via the oxo process. Some nonenes are also used in the production of nonylphenols.

Heptenes

Table 7 illustrates typical of specifications for heptenes. Though fairly common to all producers, the values can vary depending on the desired end-use application.

Thus, the boiling range and the desired ratio of dimethylpentenes to methylhexenes may determine the operating conditions in a catalytic condensation unit and the net recovery and yield of the useful fraction. The product heptenes consist of a fairly complex mixture of heptene isomers. Table 8 shows a typical composition and approximate boiling points for individual major isomer components; many other isomers can be present at lower concentrations.

Table 7 Typical heptene specifications

Parameter	Specification	Typical values
Specific gravity	0.705 min	0.711
		0.715 max
Boiling range (°C)		
IBP	85 min	85
50 %	88 min	89
		90.5 max
95 %	95 max	93
Bromine number	150 min	154
Sulfur	0.02 wt.%	–
Peroxide number	40 mg/L	–
Color	+20 saybolt min	–
Ratio of dimethylpentenes to methylhexenes	2/1 to 3/1	2.6/1

Table 8 Major isomers in the heptene fraction (>0.1 wt.% approx)

No.	Component	Wt%	Boiling point (°C)
1	4,4-Dimethyl-1-pentene	0.8	72.5
2	4,4-Dimethyl-*trans*-2-pentene	4.4	76.8
3	3,3-Dimethyl-1-pentene	0.2	77.6
4	4,4-Dimethyl-*cis*-2-pentene	0.1	80.4
5	3,4-Dimethyl-1-pentene	0.2	81.1
6	2,4-Dimethyl-1-pentene	6.2	81.7
7	2,4-Dimethyl-2-pentene	16.5	83.4
8	2,3-Dimethyl-1-pentene	7.8	84.3
9	5-Methyl-*trans*-2-hexene	1.0	86.1
10	2-Methyl-*trans*-3-hexene	0.2	86.1
11	3,4-Dimethyl-*trans*-2-pentene	16.3	87.2
12	3,4-Dimethyl-*cis*-2-pentene	4.4	87.2
13	3-Methyl-1-ethyl-1-butene	3.1	88.9
14	3-Methyl-*trans*-3-hexene	0.5	93.6
15	3-Methyl-*trans*-2-hexene	1.5	93.9
16	3-Methyl-*cis*-2-hexene	2.9	93.9
17	3-Methyl-*cis*-3-hexene	2.2	95.3
18	2-Methyl-2-hexene	2.2	95.4
19	3-Ethyl-2-pentene	1.2	96.0
20	2,3-Dimethyl-2-pentene	27.5	97.4
21	*Trans*-2-Heptene	0.6	97.9
22	*Cis*-2-Heptene	0.1	98.5

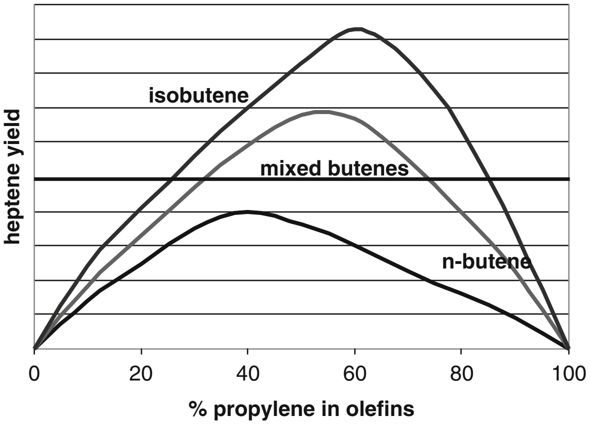


Fig. 8 Effect of olefin composition on heptene yields

As a rule, dimethylpentenes are produced mainly from isobutene, while methylhexenes tend to originate from *n*-butenes.

The relative yield of heptenes is illustrated in Fig. 8 as a function of the olefinic feed composition; as expected, higher yields of heptenes are obtained when the feed

Table 9 Typical nonene specifications

	Specification		Typical values	
Parameter	Narrow range	Wide range	Narrow range	Wide range
Specific gravity	0.738 min	0.740 min		
	0.745 max			0.745
Boiling range (°C)				
IBP	134 min	134 min	134	134
50 %	–	–	135	138
EP	143 max	155 max	142	150
Bromine number	125 min	–	127	
Sulfur	0.005 wt.% max		–	–
C_8 olefins, wt%	0.5 max		–	
C_9 olefins, wt%	90.0 min		97.3	
C_{10} olefins, wt%	3.5 max		2.7	
Olefin content (wt.%)		95 min		

mixture consists of equal proportions of propylene and butenes. Isobutene tends to produce significantly higher yields of heptenes than *n*-butene. However, because isobutene produces more dimethylpentenes, the final yield can only be calculated on the end product after fractionation that meets the required specifications.

Nonenes

Typical nonene specifications are shown in Table 9. Actually, there are several different specifications that could be called “typical,” a main characteristic being the breadth or narrowness of the cut.

A minimum olefin concentration of 95 % or higher is usually required. An olefin concentration of 95 % can be easily obtained for nonene units that process only propylene in the feed. However, in units that may also process olefinic recycle streams, as, for example, from a tetramer operation, there may be a reduction in the olefin content of the product owing to hydrogen transfer from the heavier species to the lighter olefins. Units with a high gasoline recycle may produce paraffin concentrations in the nonene fraction as high as 30–40 %, which render the nonenes unsuitable as oxo plant feed. Most nonene units today are disassociated from tetramer production and therefore this problem is seldom encountered.

Dimersol™ Process

While the catalytic condensation and InAlk processes described above make use of a supported phosphoric acid catalyst, the Institut Francçais du Pétrole (IFP) developed and commercialized a different approach based on Ziegler–Natta-catalyzed oligomerization using organometallic catalysts. In 2001, IFP created Axens as their licensing arm. Because of the nature of the catalyst, this process can be tailored to specific highly selective applications that have been identified by various names (Chauvel and Lefebvre 1989):

Dimerization of Ethylene to 1-Butene

AlphaButol™ is utilized for the selective dimerization of ethylene to 1-butene for use as a comonomer in the production of linear low-density polyethylene (LLDPE). Though not in the motor fuel range for refinery applications, its mention is included here for the sake of completeness and continuity with the other Dimersol process schemes. This type of operation is best suited for locations where LLDPE is being produced and in which there is no other local source of 1-butene. AlphaButol units have been reportedly built in Saudi Arabia and Thailand.

Dimerization of Ethylene to *n*-Butenes

Whereas the IFP AlphaButol process is selective for the production of 1-butene, the IFP Dimersol E process produces *n*-butenes and heavier oligomers. The Dimersol E process also operates at about 50 °C in the liquid phase with a Ziegler-type catalyst that can be a nickel derivative activated by an organometallic reducing agent. Whereas the AlphaButol process avoids isomerization, the Dimersol E features both dimerization and isomerization, and it produces a blend of *n*-butenes and heavier oligomers, depending on the feed composition, the actual type of catalyst, and the operating conditions. For polymer-grade ethylene, the Dimersol E process yields 30–70 % *n*-butenes with a once-through conversion of 90–100 %, with the rest being in the C_6 + gasoline fraction. Gasoline production can be further enhanced by adding propylene to the feed. It is worth noting though that in the Dimersol E process the ratio of 1-butene to 2-butene in the product is about 1:1, still well above the equilibrium ratio at 50 °C.

Dimerization of Propylene and Butenes, Separately or Combined

The Dimersol process (Fig. 9) uses an organometallic catalyst consisting of a nickel salt in combination with an alkylaluminum compound. Various modalities are available:

- Dimersol G – for the dimerization of propylene to isohexenes used in gasoline blending.
- Dimersol E – for the oligomerization of ethylene and propylene olefins contained in FCC gases and already described above for the nonselective dimerization and oligomerization of ethylene.
- Dimersol X – for the selective dimerization of propylene and butenes for the production of heptenes or for the dimerization of *n*-butenes for the production of

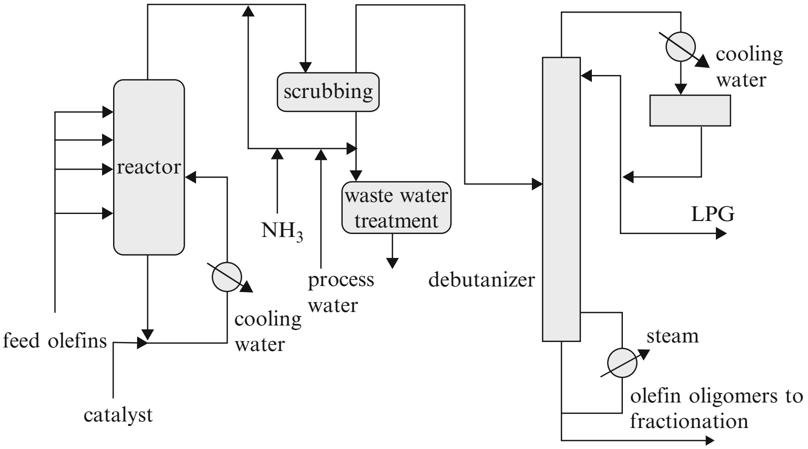


Fig. 9 Dimersol process (IFP's Axens)

octenes. These octenes are fairly linear, have a poor octane number, and are unsuited for gasoline applications. Heptenes and octenes obtained from the Dimersol X process are feedstocks for the production of plasticizer alcohols.

In all these Dimersol processes, the olefinic feedstock and the liquid catalyst are introduced into the reactor in a fashion compatible with the heat removal requirements in the reaction system. The level of conversion and the distribution of dimers and oligomers depend on the number of reactors used in series, the residence time, and the concentration of catalyst. The effluent from the reactor is circulated through a catalyst neutralization and elimination section and a water wash before fractionation for the desired cuts.

Axens' Polynaphtha

In 1986 (Gagnière 2013), IFP (now Axens) commercialized Polynaphtha, a C_3–C_4 condensation process for gasoline which employs a regenerable silica alumina catalyst in their Polynaphtha process. Multiple swing reactors are employed to permit in situ or ex situ regeneration.

Specialty Oligomerization Processes

Chevron in Richmond, California, and NPRC in Japan use or have used liquid phosphoric acid to produce propylene tetramers. There are also a few highly selective processes that are used for the production of specific dimers in petrochemical applications. Some of the most notable are:

- Sulfuric acid dimerization of isobutene for the production of trimethylpentenes, in particular a mixture of 2,2,4-trimethyl-1-pentene and 2,2,4-trimethyl-2-pentene.
- Selective dimerization of propylene to 2-methyl-1-pentene over triethylaluminum in a process developed by Scientific Design and Goodyear. This dimer can be used as an intermediate for the synthesis of isoprene.
- Selective dimerization of propylene to 4-methyl-1-pentene over organopotassium compounds or, in general, strong alkaline catalysts, in the liquid phase. 4-Methyl-1-pentene is a monomer used in the preparation of transparent plastics with a high melting point used in microwavable cookware, lab ware, and medical products and manufactured commercially by Mitsui Plastics, Inc., under the name "TPX" and by Phillips 66 under the name "Crystalor."
- Hüls AG's Octol process for the selective dimerization of *n*-butenes to highly linear octenes suitable for the manufacture of isononyl alcohol plasticizers over a solid heterogenous catalyst. The product may contain up to 20 % *n*-octenes and over 50 % methylheptenes, with a balance of dimethylhexenes, and a small amount of trimethylpentenes; the product is quite similar to that obtained with IFP's Dimersol X process.

Conclusions

Catalytic olefin condensation is one of the oldest catalytic processes used in refining and petrochemical operations and pioneered the use of acid catalysts. Many catalysts have been used over the years that have been examined, albeit briefly, in this chapter. Solid phosphoric acid catalysts (SPA) were for many years the workhorse of the industry and still command a very respectable market share. More surprisingly, this old technology is currently enjoying a bit of a revival by the introduction of highly selective, low temperature, liquid phase operations in which both sulfonic acid resins and SPA are finding growth. Zeolitic catalysts are slowly making inroads in condensation primarily to make more linear oligomers in the C_{12}–C_{24} range, for quality synthetic diesel and jet fuels.

Catalyst Suppliers

The information provided herein is correct as of the time of this writing but is subject to change without notice. The addresses provided are for the central offices; the catalysts themselves may be sourced from other geographical locations.

Dimersol catalysts are proprietary and can be obtained through Axens (IFP):

Institut Français du Pétrole	IFP, North America, Inc.
1 et 4, Avenue de Bois-Préau	100 Overlook Center, Suite 400
92852 Rueil–Malmaison Cedex	Princeton, NJ 08540
France	USA

There are two recognized suppliers of SPA catalyst:

UOP LLC	
25 East Algonquin Road	
P. O. Box 5017	
Des Plaines, IL 60017-5017	
USA	
Südchemie AG	Südchemie – United Catalysts Inc.
Lenbachplatz 6	P. O. Box 32370
80833 München	Louisville, KY 40232
Germany	USA

Sulfonic acid resins come in many forms. Preferred catalysts include, but are not limited to, highly cross-linked macroreticular resins such as those available from Rohm and Haas (AMBERLYST), Dow Chemical (DOWEX), Bayer AG, Purolite, and others. Proprietary formulations may be desirable though for specific applications in this area, and the various suppliers should be consulted accordingly.

References

A. Chauvel, G. Lefebvre, *Petrochemical Processes*, ed. Synthesis-Gas Derivatives and Major Hydrocarbons, Paris, Vol. 1, Editions Technip, Paris, pp. 183–187 (1989)

M. Gagnière, A. Pucci, E. Rousseau, Tackling the gasoline/middle distillate imbalance. Petroleum Technology Quarterly (PTQ). **Q2**(201), 31–33 (2013)

V.N. Ipatieff, R.E. Schaad, Mixed polymerization of butenes by solid phosphoric acid catalyst. Ind Eng Chem **30**, 596–599 (1938)

Isomerization in Petroleum Processing

Dana Sullivan, Stephen Metro, and Peter R. Pujadó

Contents

Abstract

Upgrading light hydrocarbon (C_4–C_7) streams in refineries, petrochemical plants, and gas processing plants has continued to increase in commercial application, as the world demand for gasoline and petrochemicals has

---

Peter R. Pujadó has retired.

D. Sullivan • S. Metro (✉)
UOP LLC, A Honeywell Company, Des Plaines, IL, USA
e-mail: dana.sullivan@honeywell.com; stephen.metro@honeywell.com

P.R. Pujadó
UOP LLC, A Honeywell Company, Kildeer, IL, USA

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_7

experienced steady growth over the past decade. Increasingly stringent regulations have been enacted in most regions of the world, driving the increased demand for clean fuels. As a result, gasoline composition has been adjusted to a greater extent using C_5–C_7 isomerization processes. Light-naphtha isomerization technology plays a key role in meeting octane demand in the gasoline pool for clean fuels and premium gasoline grades. Low octane naphtha feedstocks are processed into isomerate with an octane number ranging from 80 to 93 RON. Isomerization involves the skeletal isomerization of a paraffin to a more highly branched paraffin with the same carbon number. Several light paraffin isomerization technologies are reviewed in this chapter, including both process and catalyst technologies. Flow schemes and economics are reviewed. Catalyst technologies include Pt containing zeolitic, mixed-metal oxide, and chlorided alumina.

Keywords

Paraffins • Isomerization • Gasoline • Light naphtha • Butane • Pentane • Hexane • Octane number • Chlorided alumina • Sulfated metal oxide • Zeolite

Introduction

Upgrading light hydrocarbon (C_4–C_7) streams in refineries, petrochemical plants, and gas processing plants has continued to increase in commercial application, as the world demand for gasoline and petrochemicals has experienced steady growth over the past decade. Increasingly stringent regulations have been enacted in most regions of the world, driving the increased demand for clean fuels. As a result, gasoline composition has been adjusted to a greater extent using C_5–C_6 isomerization processes. These regulations include many clean fuel initiatives, including lead phaseout, minimization of benzene, aromatics and olefin content, and addition of oxygenates to gasoline.

Light-naphtha isomerization plays a key role in meeting octane demand in the gasoline pool for clean fuels and premium gasoline grades. Low-octane naphtha feedstocks are processed into isomerate with an octane number ranging from 80 to 93 RON, depending on the process configuration, catalyst type, and operating conditions. Isomerization involves the skeletal isomerization of a paraffin to a more highly branched paraffin with the same carbon number. As in alkylation, which is discussed elsewhere in this handbook, the more highly branched paraffins have higher octane numbers. However, because of its nature, isomerization may also affect some of the naphthene components and will also saturate aromatics. Based on its chemistry, the isomerization process is one of the most economic means available for reducing the benzene content in gasoline.

Several isomerization technologies are commercially available from various licensors. These are fixed-bed process units that employ high-activity catalysts. The reaction conditions promote isomerization and minimize hydrocracking. The first commercial isomerization process dates back to the 1930s for isomerization of normal butane to isobutane. Isomerization of C_5–C_6 paraffins for motor fuel blending was introduced in the late 1950s.

UOP developed the Butamer™ process for the isomerization of *n*-butane to isobutane, typically used as a feedstock to produce motor fuel alkylate. Isobutane produced from isomerization can also be converted to isobutylene via catalytic dehydrogenation using a process such as the UOP Oleflex™ process. Isobutylene is used to produce gasoline blending components such as MTBE and ETBE and for making petrochemicals such as butyl rubber.

The aforementioned processes are some of the most widely used in industry and form the basis of this discussion. Developments in light-naphtha isomerization are usually based on the introduction of new, more active or more stable catalysts, some of which will be discussed in more detail below.

The skeletal isomerization of paraffins is one of the many important industrial applications of acid function-promoted catalysis. Other examples of the wide commercial applications of acid-catalyzed industrial hydrocarbon reactions are the alkylation of paraffins and aromatics with olefins, transalkylation and disproportionation of aromatics, metathesis of olefins, oligomerization of olefins, etherification and hydration of olefins, and hydrocracking. Although these various applications have some similarities, they are all promoted by an acidic catalyst and often by a metal function. The specific catalytic requirements for achieving a favorable economic result have led to the proliferation of specialized catalytic materials.

History

In the 1930s, Vladimir Ipatieff and his team from UOP discovered that they could transform normal butane molecules in gasoline to isobutane using an aluminum chloride catalyst with hydrogen chloride as a cocatalyst (Remsberg and Higdon 1994). While scientifically interesting at the time, refiners did not want isobutane in their gasoline due to its high volatility. But before the decade was over, high-octane aviation fuel was being produced from alkylation and isomerization processes and became a significant factor in the war effort during World War II. The UOP Butamer™ process was the predominant process used for *n*-butane isomerization then, as it is today. HF alkylation was subsequently used to produce higher-octane motor fuel for automobiles by combining isobutane with isobutylene to form highly branched isooctane molecules with eight carbon atoms. This gasoline had a high octane number and burned cleanly in combustion engines.

Demand for high-octane fuels for automotive use continued to increase in the late 1950s and 1960s as part of postwar economic expansion. It was recognized that the light straight-run naphtha portion of crude oil, consisting of predominantly pentanes and hexanes, negatively affects gasoline quality. A catalyst similar to what was used in the Butamer process was applied by UOP scientists to pentane- and hexane-rich naphtha and found to increase octane by 12–20 numbers. This UOP process, named the Penex™ process, was soon being used in nearly all refineries.

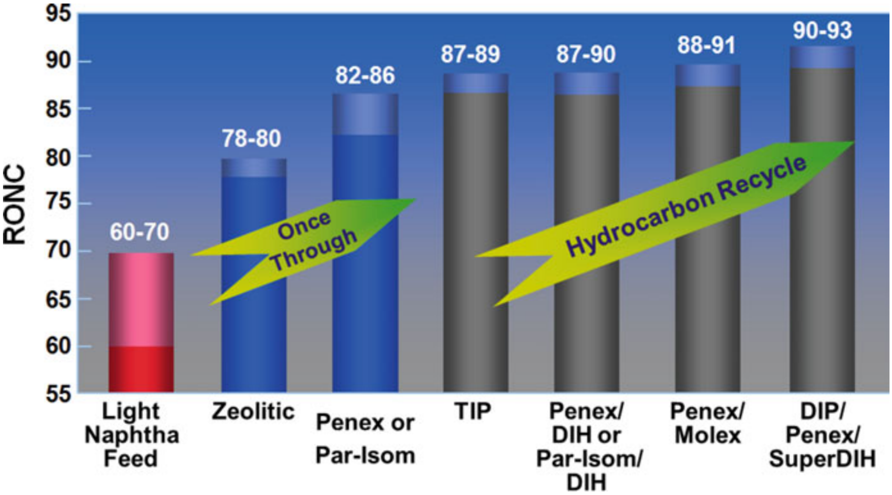


Fig. 1 Isomerization process configurations and octane values

Over the last half century, there has been an evolution in both the flow scheme and catalysts used in light-naphtha isomerization processes. Flow scheme improvements include the use of a recycle loop to circulate unreacted hydrocarbons exiting the reactor back to the reactor inlet and the use of fractionators such as a deisopentanizers (DIP) and deisohexanizers (DIH), and a process section that separates iso- and normal paraffins via a molecular sieve, rerouting the normal paraffins back to the reaction section for further yield improvements.

Catalyst advances include the use of new materials and base formulations to increase activity, selectivity, and the life of chlorided alumina-type catalysts. Other catalyst technologies were developed that did not require the continuous use of a chloriding agent during production to maintain catalyst activity and catalysts that were regenerable. Regenerable catalysts include older-generation zeolitic types, as well as more recent mixed metal oxide types (zirconia). A discussion on these types of catalysts and process technologies follows in latter sections, which are depicted in Fig. 1. A number of technology companies introduced various isomerization catalysts over the years, including Akzo Nobel NV (now Albemarle), Axens, NPP Neftekhim, Süd-Chemie AG (now Clariant), Shell Chemicals LP, and UOP (Honeywell UOP LLC).

Market Trends and Regulations

Market Trends

The gasoline available to consumers consists of a mixture of gasoline fractions from many refinery sources, including straight-run naphtha (unprocessed fraction), isomerate, alkylate, reformate, polymer, and FCC fractions. Gasoline also contains

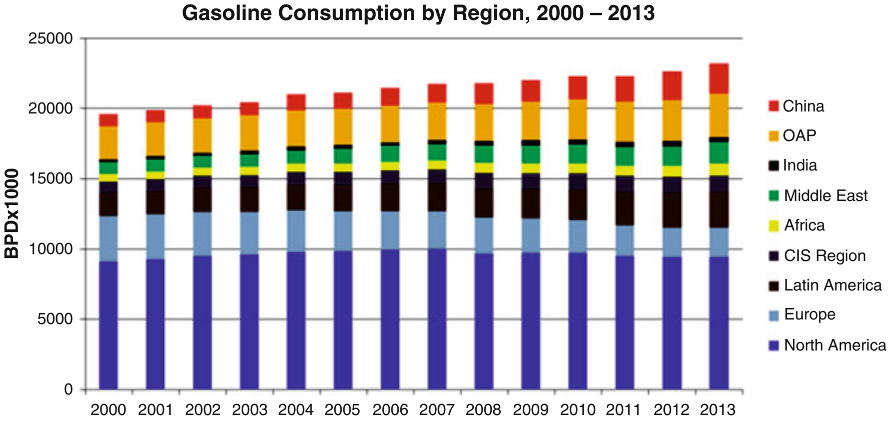


Fig. 2 Overall gasoline demand by region

additives such as ethanol, used to lower emissions via oxygenate addition, boost octane, and consume a "biofuel" source, which is typically produced from corn and sugarcane. Gasoline demand has risen from ~20 M B/D in 2000 to 23 M B/D in 2013 (IHS CERA 2014) as per Fig. 2. Gasoline demand is expected to rise to 28 M B/D over the next decade as per multiple market forecasting resources.

About half of the current demand is in developed regions such as North America, Europe, and Japan (IHS CERA 2014). Growth has been categorized as flat to declining in these regions due to the increased use of ethanol in gasoline, increased use of diesel, improved automobile fuel efficiencies, changing demographics, etc. The strongest growth over the past decade has occurred in emerging regions such as Asia, Latin America, the Middle East, and Russia, which currently make up approximately 50 % of gasoline demand (IHS CERA 2014), expected to rise by an additional 10 % over the next decade. The drivers for growth include large, growing populations and economies, increased wealth, and export of goods and services. These in turn are driving increased demand for automobiles and roadways and ultimately transportation fuels.

Isomerate makes up approximately 5 % of the total gasoline pool worldwide, highly dependent upon geographical region, typically being driven by meeting local gasoline specifications and demand. The global isomerization capacity is approximately 2.5 million barrels/day (IHS CERA 2014). While the largest installed capacity is in North America and Europe, almost 60 %, rapid growth is occurring in Russia, the Middle East, and Asia. The overall growth of isomerate over the past decade has been approximately 5 %, more than double gasoline growth, due to the increase in focus on clean fuels.

Some of the "developed" regions such as the USA and Europe, which are "octane long," have been operating their isomerization units to primarily saturate benzene to meet gasoline benzene requirements. Some allow their isomerization catalyst to deactivate from untreated feed poisoning, but still function to saturate benzene, using only the catalyst's metal function.

Table 1 Euro fuel specifications

Euro fuel specifications		Directive	EN 228	DIR 98/70	DIR 98/70	DIR 98/70	DIR 98/70
		Year	1993	1996	2000	2005	2009
		Class	Euro 1	Euro 2	Euro 3	Euro 4	Euro 5
Aromatics	Vol %	Max	No limit	No limit	42	35	35
Olefins	Vol %	Max	No limit	No limit	18	18	18
Benzene	Vol %	Max	5	5	1	1	1
Oxygen	Wt %	Max	2.5	2.5	2.7	2.7	3.7
Sulfur	ppm	Max	1,000	500	150	50	10
RON		Min	91	92	93	94	95
RVP	kPa		35–100	35–100	60–70	60–70	60–70
Lead	g/lt	Max	0.013	0.013	None	None	None

Regulations

Gasoline is subject to many local, national, and international regulations. New regulations affecting gasoline composition have been enacted in most regions of the world, driving the increase in demand for clean fuels. These regulations include many clean fuel initiatives, such as lead phaseout, minimization of RVP, limits on sulfur, benzene, aromatics, and olefin content, and addition of oxygenates. For example, Euro 5 motor fuel specifications, last updated in 2009, limit aromatics to 35 vol.%, olefins to 18 vol.%, and benzene to 1 vol.% maximum. Half a decade later, many non-EU countries are still in the planning phases of implementing either Euro IV or Euro V specifications. Refer to Table 1 for Euro I–V gasoline specifications (Euro Fuel Specifications).

In the USA, the Environmental Protection Agency (EPA) sets the fuel standards, with some variations from state to state, and California is generally being most stringent. Gasoline specifications are set by CARB, or the California Air Resources Board, and have the following fuel specifications that are similar to Euro V: 35 vol.% aromatics, maximum; 1.1 vol.% benzene, max; 10 vol.% olefins, max; 10 vol.% ethanol, min; RVP 6.4–7.2 psi; and sulfur <20 wt ppm. It should also be noted that the US EPA's Tier 3 sulfur limits have been set to 10 wt ppm maximum by 2017.

As indicated above, benzene content in gasoline is one component broadly regulated. For instance, in the USA, the Environmental Protection Agency (EPA) has implemented a Mobile Source Air Toxics (MSAT) rule to reduce hazardous air pollutants (US EPA 2014). As of 2011, the EPA requires that refiners must meet a maximum annual average gasoline benzene content of 0.62 vol.%. The maximum permissible level is 1.3 vol.% as of July 2012. These are applied to US refiners, as well as to gasoline imported to the USA. There are numerous technologies available to address lowering benzene content including prefractionation, saturation, isomerization, and extraction, and they are a subject of other literature (Shecterle 2008).

The C_5–C_6 isomerization unit is typically part of a naphtha complex used to produce gasoline. The naphtha feed is typically hydrotreated to remove contaminants harmful to downstream processes. The naphtha feed is divided into lighter and heavier fractions using a naphtha splitter. The lighter fraction, typically a C_5–C_6 hydrocarbon fraction, is sent to the isomerization unit, whereas the heavier fraction, typically C_7+ hydrocarbons, is sent to the catalytic reforming unit. The reforming unit converts these naphthas rich in paraffins and naphthenes to a product that is high in octane number and rich in aromatic hydrocarbons, using a platinum-containing acidic catalyst at elevated temperatures and pressures.

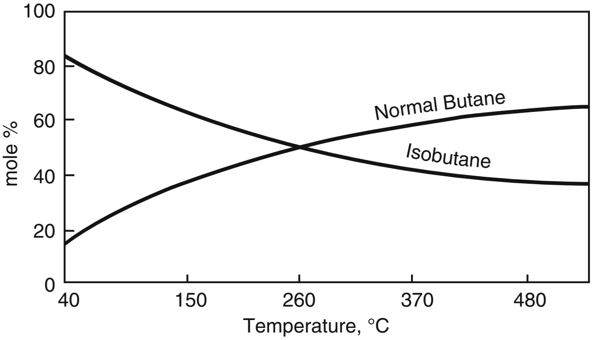
Process Chemistry of Paraffin Isomerization

The octane rating of the components used in the manufacture of the various commercial gasoline grades is indicative of the antiknock quality of a given fuel or component. The inherent octane values of different hydrocarbons have led to a variety of processing strategies to produce high-octane components for the production of high-performance motor fuel. In the case of C_5 and C_6 paraffins, the most highly branched isomers have the highest octane values. In the case of butanes, octane is somewhat irrelevant because the majority of isobutane is consumed in the production of motor fuel alkylate. Octane values for C_5 and C_6 paraffin isomers are shown in Table 2. The two empirical octane measurement methods for research (ASTM Method 2699) and motor (ASTM Method 2700) measure antiknock characteristics at two severity levels. Often, the average of these two values, or $(R + M)/2$, is used to express the overall engine performance of a gasoline component or blend. Table 2 shows that isopentane has a Research Octane Number (RON) value of nearly 30 numbers higher than *n*-pentane (Physical Constants of Hydrocarbons C3-C10 1971).

Table 2 Hydrocarbon octane values

	Research octane by ASTM 2699	Motor octane by ASTM 2700	$(R + M)/2$
n-Butane	93.8	89.6	91.7
i-Butane	100.4	97.6	99.0
n-Pentane	61.7	62.6	62.2
i-Pentane	92.3	90.3	91.3
n-Hexane	24.8	26.0	25.4
2-Methylpentane	73.4	73.5	73.4
3-Methylpentane	74.5	74.3	74.4
2,2-Dimethylbutane	91.8	93.4	92.6
2,3-Dimethylbutane	101.0	94.3	97.6

Fig. 3 Butane equilibrium



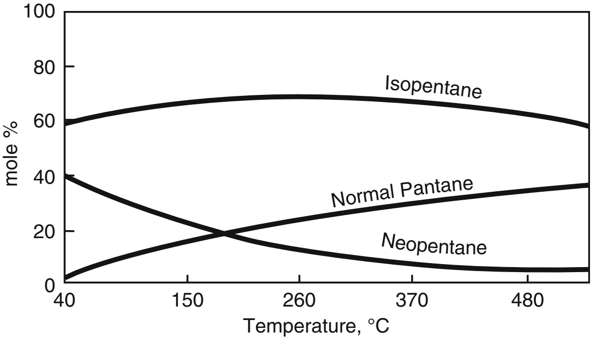


Fig. 4 Pentane equilibrium

Similarly, the multibranched hexane isomer 2,2-dimethylbutane (2,2-DMB) has a RON about 67 numbers higher than *n*-hexane. The single-branched isomer 2-methylpentane (2-MP) has a RON only about 49 numbers higher than *n*-hexane. Clearly branched isoparaffins and in particular multibranched isomers are the desired components for gasoline production.

Thermodynamic equilibria for the branched paraffin isomers are generally favored by low temperatures. Figures 3, 4, and 5 illustrate this trend (Stull et al. 1987). The most active catalyst, when all other variables are equal, is capable of producing the highest octane products.

Primary Reaction Pathways

Paraffin isomerization is most effectively catalyzed by a dual-function catalyst containing a noble metal and an acid function. The reaction is believed to proceed through an olefin intermediate, which is formed by paraffin dehydrogenation on the metal site (Reaction (1)):

$$CH_3{-}CH_2{-}CH_2{-}CH_3 \overset{Pt}{\longleftrightarrow} CH_3{-}CH_2{-}CH = CH_2 + H_2. \tag{1}$$

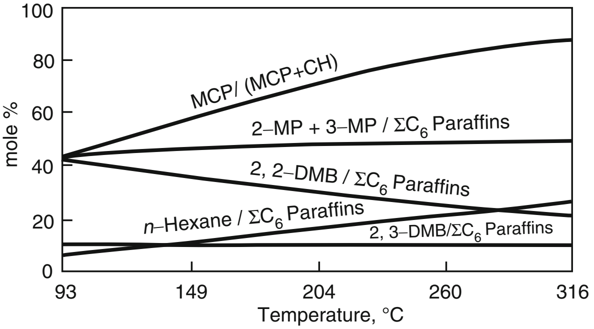
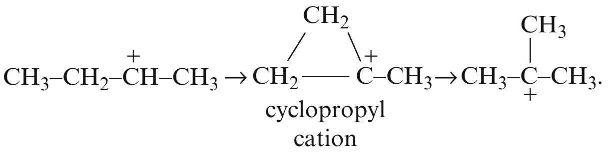


Fig. 5 C_6 fraction equilibrium

Although the equilibrium conversion of the paraffin in Reaction (1) is low at paraffin isomerization conditions, sufficient olefins are present to be converted to a carbonium ion by the strong Brønsted acid site (Reaction 2):

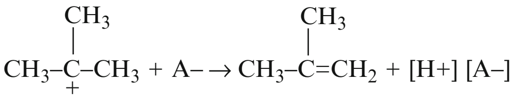
$$CH_3{-}CH_2{-}CH = CH_2 + [H^+][A^-] \rightarrow CH_3{-}CH_2{-}\overset{+}{CH}{-}CH_3 + A^-. \tag{2}$$

The formation of the carbonium ion removes product olefins from Reaction (1) and allows the equilibrium in Reaction (1) to proceed. The carbonium ion in Reaction (2) undergoes a skeletal isomerization, possibly through a cycloalkyl intermediate as shown in Reaction (3).

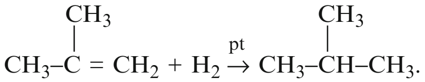


$$CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightarrow \underset{\text{cyclopropyl cation}}{CH_2\overset{CH_2}{\text{——}}\overset{+}{C}{-}CH_3} \rightarrow CH_3{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH_3. \tag{3}$$

Reaction (3) proceeds with difficulty because it requires the formation of a primary carbonium ion at some point in the reaction. Nevertheless, the strong acidity of isomerization catalysts provides enough driving force for the reaction to proceed at high rates. The mechanism of the final step is disputed. The isoparaffinic carbonium ion may be converted to an olefin through loss of a proton to the catalyst site and then quickly be hydrogenated to the analogous isoparaffin (Reactions 4A and 4B), or it may form the isoparaffin by hydride transfer from a normal paraffin, forming a normal carbonium ion intermediate as well as an isoparaffin (Santen 2012) (Reaction 5):

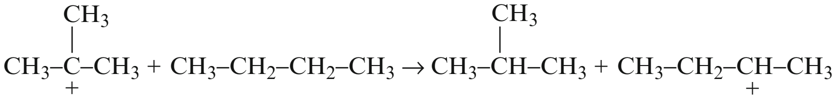


$$CH_3{-}\underset{+}{\overset{CH_3}{\overset{|}{C}}}{-}CH_3 + A- \rightarrow CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 + [H+]\,[A-] \tag{4A}$$



$$CH_3\text{–}\overset{\displaystyle CH_3}{\overset{|}{C}} = CH_2 + H_2 \xrightarrow{pt} CH_3\text{–}\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{–}CH_3. \tag{4B}$$

Or



$$CH_3\text{–}\underset{+}{\overset{\displaystyle CH_3}{\overset{|}{C}}}\text{–}CH_3 + CH_3\text{–}CH_2\text{–}CH_2\text{–}CH_3 \rightarrow CH_3\text{–}\overset{\displaystyle CH_3}{\overset{|}{C}}H\text{–}CH_3 + CH_3\text{–}CH_2\text{–}\underset{+}{C}H\text{–}CH_3 \tag{5}$$

In addition to these primary reaction pathways, there is evidence indicating the existence of a bimolecular reaction mechanism, particularly for butane isomerization. The olefinic intermediates dimerize, internal carbon atoms are protonated, skeletal isomerization occurs, and the dimer undergoes beta scission that results in the product isoparaffin. In addition to the C^{13} labeling experiments that support this mechanism, a relatively small amount of hydrocarbons containing carbon numbers higher than the feed are always found in the reaction products.

Isomerization Catalysts

Operation at the lowest temperature results in the formation of the highest octane product (Table 2 and Figs. 3, 4, and 5) in this equilibrium-limited reaction. Having the highest catalyst activity and the lowest operating temperature is important to achieve an economic operation. In the previous discussion of the primary reaction pathway, the primary functionality of a paraffin isomerization catalyst is to protonate a secondary carbon atom. All known paraffin isomerization catalysts have a combination of strong Lewis and Brønsted acid sites, which result in varying levels of protonation activity.

In addition to a strong acid function, isomerization catalysts must also be capable of hydrogenolysis, which not only assists in the protonation step but also serves to saturate olefin intermediates and aromatic hydrocarbons and to assist in the ring opening of naphthenes. This function also gives activity stability to isomerization catalysts, thereby improving the process economics.

An aluminum chloride catalyst for alkane isomerization was first developed in the 1930s (Pines 1981). The original application was for the conversion of *n*-butane to isobutane, which was, and still is, reacted with C_3, C_4, and C_5 olefins to produce motor fuel alkylate. The first application of this high-octane product was in the production of high-octane aviation gasoline. Subsequent developments of this predominantly Lewis-acid catalyst resulted in the current alumina-supported, bifunctional catalyst. UOP's I-8 catalyst is one commercial example of this catalyst system, which has seen wide commercial applications since 1981. The current state-of-the-art isomerization catalysts are UOP I-82 and I-84 catalysts and

Albemarle's ATIS-2L, introduced in the 2000s, providing higher activity and conversion for C_5/C_6 applications.

Chlorided Alumina-Type Catalysts

Chlorided alumina, the highest-activity paraffin isomerization catalyst available, increases the octane of a typical light-naphtha stream from about 70 to as high as 86 RON in a once-through paraffin isomerization unit as depicted in Fig. 1. Higher product octane, up to 93 RON, can be obtained by recycling low-octane hydrocarbons back to the reactors for further upgrade. The C_5+ yield from chlorided alumina catalysts is generally the highest from any commercial catalyst because of high catalyst selectivity and low operating temperature. Because chlorided alumina systems are not economically regenerable either within the process unit or ex situ, eventual reloading may be required, depending upon contaminant levels contained in the feed and process gas streams. While the average life of a catalyst load is 5 years, there are catalyst loads operating well beyond 20 years with diligent care and operations monitoring.

Nevertheless, the chlorided alumina system is often the most economical choice because of its inherent high activity. In addition, only chlorided alumina catalysts have enough activity to economically and effectively isomerize butanes. Approximately 85 % of the installed isomerization processes today employ chlorided alumina-type catalysts.

Zeolitic-Type Catalysts

Zeolitic isomerization catalysts, such as UOP's HS-10 Hysomer™ catalyst, operate at higher temperatures than chlorided alumina catalysts. Almost no new process units employ this technology due to unfavorable economics. The maximum product octane that can be achieved is limited by the unfavorable equilibrium at these conditions. Yields are also lower as a result of the higher operating temperature and the less selective characteristics of zeolitic catalysts. A typical octane upgrade for a once-through zeolitic isomerization unit is from 70 to about 79 RON. Higher product octanes (86–88) can be obtained in a recycle operation, such as in a UOP TIP™ unit (Total Isomerization Process) as depicted in Fig. 1. A TIP unit uses a multi-vessel vapor-phase adsorption process (IsoSiv™ process) to separate normal paraffins so they can be recycled to the reactor.

The most attractive benefit of zeolitic isomerization catalysts is that they are not permanently deactivated by water or other oxygenates and are fully regenerable. Consequently, zeolitic catalysts have often been used when revamping other process units, such as hydrotreaters or reformers to isomerization service. Sulfur can be present in the feedstock with catalysts such as the HS-10 catalyst, but performance is debited to some extent. Sulfur suppresses the platinum function as it does in any platinum-containing catalyst. Although isomerization activity is maintained, a net C_5+ product yield loss results. Feed hydrotreating is not an absolute requirement with zeolitic catalysts, but it is necessary to get the optimum performance from the catalyst. Approximately 30 zeolitic-type units still operate today.

Sulfated Metal Oxide-Type Catalysts

Sulfated metal oxide catalysts, which have been described as solid superacids, exhibit high activity for paraffin isomerization reaction (Gosling et al. 1998) when compared to zeolitic-type catalysts. These metal oxides form the basis of a more recent generation of isomerization catalysts that have been actively discussed in the scientific literature. These catalysts are most commonly tin oxide (SnO_2), zirconium oxide (ZrO_2), titanium oxide (TiO_2), tungstated zirconia, or ferric oxide (Fe_2O_3) that has been sulfated by reaction with sulfuric acid or ammonium sulfate. Sulfated alumina is not an active catalyst for hydrocarbon reactions.

A typical metal oxide catalyst, such as UOP's PI-244 Par-Isom™ catalyst, has a considerably higher activity than that of traditional zeolitic-type catalysts, and this activity advantage is equivalent to about 80 °C lower reaction temperature. The lower reaction temperature allows for a product with a significantly higher product octane, about 82 RON for a typical feed, four numbers higher than that of a zeolitic catalyst. Similar to zeolitic catalysts, the PI-244 catalyst is not permanently deactivated by water or oxygenates in the feedstock. These catalysts are also fully regenerable using a simple oxidation procedure that is comparable to the one used for zeolitic catalysts. The high activity of the PI-244 catalyst makes it an ideal choice for new units where the full performance advantage of chlorided alumina catalysts is not required or where the refiner is concerned about contaminants in the feedstock.

The performance of well-established commercial isomerization catalysts such as UOP HS-10 (zeolitic), UOP LPI-100 (an older-generation sulfated zirconia catalyst), UOP PI-244 (modified sulfated zirconia), and UOP I-82 (chlorided alumina) catalysts is compared in Fig. 6, which illustrates the octane number improvement over zeolitic catalysts for all the catalysts as a function of average reactor bed temperature. This ranking illustrates the activity advantage for the chlorided alumina-type catalyst over the zeolitic-type catalysts, an advantage that translates directly to octane improvement. This is particularly true for fixed volume systems, when considering reloading existing process units. Likewise, this ranking shows the performance benefit of the first- and second-generation sulfated zirconia-type catalysts over zeolitic. It should be noted that for unconstrained new unit designs, additional catalyst volume can be added to attain lower temperature operation and higher octane. Comparisons of chlorided alumina (I-82) and sulfated zirconia (PI-244) catalysts are provided in the following sections.

Process Options

Two process options are commercially available via either chlorided alumina-type catalyst (e.g., the Penex process with I-82) or sulfated zirconia catalyst (e.g., the Par-Isom process with PI-244). Both provide excellent upgrading of light naphtha

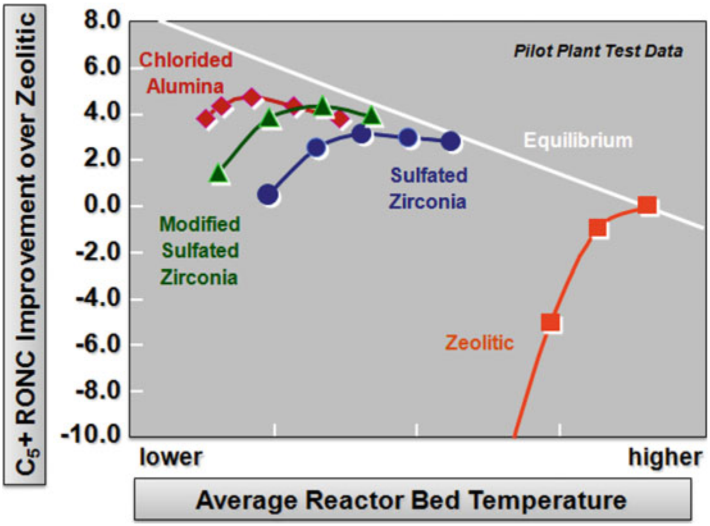


Fig. 6 Octane/activity curves for various isomerization catalyst types

with respect to octane number, yield, and octane barrels. A full techno-economic assessment is required for final process selection, with one simple example presented below as a case study.

Penex process units with chlorided alumina-type catalysts are most prevalent, historically provided the highest activity, yield, and RON. While they can employ a once-through (OT) configuration and avoid the need for an expensive recycle gas compressor and loop, it requires continuous chloride addition to maintain isomerization acid activity, requiring the use of a caustic scrubber to neutralize HCL in the off-gas and to eliminate unit corrosion (Fig. 7). Operating costs include chloride, caustic, and spent caustic disposal. In addition, these systems also require feed and make-up gas driers for moisture removal to ensure long catalyst life.

The sulfated zirconia-type units do not require the chloride or caustic, the catalyst is regenerable, but do require the use of a recycle gas compressor loop. There are benefits and trade-offs for both systems which are summarized in Table 3.

Isomerization Process Flow Schemes

The introduction of recent catalyst systems, such as the PI-244 catalyst, allows the development of new process technologies that fully utilize the characteristics of the catalyst. The process technology developed for the PI-244 catalyst is the Par-Isom™ process. A simplified flow scheme for the Par-Isom process operating in a once-through hydrocarbon configuration is shown in Fig. 8. For simplicity, a once-through hydrocarbon flow scheme is discussed in this chapter. Recycle

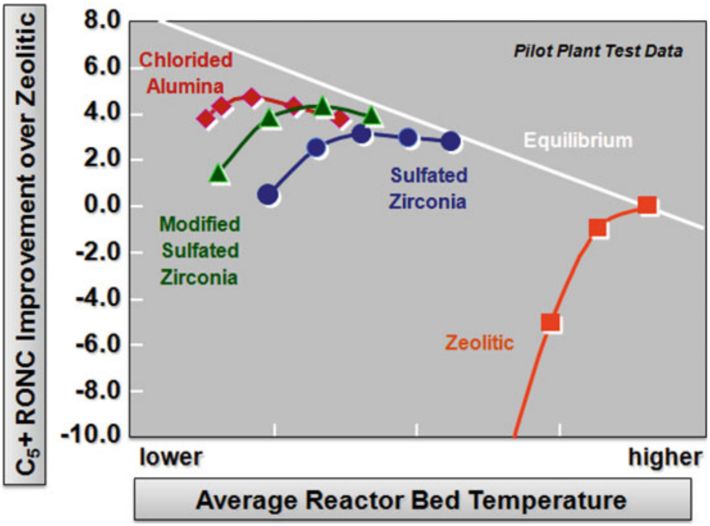


Fig. 7 Penex unit process flow scheme, hydrogen once-through (HOT)

Table 3 Comparison of process requirements for various catalyst types

	Chlorided alumina	Sulfated zirconia	Zeolitic
Chemical injection	Chloride	None	None
Contaminant sensitivity	Yes	No	No
Equipment	Dryers + scrubber	Basic	Fired heater
Spent caustic stream	Yes	No	No
Heating medium	MP steam	MP steam	Fired heater
Metallurgy	CS	CS	Alloy
Recycle compressor	No	Yes	Yes

hydrocarbon flow schemes previously developed for naphtha isomerization use either molecular sieve separation, such as in a TIP unit, or fractionation, such as a deisohexanizer (DIH) column.

The process flow scheme shown in Fig. 8 is similar to conventional once-through hydrocarbon Penex and zeolitic isomerization units. The fresh C_5–C_6 feed is combined with makeup and recycle hydrogen and directed to the charge heat exchanger, where the reactants are heated to the reaction temperature. A fired heater is not required in the Par-Isom process, because of the much lower reaction temperature needed with the PI-244 catalyst than with zeolitic catalysts. Hot oil or steam can be used as the heat source in this exchanger. The heated combined feed is then sent to the isomerization reactor.

Either one or two reactors can be used in series, depending on the specific application. Two reactors obtain the best performance from the process but at a higher capital and additional catalyst inventory costs. In a two-reactor system, the first reactor is operated at higher temperature (200–220 °C) to improve the reaction

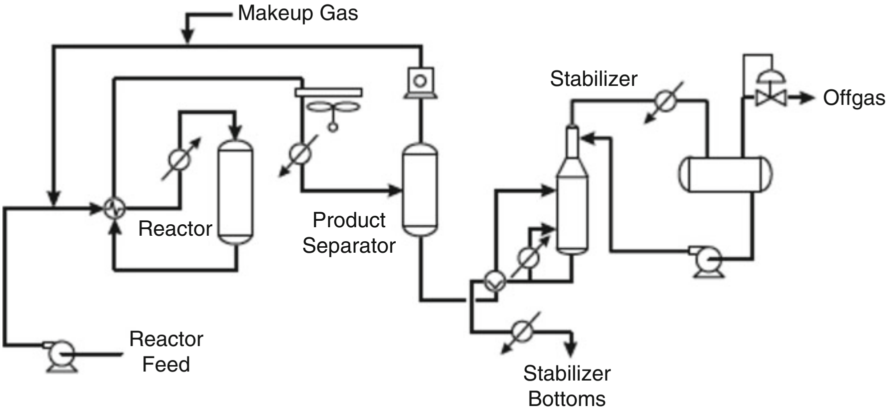


Fig. 8 Par-Isom unit process flow scheme

rate, and the second reactor is operated at a lower temperature to take advantage of the more favorable equilibrium distribution of higher-octane isomers. Two reactors are generally specified for the Par-Isom process, but a single reactor can be employed to reduce the capital and operating cost of the unit, but with a small debit in performance.

The reactor effluent is cooled and sent to a product separator, where the recycle hydrogen is separated from the other products and returned to the reactor section. The liquid product is sent to a stabilizer column, where the light ends and dissolved hydrogen are removed. The stabilized isomerate product can be sent directly to gasoline blending. In recycle flow schemes, either molecular sieve or fractionation options are used to separate the lower-octane isomers for recycling to the reactor. The selection of the separation scheme depends on the feed composition, availability of utilities, and the product octane desired.

The higher activity of the PI-244 catalyst makes it an ideal candidate for revamps of existing zeolitic isomerization units to achieve higher capacity or for revamps of idle process units, such as fixed-bed reformers or hydrotreaters to isomerization service. The reactors, recycle compressor, stabilizer, separator, and most heat exchangers can be employed in the new process flow scheme. The integration of a Par-Isom reactor into an existing semi-regenerative reforming unit can be a particularly attractive revamp opportunity for economically adding isomerization capacity to a refinery. A simple flow scheme illustrating the integrated units is shown in Fig. 9. In this configuration, a new Par-Isom reactor and charge heater are added to operate in parallel with the existing reforming unit reactors. A capacity increase can be realized by addition of another reactor in series.

The hydrogen required for the Par-Isom reactor is typically obtained from a reforming unit recycle compressor, combined with the light-naphtha charge, and sent to the Par-Isom reactor. The Par-Isom reactor effluent is typically returned to the reforming unit. The integrated units share a common product condenser, product separator, and stabilizer to minimize capital and operating costs.

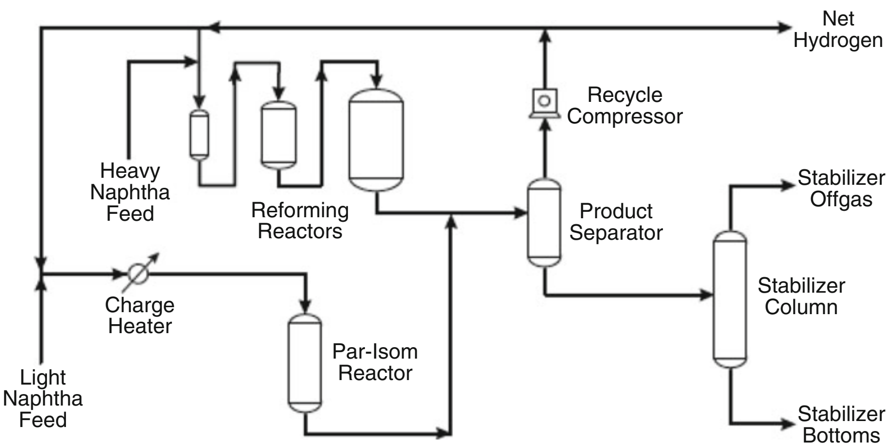


Fig. 9 Par-Isom and reforming unit revamp flow scheme

Isomerization Process Economics

The performance and economics of typical Penex and Par-Isom processes, with and without a DIH column and hydrocarbon recycle, are compared in Table 4. The case study is for a 10,000 BPD unit with a 10 X-factor feed, which is considered a light feed. X-factor is a measure of C_7+ hydrocarbons, C_6 naphthenes, and benzene.

This case study shows that a 10,000 BPD unit can produce 83.4 RON and 81,040 octane barrels with either process technology in a hydrocarbon once-through configuration (e.g., OT). C_5+ yields are well above 95 % in both cases. There will, however, be differences in quantity of catalyst required, space velocity, hydrogen to hydrocarbon ratio, and other parameters. It can be noted from the table that the total investment costs (US Gulf Coast basis) for a Penex-type unit are about 10 % higher than Par-Isom in this configuration and requires almost twice the utilities. Utilities included steam, electricity, and hydrogen for both units and chloriding agent (PERC) and caustic in the Penex unit.

Table 4 also contains comparative data for the same feed type and capacity case, except with the addition of a DIH column and hydrocarbon recycle. The DIH increases the RON by almost five numbers, from 83.4 to 88.0, and the total octane barrels by 4 %. The C_5+ yields are approximately 95 %. Utilities also increase, approximately one-third more for the Par-Isom unit, and 80 % more for the Penex unit with the recycle flow scheme. CAPEX increases from about $36M USD to $57M USD for adding a DIH to the Penex unit, whereas the CAPEX increases from $33M USD to $47M USD for the Par-Isom technology. The investment costs are less in both cases, in favor of the Par-Isom process for a given configuration.

Chlorided alumina-type catalysts have lower density (approximately half) and typically cost less from a total investment perspective, but also require added

Table 4 Isomerization unit economics for 10,000 BPD unit with a 10 X-factor (light) feed

	Units	Penex OT	Par-Isom OT	Penex-DIH	Par-Isom-DIH
Feed rate	BPD	10,000	10,000	10,000	10,000
RONC		83.4	83.4	88.0	88.0
Octane barrels		81,040	81,040	84,520	84,500
Total CAPEX	$MM	36.5	32.7	56.9	47.5
Utilities		Base	Base × 0.56	Base × 1.82	Base × 1.36

1. CAPEX based upon the US Gulf Coast prices 2014
2. Utilities are expressed on a relative basis, as costs vary on a regional basis
3. Utilities include fuel gas, electricity, hydrogen, steam (+ chloriding agents + caustic for Penex)

OT once-through hydrocarbon, *DIH* deisohexanizer

utilities such as a chloriding agent and caustic. After all variables are considered, the return on investment and profitability can be about equal for both technologies for a new unit for this particular case study (e.g., C_5–C_6 feed with a 10 X-factor), for either configuration, with or without a DIH.

While the total investment costs are higher with a DIH recycle for either technology, it is often selected for cases where higher octane is needed in a refinery's gasoline pool, particularly when complying with clean fuel specifications in some markets.

Processes based on chlorided alumina catalysts have historically been most popular due to an activity advantage, but advances in sulfated zirconia technology has closed the gap, making both choices viable. However, chlorided alumina catalysts provide greater flexibility in some applications; they can handle C_5–C_6 feeds with higher benzene content and X-factor and provide higher conversion for feeds that partially contain, or are based on, C4 hydrocarbons. It is important that any processor conduct a full techno-economic evaluation of process types and configuration, considering refinery and market objectives.

Catalyst Suppliers

For detailed up-to-date lists of catalysts and suppliers, the Oil and Gas Journal periodically publishes a comprehensive review. The main suppliers of light-naphtha isomerization catalyst are currently Albemarle, Axens IFP Group, GTC, and Honeywell UOP.

Conclusions

Light-naphtha isomerization technology, introduced in the 1930s, has undergone numerous advances to the process flow scheme and catalyst design over the course of history, and we expect to see continued interest and development in this field. The isomerization process has become increasingly important in helping refiners improve the octane of pentane- and hexane-rich naphtha and to meet the clean fuel specifications, including low-benzene-content gasoline. It has also been critical to provide isobutane to produce motor fuel alkylate as a high-octane blending component. The discussion in this chapter has been based on technology development and the relative performance of UOP's catalysts, particularly since UOP was a pioneer in this field and continues its technical leadership position today. Similar conclusions could be drawn if using equivalent catalysts and process technology from other suppliers.

Two process options are available via either chlorided alumina-type catalysts (e.g., Penex process with I-82) or sulfated zirconia catalyst (e.g., Par-Isom process with PI-244). Both provide excellent upgrading of light naphtha with respect to octane number, yield, and total octane barrels. Addition of a recycle system with DIH further increases the octane number and octane barrels, which is important for meeting growing clean fuel specifications. A full techno-economic assessment is required for final technology selection for a given application based on refinery and market objectives.

Revamping existing fixed-bed isomerization, hydrotreating, or semi-regenerative reforming units to Par-Isom-type process is an economical way to repurpose existing assets to meet octane and clean fuel demand. In most cases, the revamp can be accomplished with minimal changes to existing equipment. The high activity of the PI-244 catalyst can result in up to 4 RON higher-octane isomerate than can be achieved with zeolitic catalysts as well as higher throughput in revamp situations.

References

IHS CERA. *Annual Long-Term Strategic Workbook, Refining and Product Markets* (IHS CERA, Cambridge, MA 2014) Germany

Euro Fuel Specifications. Website: http://ec.europa.eu/environment/air/transport/fuel.htm

C.D. Gosling, R.R. Rosin, P. Bullen, T. Shimizu, T. Imai, Revamp opportunities for isomerization units. Petroleum Techonology Quarterly, Vol. 3, pp. 55–59 (1998)

Physical Constants of Hydrocarbons C3-C10, ASTM Committee D-2 on Petroleum Products and Lubricants and API Research Project 44 on Hydrocarbons and Related Compounds, American Society of Testing Materials, (1971)

H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversion* (Academic, New York, 1981), pp. 12–18

C. Remsberg, H. Higdon, *Ideas for Rent: The UOP Story*, Library of Congress Catalog Card No. 94-60759, (1994)

R. van Santen, in *Catalysis: From Principles to Applications*, 1st edn., ed. by M. Beller, A. Renken, R. van Santen (Wiley-VCH, Germany 2012), pp. 139–143

D. Shecterle, Options for Gasoline Pool Benzene Management, AiChE Ch 16, (2008). Web: http://www.aiche-fpd.org/listing/16.pdf

D.R. Stull, E.F. Westrom Jr., G.C. Sinke, *The Chemical Thermodynamics of Organic Compounds* (Robert E. Krieger, Malabar, 1987)

US EPA MSAT program regulations, 40 CFR 80 subpart, (2014). Web: http://www.epa.gov/otaq/fuels/gasolinefuels/MSAT/index.htm

Further Reading

N.A. Cusher et al., *Isomerization for Future Gasoline Requirements, Proceedings of the NPRA Annual Meeting*, 25–27 Mar 1990

R.A. Meyers, *Handbook of Petroleum Refining Processes*, 2nd edn. (McGraw-Hill, New York, 1996)

C.L. Moy et al., *Benzene Reduction for Reformulated Gasoline, Proceedings of the AIChE Spring National Meeting*, 29 Mar–2 Apr 1992

A.S. Zarchy et al., Impact of Desulfurization on the Performance of Zeolite Isomerization Catalysts, Proceedings of the AIChE Annual Meeting, 11–16 Nov 1990

Refinery Gas Treating Processes

David S. J. Jones and Steven A. Treese

Contents

Abstract

Refinery gas treating removes the so called "acid gases" (hydrogen sulfide and carbon dioxide) from the refinery gas streams. Removal of the acid gases in the refinery streams is required either to purify a gas stream for further use in a process or for environmental reasons. This chapter describes the most common sour gas treating processes. Design techniques are provided for the amine-based approaches along with a design example.

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, USA

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_11

Keywords
Refinery • Gas Treating • Amine • Absorber • Stripper • Sulfur • H2S

Introduction

Refinery gas treating is the generic term for processes used to remove the so called "acid gases," which are hydrogen sulfide and carbon dioxide, from the refinery gas streams. The acid gas removal processes used in the refinery are required either to purify a gas stream for further use in a process or for environmental reasons. Clean Air legislation now being practiced through most industrial countries requires the removal of these acid gases to very low concentrations in all gaseous effluents to the atmosphere. Hydrogen sulfide combines with the atmosphere to form very dilute sulfuric acid and carbon dioxide to form carbonic acid, both of which are considered injurious to personal health or may have other environmental impacts (greenhouse gases). These compounds also cause excessive corrosion to metals and metallic objects.

This chapter describes the processes, their chemistry, and a method of calculating the design of the more common processes.

The Process Development and Description

The use of chemically "basic" liquids to react with the acidic gases was developed in 1930. The chemical used initially was triethanolamine (TEA). However, as monoethanolamine (MEA) became commercially more available, it became the preferred liquid reactant due to its high acid gas absorption on a unit basis. The molecular weight of MEA is 61, while that for TEA is 149. As both react mole for mole with the acid gases, 2.44 lb of TEA must be circulated to achieve the same absorptive capacity as 1 lb of MEA. TEA also suffers degradation at temperatures above its boiling point; and, as this is its regeneration temperature, MEA has replaced TEA in this service. Since 1955 numerous alternative processes to MEA have been developed. These have fewer corrosion problems and are to a large extent more energy efficient. Inhibitor systems have, however, been developed which have eliminated much of the MEA corrosion problems. Some of these newer processes also are designed to selectively remove the H_2S, leaving the CO_2 to remain in the gas stream.

The process flow and description of the more common processes are essentially the same. This process flow is shown in Fig. 1.

For product gas streams which must meet lower than 1 grain per scf (standard cubic foot) of H_2S ($\sim$4.2 vol ppm), MEA (or caustic absorption) must be used. This amine, however, is degraded by certain sulfide compounds found in gas from thermal crackers. The most common compound that degrades MEA is carbonyl sulfide (COS). MEA can, however, be regenerated by batch or continuous vaporization and disposal of the sludge formed by the degradation.

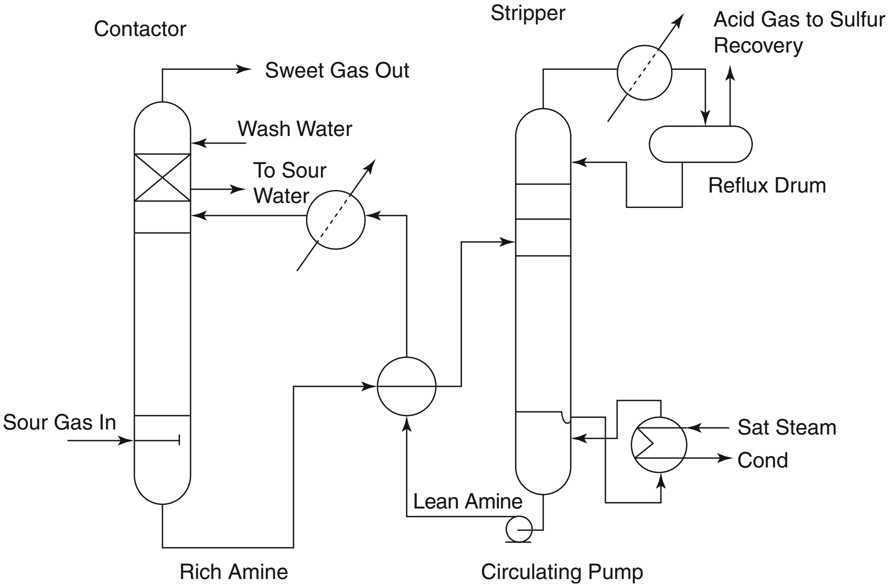


Fig. 1 Schematic drawing of a typical amine treating unit

Referring to the above flow sheet, sour gas (rich in H_2S) enters the bottom of the trayed absorber (or contactor). Lean amine is introduced at the top tray of the absorber section to move down the column. Contact between the gas and amine liquid on the trays results in the H_2S in the gas being absorbed into the amine. The sweet gas is water washed to remove any entrained amine before leaving the top of the contactor.

Rich amine leaves the bottom of the contactor to enter a surge drum. If the contactor pressure is high enough, a flash stream of H_2S can be routed from the drum to a trayed stripper. The liquid from the drum is preheated before entering a stripping column on the top stripping tray. This stripper is reboiled with 50 psig saturated steam. Saturated 50 psig steam is used because higher temperatures cause amines to break down. The H_2S is stripped off and leaves the reflux drum usually to a sulfur production plant. Sulfur is produced in this plant by burning H_2S with a controlled air stream.

The lean amine leaves the stripper bottom and is cooled. The cooled stream is routed back to the contactor.

Common Processes

There are several liquid solvents in commercial use for the removal of H_2S and CO_2 from refinery gases. Among the more common are the amines. These include:

MEA	Monoethanolamine
DEA	Diethanolamine
DGA	Diglycolamine
MDEA	Methyldiethanolamine

In addition to these amine-based solvents, there are also a few hot potassium carbonate processes, Sulfinol, and DIPA (diisopropanolamine). These latter two processes are marketed by the Shell Oil Company and are quite common in worldwide usage. They are described in the next section.

It is not the intent here to detail all of these processes with their various properties. The four amine solvents will however be described and discussed, and some mention will be made of the other processes.

Monoethanolamine (MEA)

This is one of the most common acid gas absorption processes. Normally 15–20 wt % MEA in water is circulated down through a trayed absorber to provide intimate contact with the sour gas. The rich solution is routed to a steam stripping column where it is heated to about 250 °F at 10 psig to strip out the acid gases. The lean MEA solution is then returned to the absorber.

MEA is the most basic (and thus reactive) of the ethanolamines. MEA will completely sweeten sour gases, removing nearly all acid gases if desired. The process is well proven in refinery operations.

Like all of the amine solvents used for acid gas removal, MEA depends upon its amino nitrogen group to react with the acidic CO_2 and H_2S in performing their absorption. The particular amines are selected with a hydroxyl group which increases their molecular weight and lowers their vapor pressures, thus yielding minimum solvent losses to the gas stream. MEA is considered a chemically stable compound. If there are no other chemicals present, it will not suffer degradation or decomposition at temperatures up to its normal boiling point.

The process reactions are given below:

$$\begin{gathered}HOCH_2CH_2NH_2 = RNH_2\\ 2RNH_2 + H_2S \underset{\text{High temp}}{\overset{\text{Low temp}}{\rightleftharpoons}} (RNH_3)_2S\\ (RNH_3)_2S + H_2S \underset{\text{High temp}}{\overset{\text{Low temp}}{\rightleftharpoons}} 2RNH_3HS\end{gathered} \tag{1,2}$$

Some of the degradation products formed in these systems are highly corrosive. They are usually removed by filtration or reclaimer operations. Filtration will remove corrosion by-products such as iron sulfide. Reclaiming is designed to remove heat-stable salts formed by the irreversible reaction of MEA with COS and CS_2 (carbonyl sulfide and carbon disulfide) and mercaptans. The reclaimer operates on a side stream of 1–3 % of the total MEA circulation. It is operated as a stream stripping kettle to boil water and MEA overhead while retaining the higher boiling point heat-stable salts. When the kettle liquids become saturated at a constant boiling point with the degradation products, they are shut in and dumped to the drain. Proprietary chemical treatments, not covered here, are also available on a contract basis to remove degradation products. Union Carbide has developed a well-proven corrosion inhibitor system for MEA that allows solution strengths of 28–32 %. The inhibitor requires payment of a royalty. The inhibitor chemicals are both expensive and hazardous for personnel to handle. The system does reduce corrosion problems to nearly zero and allows much higher system capacity for the same size equipment. In addition to the chemical degradation mentioned above, MEA oxidizes when exposed to air. Storage and surge tanks must be provided with inert blanket gases such as N_2 or sweet natural gas to avoid this degradation.

Amine systems foam rather easily resulting in excessive amine carry-over in the contactor. Foaming can be caused by solids such as carbon or iron sulfide; condensed hydrocarbon liquids from the gas stream; degradation products; and almost any foreign material introduced to the system such as valve grease, excess corrosion inhibitor, etc. Some of these items, such as iron sulfide or carbon particles, are removed by cartridge filters. Hydrocarbon liquids are usually removed by the use of a carbon bed filter on a lean amine side stream (about 10 % of total flow). Corrosion by-products are removed by reclaiming as noted above.

High skin temperatures on the reboiler/reclaimer tubes promote amine degradation. Steam or hot oil used for the reboiler should be limited to a maximum of 285 °F (140 °C) to avoid excessive temperatures. The reclaimer should not see hot oil or steam above 415 °F (213 °C).

MEA is nonselective in absorbing acid gases. It will absorb H_2S faster than CO_2, but the difference is not significant enough to allow its use to separate them. With the lowest molecular weight of the common amines, it has a greater carrying capacity for acid gases on a unit weight or volume basis. This generally means less pure amine circulation to remove a given amount of acid gases.

Because the solvent is in solution with water, the gas with which it comes in intimate contact will leave the contactor at its water saturation point. If dehydration is necessary, it must be done after the MEA system.

MEA has a vapor pressure 30 times that of DEA (300 times that of TEA and DGA) at the same temperature. This causes MEA losses of 1–3 lb/MMscf compared to 1/4–1/2 lb/MMscf for the other amine systems using the same system design parameters. Entrainment and leakage losses prevent low vapor pressure amines from attaining the predicted losses.

Diethanolamine (DEA)

DEA does not degrade when contacted with CS_2, COS, and mercaptans as does MEA. However, for product gas streams which must meet specifications lower than 1 grain per scf of H_2S, MEA must be used. Because of this, DEA has been developed as a preferred solvent when these chemicals are present in the stream to be treated.

The reaction with acid gas for any of the amines is a mole-to-mole reaction. As shown in Table 1, the molecular weight of DEA is 1.7 times that of MEA. Even after correcting for density, it requires 1.6 lb of DEA to react with the same amount of acid gas as 1 lb of MEA.

Table 1 Comparison of H_2S and CO_2 solvents

Formula	MEA	DEA	MDEA	DGA	DIPA	Sulfinol	Sulfolane
Molecular wt	61.1	105.1	119.2	105.14	133.19		120.17
Boiling point (°F)	338.5	515.1	477	405.5	479.7		545
Boiling range, 5–95 % (°F)	336.7–	232–	–	205–230	–		–
	341.06	336.7					
Freezing point (°F)	50.5	77.2	−9.3	9.5	107.6		81.7
Sp. Gr., 77 °F 140 °F	1.0113	1.0881	1.0418	1.0572	–		1.256
	0.9844	(86 °F)	(68 °F)	1.022	0.981		(86 °F)
		1.0693			(129 °F)		1.235
Pounds per gallon, 77 °F	8.45	9.09	8.68	8.82	8.3		10.46
		(86 °F)			(86 °F)		(86 °F)
Abs. visc., cPs., 77 °F 140 °F	18.95	351.9	0.68 cSt (100 °F)	40	870		12.1
					(86 °F)		(86 °F)
	5.03	(86 °F)	0.28 cSt (212 °F)				
		53.85		6.8	86		4.9
					(129 °F)		
Flash point (°F)	200	295	265	260	255		350
Fire point (°F)	205	330		285	275		380
Sp. ht. Btu/lb (°F)	0.663	0.605	0.535	0.571	0.815		0.35
Critical temp. (°F)	646.3	827.8	662	765.6	–		982.4
Critical press. atm	44.1	32.3		37.22	–		52.2
Ht. of vaporiz. (Btu/lb)	357.94	267.00		219.14	202.72		225.7
Ht. of reaction – CO_2 Btu/lb (approx)	825	620		850		580	
Ht. of reaction – H_2S, Btu/lb (approx)	650	550		674		500	
Normal w% soln	15–25	25–35	50–60	50–70		Varies	

MEA = $HOC_2\ H_4NH_2$
DEA = $(HOC_2H_4)_2NH$
DGA = $HOCH_2CH_2OCH_2C_2H_4NH_2$
DIPA = $(HOC_3\ H_6)_2NH$
Sulfolane = $(CH_2)_4SO_2$
MDEA = $(HOC_2H_4)_2NCH_3$

DEA is a weaker base (less reactive) than MEA. This has allowed DEA to be circulated at about twice the solution strength of MEA without corrosion problems. DEA systems are commonly operated at strengths up to 30 wt% in water, and it is not unusual to see them as high as 35 wt%. This results in the DEA solution circulation rate usually being a little less than MEA for the same system design parameters.

The process reactions are shown below:

$$\begin{gathered}\mathrm{HOCH_2CH_2NHCH_2CH_2OH = R_2NH = DEA}\\ \mathrm{2R_2NH + H_2S \underset{High\ \ temp}{\overset{Low\ \ temp}{\rightleftharpoons}} (R_2NH_2)_2S}\\ \mathrm{(R_2NH_2)_2S + H_2S \underset{High\ \ temp}{\overset{Low\ \ temp}{\rightleftharpoons}} 2R_2NH_2HS}\end{gathered} \qquad (3,4)$$

Because the system has fewer corrosion problems and removes acid gases to nearly pipeline specifications, it has been installed as the predominant system in recent years.

Diglycolamine (DGA)

This process has been developed by the Fluor Company. It originally began as a combination of 15 % MEA, 80 % triethylene glycol, and 5 % water. The system would both sweeten and dehydrate (to the same level as 95 % TEG) the gas in a single step. The high vapor release during regeneration (both water vapors and acid gases) causes severe erosion/corrosion problems in the amine/amine exchanger and in the regeneration column. This system has generally been abandoned.

The present system uses 2-(2-aminoethoxy)ethanol at a recommended solution strength of 60 wt% in water. DGA has almost the same molecular weight as DEA and reacts mole for mole with acid gases. DGA seems to tie up acid gases more effectively so that the higher concentration of acid gas per gallon of solution does not cause corrosion problems as experienced with the usual amine systems.

The system reactions are given below.

$$\begin{gathered}\mathrm{HOCH_2CH_2OCH_2CH_2NH_2 = RNH_2 = DGA}\\ \mathrm{2RNH_2 + H_2S \underset{High\ \ temp}{\overset{Low\ \ temp}{\rightleftharpoons}} (RNH_3)_2S}\\ \mathrm{(RNH_3)_2S + H_2S \underset{High\ \ temp}{\overset{Low\ \ temp}{\rightleftharpoons}} 2RNH_3HS}\end{gathered} \qquad (5,6)$$

DGA does react with COS and mercaptans similarly to MEA but forms N, N1, *bis* (hydroxy, ethoxy ethyl) urea, BHEEU. BHEEU can only be detected using an infrared test rather than chromatography. Normal operating levels of 2–4 % BHEEU are carried in the DGA without corrosion problems. BHEEU is removed by the use of a reclaimer identical to that for an MEA system but operated at 385 °F (196 °C). Materials of construction are the same as those for MEA systems. Proprietary chemical processes are available for sidestream removal of degradation products.

There has been a concern that DGA might be a good solvent for unsaturated hydrocarbons. A survey of the DGA users indicates that many of the systems are operated on gas containing concentrations of C_5+ above 2 % without any indication of hydrocarbon loading of the system.

Those systems near their hydrocarbon dew point are usually installed with a flash tank on the rich amine from the absorber. The flash tank is operated at a reduced pressure, just high enough to get into the plant fuel gas system. This reduces the vapor load on the regenerator column. (A similar system is recommended on MEA systems operating near the hydrocarbon dew point.)

DGA allows H_2S removal to less than ¼ grain per 100 scf and removes CO_2 to levels of about 200 ppm using normal absorber design parameters.

Methyl Diethanolamine (MDEA)

The amine that is growing in popularity for H_2S removal from gases is methyl diethanolamine. MDEA has taken over many of the applications formerly allocated to MEA and DEA.

MDEA is a tertiary amine that selectively removes H_2S, with less affinity for CO_2. This means that the sour gas from MDEA regeneration contains less CO_2 and places a lower volume load on the sulfur recovery units. MDEA is relatively noncorrosive and is commonly used at 50 % concentration without corrosion inhibitors. It is not degraded significantly by impurities in the gas and has a relatively low heat of vaporization and specific heat.

The MDEA reactions are similar to the absorption reactions of other amines. It is a somewhat weaker base in the reactions.

The process know-how for applying MDEA is offered by several vendors, but can also be applied as open art. MDEA can typically pick up about 0.3–0.5 mole H_2S per mole MDEA. In a typical 50 % solution, this amounts to 4.1–6.8 scf of H_2S per gallon, significantly more than MEA or DEA at their normal concentration levels. It has been successfully retrofit into MEA and DEA systems for increasing capacity with few other changes. Some of these retrofits have actually been done online while the systems were in operation.

MDEA is capable of meeting ¼ grain H_2S per 100 scf standard for fuel gases, but leaves more CO_2 in the gas than the alternative amines.

Other Gas Treating Processes

Hot Potassium Carbonate (Benfield, Catacarb)

This basic process concept has been known since the early 1900s. It was not an economical, practically-demonstrated process until the mid-1950s. Since that time, the process has been used for bulk removal of acid gases where residual CO_2 content was not needed in the ppm range.

The process is very similar to the amine processes. High temperatures favor high solubility of potassium carbonate (PC) in water leading to high concentrations of

PC. High PC concentrations mean higher carrying capacity of acid gases in the system. Hence, these processes operate at somewhat elevated temperatures.

The system is ideal for streams having CO_2 partial pressures of 30–90 psi (205–620 kPa). It has a high affinity for H_2S so that pipeline specification for H_2S can easily be reached at about 4 ppm. A stream with little or no CO_2 is not suited for the process due to making regeneration of the lean PC extremely difficult.

This process is often found as part of the hydrogen plant in those refineries that need to produce hydrogen.

Sulfinol

This is a proprietary system developed by Shell Oil Company. The process uses a solution containing both a chemically reactive component, diisopropanolamine (DIPA), and a physical solvent, tetrahydrothiophene 1–1 dioxide (Sulfolane).

Sulfolane is a very active solvent for H_2S, COS, and the mercaptans. CO_2 is also soluble in it, but not nearly as much as the S compounds are. Because of this, Sulfinol systems are most economically attractive (compared to amine systems) for H_2S/CO_2 ratios greater than 1:1. If the bulk of the acid gas can be dissolved in the Sulfolane, the system is much cheaper to operate than amine. The acid gases are picked up and released with very little heat increase or heat required. The solubility of acid gases is much higher in Sulfinol than for the amines. Sulfinol loadings are limited to 4–6 scf acid gas/gal solvent versus 2.5 scf acid gas/gal amine solution. In addition, the heat capacity of Sulfolane is about half that of the amines, further reducing the regeneration heat required.

Miscellaneous Processes

Other sweetening liquid processes such as Vetrocoke, Stretford, and Rectisol have found high usage in the coal gasification and natural gas industries. They have not reached the prominence of the amines or the PC processes in oil refining. Table 1 summarizes a comparison of the common solvents.

Calculating the Amine Circulation Rate

The circulation rate for amine solvents is important to ensure effective treatment of the sour gas. It is important also because it is a major contribution to the operating costs of the plant. These costs include pumping costs and steam to the reboiler and air cooler/condenser costs. This section provides a calculation method to establish this circulating rate. It is based on some fixed parameters which have been accepted as the optimum. These steps are:

Step 1. In DEA and MEA treating processes, a ratio of the amine to H_2S is about 3:1 mole-mole.

Step 2. Obtain gas feed rate and its composition (from plant and lab tests). Determine its mole weight and the volume percent H_2S.

Step 3. Fix the weight percent of amine in the recirculating amine solution. This will be between 15 % and 20 % weight of DEA or MEA in water.

Step 4. Calculate the H_2S in moles/h that is in the feed. This is done by converting the volume flow of gas to moles and using lab data to provide moles/h of H_2S.

Step 5. Calculate the amount of H_2S to be left in the lean gas. This is usually 10 grains/100 scf with DEA as absorbent and 3 grains/100 scf with MEA as absorbent (1 grain = 0.0648 g or 0.0022857 oz).

Step 6. Calculate H_2S absorbed. This is the difference between Step 4 and Step 5.

Step 7. Using the ratio 3:1 fixed in Step 1, calculate the rate of DEA (or MEA) that will be required.

Step 8. The mole weight of DEA is 105.1 and the mole weight of MEA is 61.1. Calculate weight of the amine using percent weight of amine in solution; calculate weight per unit time of solution.

Step 9. Using the data from step 2, calculate the solution flow rate in gallons (or other volumetric unit) per hour or per minute.

Calculating the Number of Theoretical Trays in an Amine Contactor

There are several accepted methods to calculate theoretical trays in amine contactors. It is common today to use process simulation software (HYSYS, Pro/II, and others) to perform the design calculations for amine contactors. This allows case studies to optimize the process design. The details of the computer simulations are beyond the scope of this handbook.

A manual approach to the calculations is described here. It is helpful to understand the manual approach to establish the background and limitations behind the computerized calculations.

Among the manual approaches are the McCabe-Thiele graphical method and the calculation method described by the following steps. The described calculation method is considered by many to be the sounder and more accurate of the manual methods available.

The following steps describe this calculation procedure:

Step 1. The equation to determine the number of theoretical trays is

$$N = \frac{(\mathrm{Log}\, 1/q(A-1))}{(\mathrm{Log} A)} - (1) \tag{7}$$

where:

- N = number of theoretical trays
- q = mole H_2S in lean gas/mole H_2S in feed gas
- A = the absorption factor $L/V \cdot K$

Step 2. Calculate H_2S in lean gas in moles/h and mole H_2S in the rich gas. Divide H_2S in lean gas by that in the feed. This is q.

Step 3. Calculate the amine circulation rate in mol/h amine, lb/h amine, and lb/h solution (about 20 vol.%). Resolve to gal/h of solution.

Step 4. Using the grains/h of H_2S leaving in the richer amine (i.e., grains in feed gas less grains in product gas), calculate grains per gallon absorbed by the amine solution. Add to that the value the H_2S residual in the lean amine. The sum of these is the grains of H_2S per gallon of amine and is the value used in Fig. 2 to determine the partial pressure of H_2S in MEA.

Step 5. The absorption factor is obtained from the equation

$$A = \frac{a(1 + Rr)(1 - q)}{pp/P} \tag{8}$$

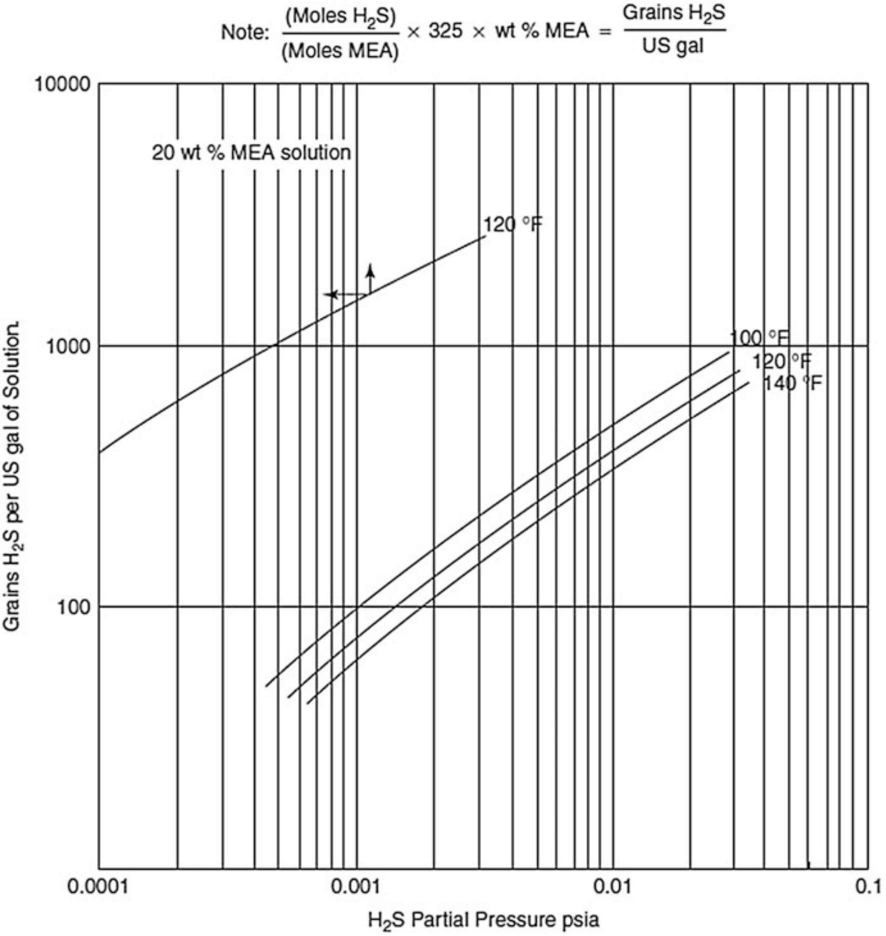


Fig. 2 (continued)

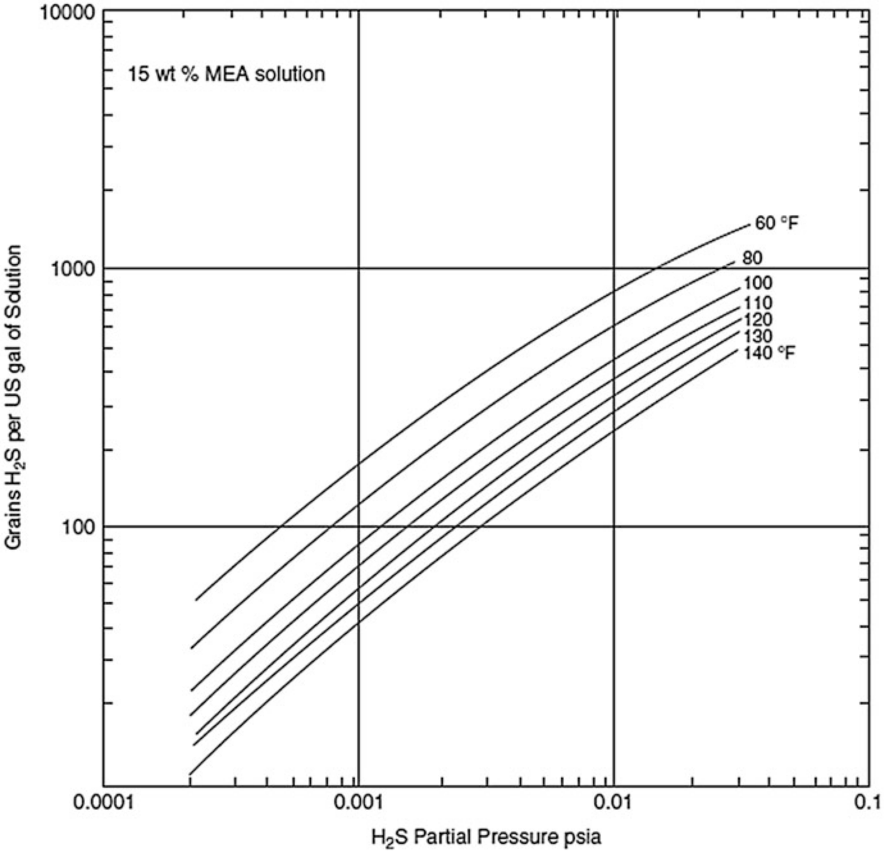


Fig. 2 (**a**, **b**) Partial pressure of H_2S in 15 and 20 w% MEA solution

where:

- A = the absorption factor
- a = mole fraction of H_2S in gas feed
- R = mole MEA/mole H_2S absorbed
- r = residual H_2S in lean MEA solution (mole H_2S per mole MEA)
- pp = partial pressure of H_2S in rich solution, psia
- P = system pressure (tower pressure), psia

Step 6. Solve for A. Then solve the equation given in Step 1 for N. Divide N by an efficiency factor (usually about 15 % for absorbers) to determine actual number of trays.

An example calculation is given in the Appendix of this chapter, along with other applicable charts and tables.

Calculating Absorber Tray Size and Design

This procedure is similar to those described in other sections of this handbook. Emphasis is made here, however, to the foaming tendencies of MEA and DEA. Most of these units contain facilities to inject antifoaming chemicals. Under normal operation, these chemicals subdue foaming to a large extent, particularly in the contactors. The addition of a filter in the rich amine line also helps combat severe foaming.

It is believed that foaming is enhanced by the absorption of large quantities of hydrocarbons into the amine stream. This can occur quite easily if the temperature or pressure change forces the hydrocarbon gas into a condition below its dew point. The presence of large quantities of impurities such as COS (carbonyl sulfide) or the tarry derivative of COS may also induce foaming. The addition of the filter and reclaimer usually solves this problem to a large extent.

Loading of amine towers nevertheless is critical due to the foaming nature. Consequently the towers are designed with more latitude than most other towers. In evaluating its performance also the acceptable level of flooding is lower by 20–30 % than that for normal towers.

The calculation to evaluate the tower flooding follows the same steps as those described in the chapter on "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook. In this case, however, the calculated value for V_L is multiplied by a system factor between 20 % and 30 %. If the unit is being used in service where a high concentration of impurities is present, a figure of 30 % should be used.

Calculating the Heat Transfer Area for the Lean/Rich Amine Exchanger

The amine in the contactor picks up the heat of reaction which occurs with the absorption of H_2S. On leaving the amine contactor or absorber, the rich amine is heat exchanged against hot lean amine leaving the bottom of the stripper. The performance of this exchanger is critical to the process as a whole. Usually the rich amine receives no other heat before it enters the stripper. As in light ends towers, the feed condition is vital to the proper operation of the tower. The purpose of this section is to provide a calculation procedure to evaluate the heat transfer coefficient of this exchanger. The following steps give the procedure:

Step 1. Using lab data for operational units or the design specification for those units to be designed, determine the quantity of H_2S absorbed in the contactor.

Step 2. From the data given in Table 1, calculate the total heat of reaction in Btu/h.

Step 3. Set the temperature of the lean gas leaving the absorber to be the same as the amine entering.

Table 2 The heat balance for example case

Stream	V or L	lb/h	°F	Btu/lb	MMBtu/h
In					
Rich product gas	V	34,722	100	350	12.153
Lean amine soln	L	194,747	105	98	19.085
Heat of reaction				650	4.696[a]
Total in					35.928
Out					
Lean product gas	V	34,722	105	355	12.326
Rich amine soln	L	194,747	By	Diff	23.602
Total out					35.928

[a] 7,225 lb of H_2S absorbed/h

Step 4. Carry out a heat balance over the contactor with the rich amine temperature being the unknown. Equate and solve for this.

Step 5. From plant data (or the Design Spec), apply the temperatures and flow in and out of the exchanger to calculate its heat duty in Btu/h.

Step 6. Calculate the LMTD (log mean temperature difference) and from Table 2 establish the overall heat transfer coefficient U in Btu/h sq. ft. °F.

Step 7. Using the energy equation

$$Q = U \ A\Delta T_M \tag{9}$$

where

Q = the duty in Btu/h
A = the area in sq. ft.
ΔT_{M} = the log mean temperature difference in °F
U = the overall heat transfer coefficient in Btu/h sq. ft. °F.

calculate the value for A in sq. ft.

The Stripper Design and Performance

This evaluation is based on reconciling the steam used for stripping the rich amine. The quantity of steam is a major operating cost in this type of plant and therefore deserves attention. An acceptable level of steam usage is about 0.8–1.1 lb steam/gal of circulating solution for MEA and 1.1–1.3 lb steam/gal in the case of DEA. Following is a procedure to calculate this steam rate.

Step 1. From plant data design specification, ascertain the feed rate of rich amine to the stripper and its composition in terms of H_2S, water, MEA (or DEA), and hydrocarbons.

Step 2. Calculate recycle rate of lean amine leaving the bottom of the tower. Obtain from the lab data or design specification its composition in terms of residual H_2S, water, MEA (or DEA), and hydrocarbon (if any).

Step 3. Develop the material balance over the tower.

Step 4. Using the data in Step 3, set the external tower top reflux ratio as 2:1, and calculate the heat balance over the tower top to find the condenser duty.

Step 5. Calculate the heat entering with the rich amine feed before the preheat exchangers (see previous section above).

Step 6. Using plant data for lean amine temperature in and out of the preheat exchangers, calculate its duty. Add the duty to the enthalpy from Step 5 to give feed enthalpy into the tower.

Step 7. Calculate the overall heat balance over the stripper to find the reboiler duty. Remember to add in the heat of dissociation which is equal to the heat of reaction in the contactor (see previous section above).

Step 8. Saturated 50 psig steam is usually used as the heating medium. Calculate the amount of steam from its enthalpy data (steam tables) and the reboiler duty.

Step 9. If the steam usage is excessive, check overhead stream and the lean amine concentration. It is possible that a high volume of water is being evaporated. If this is the case, reduce the reboiler duty to maintain the amine concentration and H_2S concentration.

Removing Degradation Impurities from MEA

Although MEA (monoethanolamine) is the most efficient absorbent in the amine family, it has one major shortcoming. It is readily degraded by certain sulfur compounds such as carbonyl sulfide (COS) and by carbon disulfides. Both these compounds are found in significant quantities in gases from cracking processes such as thermal crackers and catalytic crackers.

It is difficult if not impossible under normal refinery conditions to remove these sulfides from the gas. What can be done and is the normal practice is to remove the product of degradation and return the “clean” amine to the system. Two items of equipment are added to the process to achieve this. These are a filter and a reclaimer. The filter is a normal leaf-type filter contained in two filter casings. These are piped up in parallel with one on stream and the other shut down for cleaning and as spare.

Reclaimers are really kettle-type reboilers. They take as feed a portion of the lean amine leaving the stripper. This stream is vaporized and the vapor returned to the stripping tower. The residue or sludge is the product of degradation and is dumped to waste. Reclaimers can be designed to operate continuously or on a batch basis. Steam is used as the heating medium. As in the case of the stripper reboilers, the heating steam temperature to the reclaimer is also carefully controlled. Thus the steam medium is saturated 50 psig steam. It must be remembered that the duty to condense the vaporized amine from the reclaimer must be added to the stripper overhead condenser duty. It must also be included in any tower loading exercise that may follow. As noted previously, there are also proprietary methods for reclaiming that do not involve a reclaimer/reboiler arrangement. These are provided as a contract service and are beyond the scope of this handbook.

Appendix Process Design of an Amine Gas Treating Unit

The following is an extract from a design specification and defines the parameters of this example:

1. Unit required is a gas treating unit for the removal of H_2S from a hydrotreater recycle gas stream. The feed to the hydrotreater consists of gas oil from straight run source and streams from a thermal cracker and a catalytic cracker. The recycle gas will therefore contain some COS.
2. The feed gas shall have the following properties:
   - The mole weight of the gas is 10.5.
   - The H_2S content of feed gas is 4,048 grains/100 scf.
   - The gas rate is 30 MMscf/day
   - The pressure of the gas at the outlet of the contactor is 320 psig.
3. Product gas shall have a H_2S content no greater than 0.1 grain/100 scf.
4. The amine solvent to be used shall be monoethanolamine:
   - Amine ratio to H_2S shall be 3.0 mole amine to 1.0 mole H_2S.
   - The amine solution shall be 20 % by weight in water.
   - Residual H_2S in the lean amine solution shall be no greater than 0.09 mole per mole of MEA.
   - Protection against degradation of the amine shall be included.

The Contactor Design

Calculating the Amine Solution Circulation Rate

$$\begin{aligned}\text{Feed gas rate} &= 30\,\text{MMscf/day}\\ &= 3{,}306.9\,\text{mol/h}\\ &= 34{,}722\,\text{lb/h}\end{aligned}$$

$$\begin{aligned}H_2S \text{ in feed} &= \frac{4{,}048 \times 0.0022857}{16} = 0.578\,\text{lb/100}\,\text{scf}\\ &= 5{,}100\,\text{mol/day} = 1.928\,\text{MMscf/day}\\ &= 212.5\,\text{mol/h}\end{aligned}$$

$$\begin{aligned}H_2S\ \text{in product gas} &= 0.1\,\text{grain}/100\,\text{scf}\\ &= 0.126\,\text{mol}/\text{day}\\ &= 0.00521\,\text{mol}/\text{h}\end{aligned}$$

$$\begin{aligned}H_2S\ \text{absorbed in amine} &= 212.5 - 0.00521\\ &= 212.49\,\text{mol}/\text{h}\end{aligned}$$

The amine ratio is 3.0 mol amine per mole H_2S.

Moles amine circulating = 637.47 mol/h = 38,949 lb/h (mol wt. MEA = 61.1), or for 20 % wt solution = 194,747 lb/h, made up of 155,798 lb water and 38,949 amine.

lb/gal MEA = 8.45
lb/gal water = 8.328
MEA gals/h = 4,609
Water gals/h = 18,708

Amine solution circulation rate = 23,317 gals/h (volumes are additive in these solutions).

Calculating the Number of Trays and the Overall Dimensions of the Contactor

The number of theoretical stages required in the contactor will be calculated using the equation

$$N = \frac{(\text{Log}\,1/q(A-1))}{(\text{Log}\ A)} - 1 \tag{10}$$

where:

N = number of theoretical trays
q = mole H_2S in lean gas/mole H_2S in feed gas
A = the absorption factor $L/V \cdot K$

$$\begin{aligned}\text{“}q\text{” in this case} &= \frac{\text{moles } H_2S \text{ in lean gas}}{\text{moles } H_2S \text{ in feed gas}}\\ &= \frac{0.00521}{212.5}\\ &= 2.45 \times 10^{-5}\end{aligned}$$

$$\begin{aligned}
\text{Total moles of acid gas absorbed} &= 212.49\,\text{mol/h}\\
\text{Acid gas residual in the lean amine} &= 57.37\,\text{mol/h}\\
\text{Total acid gas in grains/h} &= \frac{269.87 \times 34 \times 16}{0.0023}\\
&= 63.83 \times 10^{6}\text{grains/h}\\
\text{Total MEA solution} &= 23{,}317\text{gal/h}
\end{aligned}$$

Then grains acid gas per gal of amine solution = 2,738 grains H_2S/gal MEA.

From Fig. 2a for 20 % MEA solution, the H_2S partial pressure is 0.33 psia.

Using the following equation, the absorption factor A is calculated:

$$A = \frac{a(1 + Rr)(1 - q)}{pp/P} \tag{11}$$

$$\text{“}a\text{”is the mole fraction of } H_2S \text{ in feed gas} = \frac{212.5}{3,306.9} = 0.0643$$

R = mole MEA per mole acid gas absorbed = 3.0
r = 0.09 mole H_2S per mole lean MEA

Then

$$\begin{aligned}
A &= \frac{0.0643 \times \{1 + (3.0 \times 0.09)\} \times \{1 - (2.45 \times 10^{-5})\}}{0.33 \div 335}\\
&= 82.1
\end{aligned}$$

Therefore

$$\begin{aligned}
N &= \frac{\log\{(1 \div 2.45 \times 10^{-5}) \times (82.1 - 1)\}}{\log 82.1} = \frac{\log(3.283 \times 10^{6})}{\log 82.1}\\
&= \frac{6.5}{1.91} = 3.4\,\text{theoretical trays}
\end{aligned}$$

Set tray efficiency at 15 %; then actual number of trays = 23 (including reboiler).

MEA has a tendency to foam; therefore set tray spacing at 30 in (1.5 ft).

Then trayed section will have a height of 22 × 1.5 ft = 33 ft.

Calculating the Contactor Diameter

Use foaming factor of 60 %.

Feed gas to the contactor is 30 MMscf/day.

Temperature of gas is 100 °F and its pressure is 335 psia (these are average conditions).

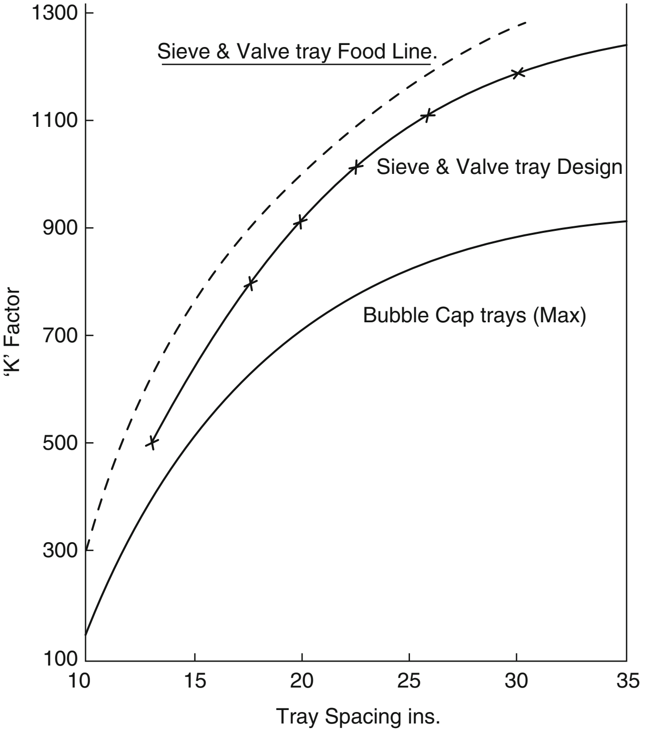


Fig. 3 The Brown and Souders flood constant

$$\text{Then actual cubic feet per second(ACFS)} = \frac{30 \times 10^6 \times 14.7 \times 580}{24 \times 3{,}600 \times 520 \times 335} = 16.41\,\text{cfs}$$

Feed gas in lb/h is 34,722 = 9.645 lb/s.

$$\rho_\text{v} = \frac{9.645}{16.41} = 0.588\text{lb/cuft}$$

lb/h of MEA solution is 194,747.

gals/h is 23,317.

And cubic ft/h is 3,117.

Then lb/cuft = 62.48 and at 120 °F (MEA inlet temperature) = 62.1 lb/cuft.

Loading at flood: $K_\text{f}\sqrt{\{\rho_\text{v} \times (\rho_1 - \rho_\text{v})\}}$

K_f is 1,280 from Fig. 3 and, inserting a 60 % foam factor, $K_\text{f} = 768$.

Loading = $768 \times \sqrt{36.17} = 4{,}619\text{lb/h sq. ft.}$

Let design load be 70 % of flood = 3,233 lb/h·sq. ft.

$$\text{Cross} - \text{sectional area of tray(and towerI/D)} = \frac{34{,}722}{3{,}233} = 10.74\,\text{sq. ft.}$$

Internal diameter of tower (calculated) = 3.7 ft

Call it 4 ft. = 12.6 sq. ft. cross-sectional area.

The actual tray design will be done by others (tray manufacturer) to protect the guarantee requirements.

Calculate the Amine Holdup in the Bottom of the Tower

The minimum liquid holdup will be 1 min from NLL to empty.

The volume of amine in 1 min $= \frac{3{,}117}{60} = 51.95\,\text{cuft}$

Then NLL will be $= \frac{51.95}{12.6} = 4.1\,\text{ft}$ say 4 ft

Then HLL will be set at 8 f. and LLL at 4 f. above tangent.

Add a further 4 f. from HLL to bottom tray.

The Overall Dimensions of the Contactor

The height of the contactor is as follows:

From bottom tangent line:

$$\begin{aligned}
&\text{To bottom tray} = 12\,\text{ft}\\
&\text{To top absorbing tray} = 45\,\text{ft}\\
&\text{To wash water drawoff} = 48\,\text{ft}(\text{bottom of chimney tray})\\
&\text{To top of wash section} = 54\,\text{ft}\\
&\text{To top tangent} = 58\,\text{ft}
\end{aligned}$$

Overall dimensions for the contactor are 4 f. ID × 58 f. Tan-Tan.

Calculating the Heat Balance over the Contactor

The rich gas flow will enter at 100 °F and 320 psig and will have an enthalpy of 350 Btu/lb. Its flow rate is 34,722 lb/h.

The heat of reaction is calculated at 650 Btu/lb of H_2S absorbed.

The lean amine solution enters at a temperature of 105 °F which will be set by heat transfer. The lean product gas will leave at about the same temperature.

The rich amine leaving the contactor is determined by difference

$$\begin{aligned}
\text{Temperature of rich amine out} &= \frac{23.602 \times 10^6}{(38{,}949 \times 0.663) + 155{,}798}\\
&= 129.95\,\text{say}\,130^\circ\text{F}
\end{aligned}$$

The Heat Exchanger Design

The hot lean amine stream to the contactor will be cooled from the stripper bottom temperature first by heat exchange against the rich amine leaving the contactor. It will then be trim cooled to the contactor inlet temperature by either water or air. The following is the calculation to determine the size of the lean/rich amine exchanger.

The lean amine from the stripper will be cooled to 175 °F in the heat exchange with the rich amine leaving the contactor. The duty of this exchanger is

$$\{38{,}949 \times 0.663 \times (249 - 175)\} + (155{,}798 \times 74) = 13.44\text{MMBtu/h}$$

The figure 240 °F is a value for the stripper bottom temperature estimated by a quick bubble point calculation of the lean amine at the stripper bottom conditions of temperature and pressure. This will be checked later.

Temperature of the rich amine feed to the stripper (T) is as follows:

$$\begin{aligned}(23.602 + 13.44) &= (38{,}949 \times 0.663 \times T) + 155{,}798T \\ T &= 204\,^{\circ}\text{F}\end{aligned}$$

The overall heat transfer coefficient for the amine exchanger can be taken as 100 Btu/h sq. ft. °F (this will be checked by the exchanger manufacturer). The exchanger size is

$$\begin{aligned}\text{LMTD}\,249 &\rightarrow 175 \\ 204 &\leftarrow 130 = 45\,^{\circ}\text{F}\end{aligned}$$

$$\begin{aligned}\text{Area} &= \frac{13{,}440{,}000}{45 \times 100} \\ &= 2{,}987\,\text{sq.ft.}\end{aligned}$$

The Stripper Design

Total moles of acid gas infeed = moles absorbed = 212.49 mol/h

$$\text{Residual acid gas} = 57.37\text{mol/h}$$

$$\text{Total acid gas} = 269.86\text{mol/h}$$

$$\text{Moles amine} = 637.47\ \text{mol/h}$$

$$\text{(This assumes no losses)}$$

$$\begin{aligned}&\text{Moles water} = 8{,}655\ \text{mol/h} \\ &\text{Moles hydrocarbon dissolved} = 1.8\ \text{mol/h as C5}\end{aligned}$$

The Material Balance

The material balance over the stripper is given in Table 3.

The following calculation establishes the composition of the overhead product and the composition of the liquid reflux stream, thus:

Let x be the moles per hour of water in the overhead product. The H_2S content is established by the total in the feed less the residual H_2S in the bottom product – the lean amine. It is assumed that all the hydrocarbons will leave with the overhead vapor product. The value of x is found by the dew point calculation of the overhead product at the reflux drum conditions of temperature and pressure in Table 4.

Table 3 Example of amine stripper material balance

Comp	MW	lb/gal	Feed			O/heads			Lean amine		
			Mol/h	lb/h	GPH	Mol/h	lb/h	GPH	Mol/h	lb/h	GPH
H_2S	34	6.55	270	9,180	1,401	212.5	7,225	1,103	57.5	1,955	298
H_2O	18	8.33	8,655	155,790	18,702	8.43	151	18	8,646.6	155,639	18,684
HC	72	5.25	1.8	130	25	1.8	130	25	Nil	Nil	Nil
MEA	61	8.45	637.5	38,888	4,602	Nil	Nil	Nil	637.5	38,888	4,602
Total			9,564.3	203,988	24,730	222.73	7,506	1,146	9,341.6	196,482	23,484

Table 4 Example of calculation of overhead product and reflux compositions

Comp	Mol/h	K at 100 °F	$x = y/k$
H_2S	212.5	14.75	14.40678
H_2O	x	0.041	$x/0.041$
C5's	1.8	0.67	2.686567
	214.3		17.09335
	$214.3 + x$		$17.09 + x/0.41$
	197.21		$x/0.041 + x$
		$x = 8.43$	
		Mol/h	lb/h
H_2S	0.065	=29.5	1,003
H_2O	0.923	=419.6	7,553
HC	0.012	=5.5	396
		=454.6	8,952

Table 5 Example of calculation of overhead vapor composition

	Product			
	Moles/h	Reflux	Total	Mole fraction
H_2S	212.5	29.5	242	0.357
H_2O	8.43	419.6	428.03	0.632
HC	1.8	5.5	7.3	0.011
	222.73	454.6	677.33	1.000

The reflux drum conditions were set at 23 psia pressure and 100 °F, and the dew point calculation at these conditions gave a reflux stream composition as shown in Table 4.

Mole reflux is 2× product vapor.

Tower Top Conditions and Condenser Duty

The tower top pressure shall be the reflux drum pressure plus, say, 3 psi pressure drop over the condenser and about 0.7 psi for piping and other losses. Then the tower top pressure will be 26.7 psia. The total overhead vapor will be product plus reflux as shown in Table 5.

The dew point calculation gave the tower top temperature of 218 °F.

The condenser duty is calculated from the following heat balance over the tower top (refer to envelope 1 in Fig. 4). The heat balance is shown in Table 6.

Condenser duty to strip vapors from the feed is 8.125 MMBtu/h. To this will be added the vapor from the reclaimer that has to be condensed. This will be done later.

To Calculate the Internal Reflux from the Top Tray

Knowing the condenser duty, the internal reflux × lb/h can be calculated from the heat balance over the tower top as shown in envelope 2 of Fig. 4. See Table 7.

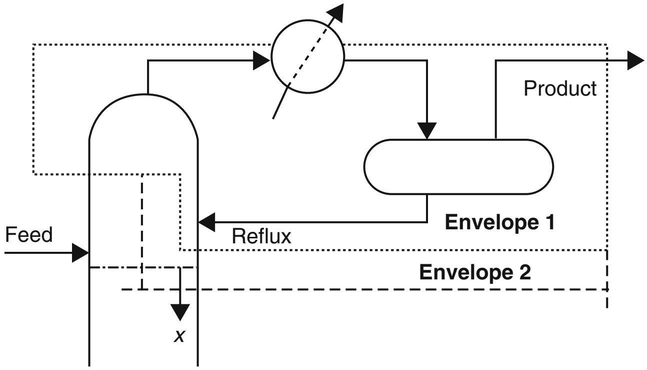


Fig. 4 Heat balance envelopes for tower overhead

Table 6 Overhead heat balance example

Stream	V or L	°F	lb/h	Btu/lb	MMBtu/h
In					
Total O/head	V	218	16,458	615	10.122
Total in					10.122
Out					
Prod	V	100	7,506	155.7	1.169
Reflux	L	100	8,952	92.5	0.828
Condenser	By	Diff			8.125
Total out			16,458		10.122

Solving for x:

$$9.294 + 222x = 0.923 + 1{,}162x$$
$$x = 8{,}905\,\mathrm{lb/h}$$

$$\text{Mole weight of reflux} = 18.5(\text{from the dew point calculation})$$
$$\text{Moles/h reflux} = 481$$

The moles of vapor from the reclaimer will be added to this figure when calculating the vapor loading over the top tray. Two trays above the feed tray will be provided as wash trays.

The Stripper Bottom Conditions and Reboiler Duty

The pressure at the bottom of the tower is fixed at 34 psia. This allows a pressure drop of about 0.35 psi per tray which is estimated as a total of 20 trays. The tower

Table 7 Example of internal reflux from top tray calculation

Stream	V or L	°F	lb/h	Btu/lb	MMBtu/h
In					
Int. reflux	V	222	x	1,162	1,162x
Product	V	222	7,506	123	0.923
Total in			7,506 + x		0.923 + 1,162x
Out					
Prod	V	100	7,506	155.7	1.169
Reflux	L	222	x	222	222x
Condenser					8.125
Total out			7,506 + x		9.294 + 222x

Table 8 Example of calculation of stripper bottom composition

Temperature			249 °F	
Comp	Moles/h	Mole frac	K@ 34 psia	$y = xk$
H_2S	57.5	0.0062	45.4	0.2815
Water	8646.6	0.9256	0.79	0.7312
MEA	637.5	0.0682	0.09	0.0057
Total	9,341.6	1.0000		1.0184

Table 9 Calculation of reboiler duty

Stream	V or L	°F	lb/h	Btu/lb	MMBtu/h
In					
Feed	V + L	204	203,988	181.7	37.06
Reboiler			By Diff		22.049
Total in			203,988		59.109
Out					
O/head prod	V	100	7,506	155.7	1.169
Bottoms	L	249	196,482	230	45.179
Ht. of reaction					4.696
Condenser					8.125
Total out			203,988		59.109

bottom temperature is calculated by a bubble point calculation of the bottom product at this pressure of 34 psia (see Table 8).

Enthalpy of bottom product = 230 Btu/lb as liquid.

Calculating the Reboiler Duty

This is determined from the overall tower heat balance as shown in Table 9.

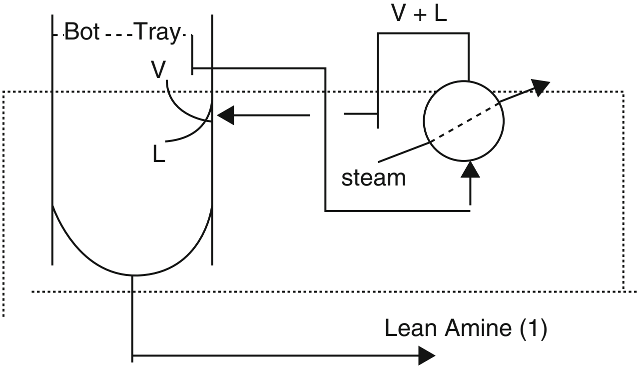


Fig. 5 Tower bottom heat balance loop

Table 10 Bottom tray condition calculation

Stream	V or L	°F	lb/h	Btu/lb	MMBtu/h
In					
Bot prod	L	240	196,482	224	44.012
Stripout	L	240	*x*	224	224*x*
Reboiler					22.049
Total in			196,482 + *x*		66.061 + 224*x*
Out					
Stripout	V	249	*x*	1,035	1,035*x*
Bottoms	L	249	196,482	230	45.179
Total out			196,482 + *x*		45.179 + 1,035*x*

Vapor/Liquid on Bottom Tray

The bottom tray will have a temperature of 240 °F (see Fig. 5 and Table 10). In the following heat balance, let the lb/h of the stripout vapors to the tray be *x*:

$$\begin{aligned} x = 25{,}748\ \mathrm{lb/h}\quad & \text{Mole wt} && = 23.08\\ & \text{Mol/h} && = 1{,}115.6\\ & \text{V/Lat bottom tray} && = 1{,}115.6/10{,}457\\ & && = 0.107 \end{aligned}$$

To Calculate the Number of Theoretical Trays in the Stripper

The Kremser equation which is shown graphically in Fig. 6 will be used for this calculation.

The V/L factor calculated above will be used for this equation. A tower average *K* value for each component in the feed will also be used. The calculation is shown in Table 11.

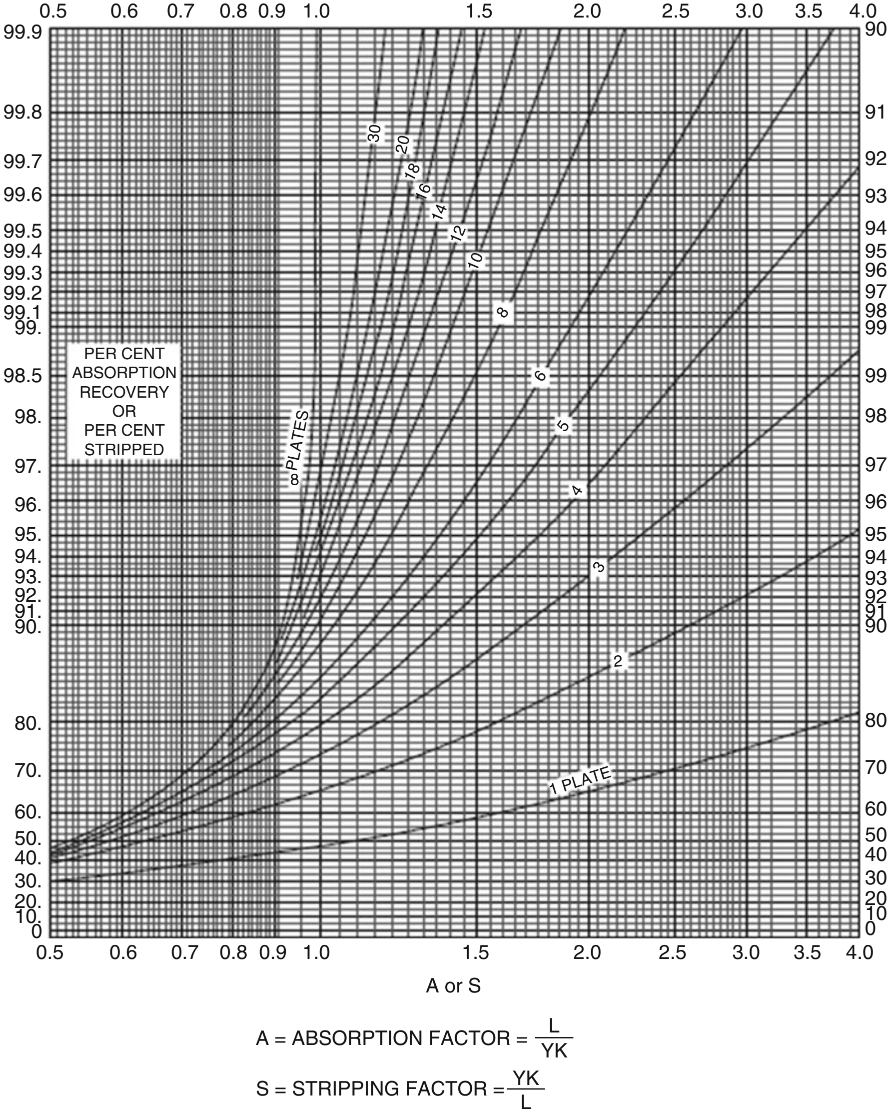


Fig. 6 The Kremser equation and correlation

Three theoretical trays will achieve the stripping required. Stripping trays have poor efficiency between 12 % and 18 %. Use 15 % in this case; then actual trays will be 3/0.15 = 20 actual trays.

The anomaly for the amount of HC stripped in the above calculation stems from the assumption that the HC is pentane. It is probably a heavier hydrocarbon.

Table 11 Estimated number of theoretical trays

Component	Mol/h	Ave K	VK/L	Stripout %	Mol/h
H_2S	270	44	4.7	100	270
H_2O	8,655	0.72	0.08	<0.5	8.0
HC	1.8	3.5	0.37	50	0.9
MEA	637.6	0.1	0.01	0	0
Total	8,564.3				278.9
Notes			Use 3 trays	From Fig. 6	

Table 12 Reclaimer material balance and heat duty

Stream	V or L	°F	lb/h	Btu/lb	MMBtu/h
In					
Feed	L	249	3,930	230	0.935
Reclaimer			By diff		2.130
Total in			3,930		3.065
Out					
Rec vapor	V	260	2,851	1,070	3.051
Sludge	L	260	79	182	0.014
Total out			3,930		3.065

Calculating the Reclaimer Duty and Size

A slip stream of 2 wt% of lean amine solution will be routed through the reclaimer. It will be vaporized to leave a sludge stream of 2 % of the reclaimer feed. The operation will be continuous, and the vapor will be routed back to the tower entering below the bottom tray. The material balance over the reclaimer is shown in Table 12.

A typical heat flux over a kettle reboiler is 26,500 Btu/h sq. ft, therefore the area for heat transfer = 80 sq. ft.

The vapor generated by the reclaimer will be added to the vapor load at the bottom tray. Likewise, this amount as liquid will be added to the tray liquid load. The condenser duty will also be increased to accommodate the reclaimer duty. Thus

$$\begin{aligned}\text{Total condenser duty} &= 8.125 + 2.130 = 10.255\,\text{MMBtu/h}\\ \text{Vapor load to bottom tray} &= \text{stripout} + \text{reclaimed vapor}\\ &= 25{,}748\ \text{lb/h} + 2{,}851/\text{h}\\ &= 28{,}599\ \text{lb/h}\\ \text{Mol/h} &= 1{,}115.6 + 135.8\\ &= 1{,}251.4\end{aligned}$$

Stripper Tower Dimensions

As in the case of the contactor, the cross-sectional area of the stripper will be calculated using the Brown and Souders method as follows:

Cross-sectional area of the tower will be based on the loadings over the bottom tray; thus

$$\begin{aligned}\text{Total vapor to tray} &= 1{,}251.4\ \text{mol/h}\\ \text{In actual cubic feet/s} &= \frac{1{,}251.4 \times 378 \times 700 \times 14.7}{520 \times 34 \times 3{,}600}\\ &= 76.47\,\text{ACFS}\\ \rho_\text{v} = 7.85/76.47 &= 0.104\text{lb/cuft}\end{aligned}$$

$$\begin{aligned}\text{Total liquid from the bottom tray} &= \text{stripout} + \text{product} + \text{reclaimer liq}\\ &= 25{,}748 + 196{,}482 + 2{,}851\\ &= 225{,}081\text{lb/h}\end{aligned}$$

$$\begin{aligned}\text{lb/gal of liquid at } 240\,^\circ\text{F} &= 7.87\\ \text{Gals per hour} &= 28{,}600 \text{ and cubic ft/h is } 3{,}823\\ \rho_1 &= 58.87\text{lb/cuft.}\end{aligned}$$

Loading at flood $= K_\text{f}\sqrt{\{\rho_\text{v} \times (\rho_1 - \rho_\text{v})\}}$.

From Fig. 5 K_f = 1,280 and at 60 % = 768

$$\begin{aligned}\text{Then loading} &= 768 \times 2.47\\ &= 1{,}899\text{lb/h sq. ft.}\end{aligned}$$

Let loading be 80 % flood = 1,519:

$$\begin{aligned}\text{Cross}-\text{sectional area} &= \frac{28{,}599}{1{,}519}\\ &= 18.8\,\text{sq.ft.}\\ \text{and diameter} &= 4.9\,\text{ft call it } 5\,\text{ft or } 19.6\,\text{sq. ft.}\end{aligned}$$

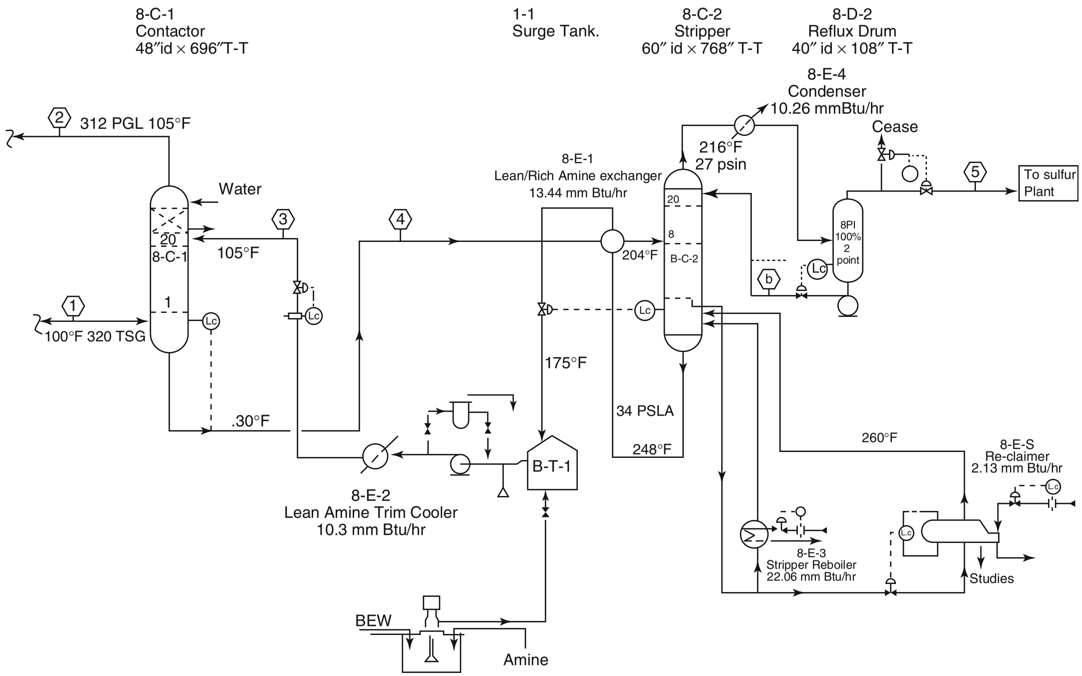
Tower will contain 20 valve-type trays made up of 18 stripping trays and 2 rectifying trays. As in the case of the contactor trays, they will be spaced at 30 in. Trayed section will therefore be 19 × 30 in. = 570 in or 47 f. 6 in. from bottom to top tray.

The bottom of the tower (from bottom tray to bottom tangent) will be sized to cater for a 2 min holdup of liquid to the HLL. Thus

$$\begin{aligned}\text{Total liquid from bottom reboiler} &= 196{,}482 + 2{,}851\\ &= 199{,}333\,\text{lb/h}\end{aligned}$$

$$\begin{aligned}\text{lb/gal at } 60\,^\circ\text{F} = 8.35, \text{and at } 249\,^\circ\text{F} &= 7.89\,\text{lb/gal}\\ \text{Then gals/h of total bottoms} &= 199{,}333/7.891\\ &= 25{,}264\,\text{gal/h}\\ &= 421\,\text{GPM}\end{aligned}$$

or 56.3 cubic ft/min



Stream	1	2	3	4	5	6
Comp Molas/nr	Sour Recycle Gas	Sweet Recycle Gas	Lean Amine	Rich Amine	Acid Gas	Stripper Reflux
H2S	212.5	(neg)	57.5	270	212.5	29.5
HOS	Nil	Nil	8646.6	8655	8.4	419.6
HC	3094.4	3092.6	Nil	1.8	1.8	5.5
MEA	Nil	Nil	637.5	637.5	Nil	Nil
Total	3306.9	3092.6	9341.6	9364.3	222.7	454.6
Lbs/nr	34722	27462	196482	203988	7506	8952
GPM (mmSSFD)	(30)	(28)	391	412	(0.2)	15

Fig. 7 The preliminary process flow sheet for a MEA treating plant

Volume resident over 3 min = 168.9, say, 169 cubic ft.

Height of HLL = 8.6; allow 4 f. from HLL to bottom tray.

Summary of stripper height (all dimensions from bottom tangent)

To bottom tray	12 f. 6 in.
Trayed section	47 f. 6 in.
Top tray to top tangent	4 ft
Total height	64 ft

There will be a 15 f. skirt to give the total height above grade of 79 ft.

This completes the process design of the major items of equipment. These and the smaller items of equipment are shown in the following preliminary process flow sheet Fig. 7.

Upgrading the Bottom of the Barrel

David S. J. Jones

Contents

Abstract

Crude oils usually contain substantial yields of heavy hydrocarbons boiling above 600–800 °F. These are referred to as atmospheric and vacuum residual oils, residua, or resids. Resids were primarily used for many years as heavy fuel oils (bunker oil) or various tar or asphalt products. Modern refinery economics

---

David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_8

and environmental regulations make the processing of residua to light oils and feedstocks for other units desirable and, indeed, necessary in many areas. Several process approaches are available for resid conversion. In this chapter, we explore several of the resid conversion processes, including thermal cracking, visbreaking, delayed coking, Flexicoking™, deep oil FCC, and residuum hydrocracking. A detailed design example of thermal cracker key equipment is provided.

Keywords
Refinery • Crude oil • Residuum • Resid • Coking • Visbreaking • Thermal cracking • Fuel oil

Introduction

The highest yield of straight-run product as a percentage on crude is usually the residue from the atmospheric distillation of the crude feed. In most Middle East crudes, this ranges from around 40 vol.% for the lighter crude oils to 50 % and higher in case of the heavier oils. It can be, and often is, the major factor in crude oil slate selection and in the operation of the refinery itself. In most cases, a large portion of the residue can be blended off to meet the fuel oil product in the refinery's production plan. In other cases, perhaps equally as common, a major portion of the atmospheric residue is further distilled, under vacuum, to distillates which can be processed to meet gasoline and middle distillate product slates or lube oil blending stocks. The residue from this vacuum distillation, now considerably smaller in volume, is routed to fuel oil or to a bitumen product pool.

There are cases however where the quantities of both atmospheric and vacuum residues are high enough to limit the refinery's throughput or limit its production of the more valuable products and thus limit the refinery's profitability. In such cases, the conversion of these residues becomes attractive and, in some cases, absolutely imperative. This latter case refers to those refineries that have no or a very small fuel oil market. The upgrading of these residues is accomplished by the indirect processing of the atmospheric residue, processing the distillates by catalytic cracking or hydrocracking and then thermally cracking the vacuum residue. Most of the processes involved with the conversion of the vacuum distillates are described in other chapters of this handbook dealing with hydrocracking and fluid catalytic cracking.

Direct upgrading of the atmospheric residue by the thermal cracking processes has long been the "workhorse" of the industry in processing the "bottom of the barrel." However, some catalytic processes have been developed which demonstrate a more efficient and effective method than the thermal cracking routes. This chapter deals with the direct processing of crude oil residuum and is divided into the following parts:

- Thermal cracking
- "Deep oil" fluid catalytic cracking
- Residuum hydrocracking and desulfurization

The Thermal Cracking Processes

Thermal cracking processes refer to those that convert the residuum feed (whether atmospheric or vacuum residues) into higher-grade products such as naphtha and middle distillates, by heat at high temperature alone. That is, no catalyst or chemicals are used in the conversion. The processes themselves are:

- Visbreaking
- Thermal cracking
- Coking

Certain confusion exists in the definition of visbreaking and thermal cracking. Differentiation is based on the type of feedstock, severity of cracking, or the final result. Strictly speaking, the term visbreaking should refer only to the viscosity reduction of heavy stock as the process' main objective.

Applications of the Thermal Cracking Processes

In a simple refinery, without vacuum distillation facilities, the residue from the crude oil atmospheric distillation, typically boiling above 650 °F or 700 °F, constitutes the bulk of the heavy fuel oil produced. In cases where incremental production of light and middle distillates at the expense of fuel oil is desired, one-stage thermal cracking of the residue is an easy and cost-effective solution. The residue is cracked in a specially designed heater; the effluent from the heater is quenched and routed to a fractionator, sometimes with a pre-flash; and the products of cracking, such as light gases, naphtha, gas oil, and residue, are separated in the conventional manner. Some 20 % of the residue feed can be converted into lighter products, mostly gas oil, by this process. Figure 1 shows a typical one-stage thermal cracker.

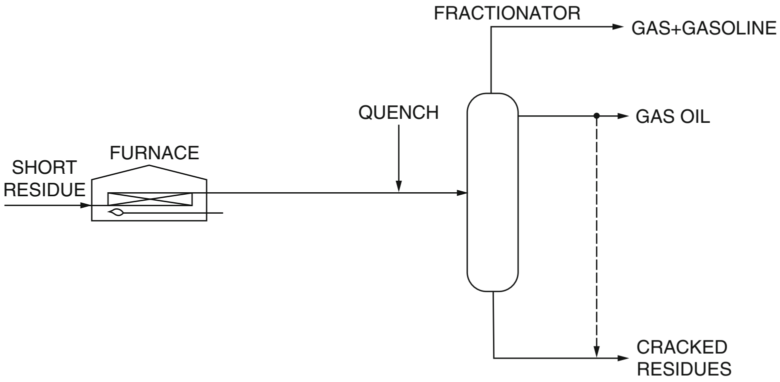


Fig. 1 One-stage thermal cracker

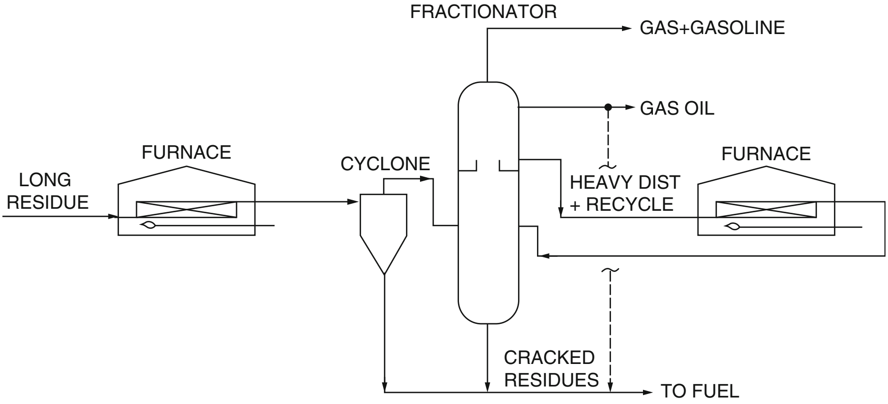


Fig. 2 Two-stage thermal cracker

For increased gas oil production, a somewhat more complicated scheme can be applied. The residue feed in this case is first cracked in the heater and the effluent flashed, and the hot vapors from the flash drum are routed to a fractionating tower where a heavy gas oil is recovered as the bottom product. This is, in turn, cracked in a second heater and under more severe conditions to yield additional quantities of light distillate products and gas oil. Typically, the first (residue) heater is operated at 15–20 psig and a coil outlet temperature of 900 °F. The second (gas oil) heater operates at around 250–300 psig and a coil outlet temperature of 930 °F. This process is a two-stage thermal cracker and is shown in Fig. 2.

The Visbreaker Process

The visbreaker process configuration is very similar to the one-stage thermal cracker as shown in Fig. 1. More often than not, though, an additional piece of equipment is added immediately after the heater. This is a simple soaking drum which prolongs the time the heater effluent remains at the cracking temperature without being subjected to further heat input and higher temperatures. The objective here is to maintain good fuel oil stability while still converting sufficient amounts of the feed to gas oil and thus lowering the residue viscosity to fuel oil specification. By providing a soaking drum, suitable conversion is obtained by residence time at moderate temperature and pressure conditions without impairing the resulting fuel oil stability. Visbreaker heater outlet temperature can be as low as 830 °F to meet viscosity specification. This process configuration is shown in Fig. 3.

The Coking Processes

Coking is the most severe form of thermal cracking, in which all the residue feed is converted into light ends, naphtha, middle distillate, and a solid material,

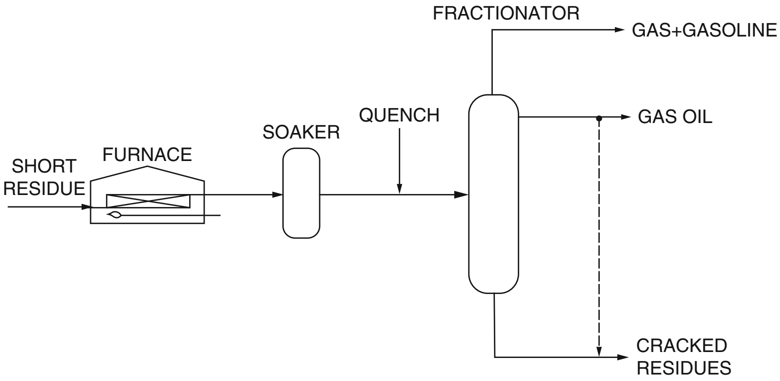


Fig. 3 A typical visbreaker

coke. No residual fuel oil is left. This process is particularly useful in handling very heavy crudes such as Bachaquero or the Canadian "heavy oil" crudes. A suitable market for the coke must be found, and coke quality requirements may impose further processing such as calcining with, of course, a resulting additional cost.

Two major types of coking processes are in operation today: these are the delayed coking process and the fluid coking process. The intricacies, delicate operation, and cost of the conventional fluid process make it an unlikely contender when simple and cheap ways to convert residues into more valuable products are desired. A fairly recent development of the fluid coking process, however, allows for the conversion of the coke into low-Btu gas. Only the delayed coking process and a proprietary process for fluid coking will be discussed here.

Delayed Coking Process

The delayed coking process is illustrated in Fig. 4.

The fuel oil or heavy oil feed is routed to a cracking furnace similar to other thermal cracking processes. The effluent from the furnace is sent to one of a set of several coking drums without quenching. The effluent is normally at a coil outlet temperature of around 920 °F and at a pressure of 30–50 psig and the coking drum is filled in about 12–24 h. The vapors leaving the top of the drum while filling are routed to the fractionator, where they are fractionated to the distillate products. The very long residence period of the effluent in the coking drums results in the complete destruction of the heavy fractions, and a solid residue rich in carbon is left in the drum as coke.

When the drum is full of coke, it is cooled and the top and bottom of the drum are opened. Special high-pressure water jets are used to cut and remove the coke through the drum's bottom opening.

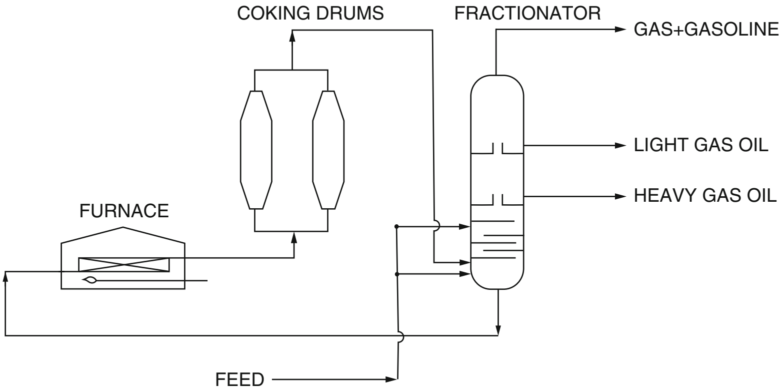


Fig. 4 A delayed coker

Table 1 Comparison of yields from thermal cracking processes, wt% on feed

	Thermal cracker	Visbreaker	Delayed coker
Feedstock	Atmospheric residue	Vacuum residue	Atmospheric residue
Butane and lighter	4.0	2.5	7.5
C5–330 °F naphtha	7.0	4.5	15.5
330–660 °F gas oil	26.0	13.0	59.0
Cracked residue	63.0	80.0	18.0 as coke

Table 1 gives a rough comparison of yields from the various thermal cracking processes. The two-stage thermal cracker as shown in Fig. 2 is represented in Table 1.

Flexicoking™ (Fluid Coking)

Flexicoking™ is a thermal conversion process licensed by Exxon Research and Engineering Company. The process itself is an extension of the traditional fluid coking process. The extension allows for the gasification of the major portion of the coke make to produce a low-Btu gas. The gasification step follows closely the concepts used in coal gasification processes.

Figure 5 is a simplified flow diagram of the Flexicoking™ process.

Heavy residuum feed is introduced into the reactor vessel where it is thermally cracked. The heat for cracking is supplied by a fluidized bed of hot coke transferred to the reactor from the heater vessel. The vapor products of the reaction leave the reactor zone to enter the scrubber section. Fine coke and some of the heavy oil particles are removed from the cracked products in the scrubber zone and returned to mix with the fresh feed entering the reactor. The reactor products subsequently

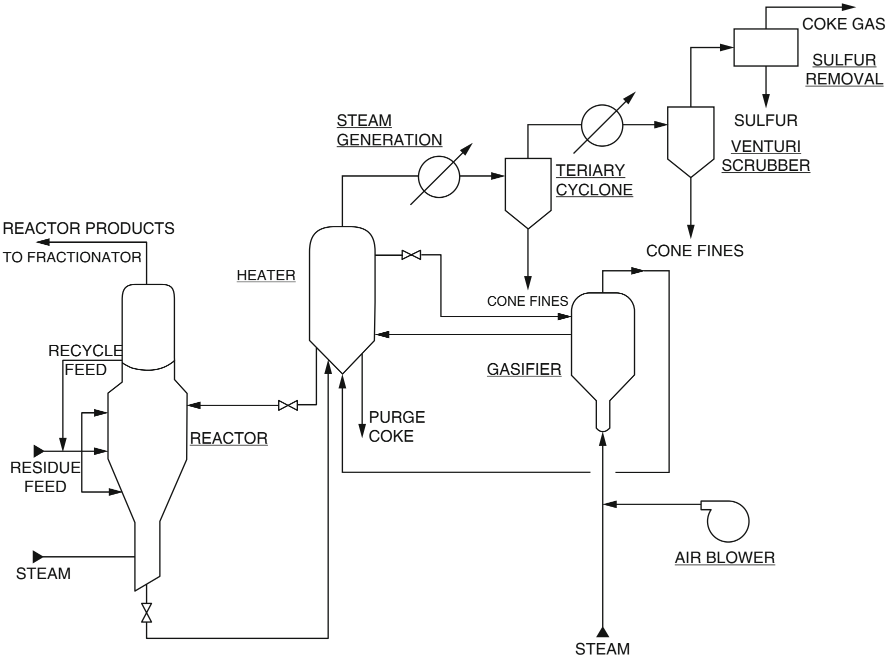


Fig. 5 The Flexicoking^{TM} process

leave the scrubber and are routed to a conventional fractionating facility. Steam is introduced to the bottom of the reactor to maintain a fluid bed of coke and to strip the excess coke leaving the reactor free from entrained oil.

The coke leaving the reactor enters the heater vessel, where sufficient coke is converted into CO/CO_2 in the presence of air. This conversion of the coke provides the heat for cracking which is subsequently transmitted to the reactor by a hot coke stream. The net coke make leaves the heater and enters the gasifier vessel. Air and steam are introduced into the gasifier to react with the coke producing a low-Btu gas consisting predominately of hydrogen, CO, CO_2, and nitrogen. This gas together with some excess air is transferred to the heater and leaves this vessel to be suitably cleaned and cooled.

Flexicoking^{TM} is an extinctive process. By continuous recycle of heavy oil stream, all the feed is converted into distillate fractions, refinery gas, and low-Btu gas. There is a very small coke purge stream which amounts to about 0.4–0.8 wt% of fresh feed. When suitably hydrotreated, the fractionated streams from the Flexicoker^{TM} provide good-quality products. Hydrotreated coker naphtha provides an excellent high-naphthene feed to the catalytic reformer. Typical yields from a Flexicoker^{TM} based on Arabian residue are shown in Table 2.

This process is quite flexible as to the quality of the feedstock: most of the metals are removed with the coke purge. Conradson carbon content of the feed does not

Table 2 Typical operating conditions and yields from flexi-coking

Feed	
Cut range, °F TBP	+1,050
°API	3.0
Sulfur, wt%	6.0
Nitrogen, wt-ppm	4,800
Conradson carbon, wt%	27.7
Metals, wt-ppm	269
Yields based on fresh feed	
H_2S, wt%	1.45
C_4s and lighter, wt%	10.29
C_5 to 370 °F, LV%	15.0
370–650 °F, LV%	16.7
650–975 °F, LV%	28.4
Purge coke, wt%	0.69
Coker gas, Scf/Bbl	10.79 (LHV =127 Btu/Scf)

affect the yield as may be expected. Where an economic use can be found for the low-Btu gas, the process offers an attractive route for upgrading low-quality fuel oil.

The Principles and Correlations Associated with Thermal Cracking Processes

The Soaking Volume Concept

The design of a thermal cracker is keyed to the configuration and temperature profile across the heater and soaking drum or soaking coil. The degree of cracking is dependent on this temperature profile and the residence time of the oil under these conditions.

The thermal cracking reaction is accepted as being of the first order thus it complies with the equation:

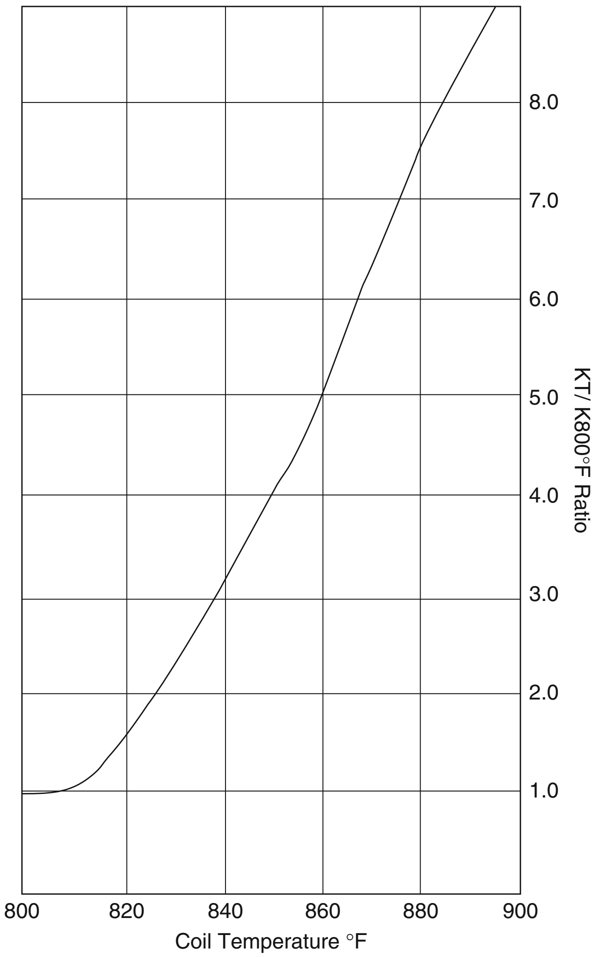
$$\text{In}\,(\text{conv}) = (\text{A})e^{-E/RT\times t} \tag{1}$$

where

$$\begin{aligned} A, E, R &= \text{constants} \\ t &= \text{reaction time} \\ T &= \text{reaction temperature} \end{aligned}$$

The thermal cracking reaction occurs in the heater along a curve of increasing temperature. In this concept of design, the cracking progression is expressed by a soaking volume factor (SVF) which is defined by the following equation:

Fig. 6 Temperature versus the $K_T/K_{800°F}$ ratio



$$F = 1/D\int_0^V \frac{P_s}{P_o}\cdot\frac{K_t}{K_0}dv \tag{2}$$

where

V = coil volume
D = feed rate
K_t = reaction rate constant at any given temperature
K_o, P_o = standard reference value for K_t and P_t
P_t = pressure at a given point in coil

The standard reference temperature for thermal cracking is taken as 800 °F. A curve giving value of K_t/K_o at a typical thermal cracking heater is given in Fig. 6.

The curve was produced from experimental results using a normal accepted pressure drop profile across the heater. For simplicity, the curve is related to temperature versus the factor $K_t/K_{800\ ^\circ\mathrm{F}}$.

The Soaking Volume Factor

The soaking volume factor is related to product yields and the degree of conversion. The definitions of these items are discussed in the following sections.

The Degree of Conversion

The relationship of the soaking volume factor to the degree of conversion is given in Fig. 7. These curves were the result of experimental data from the laboratory cracking of many feedstocks. The family of curves given in Fig. 7 demonstrates the comparative ease of cracking the large molecular structure of short residue to that of increasing wax distillate content. Conversion is measured by the result of gas and gasoline (to an end point of 257 °F) produced.

Product Yields

A family of curves given in Figs. 8 and 9 shows the relationship of the soaking volume factor to the yield of products of thermal cracking. Figure 8 shows the yields when cracking wax distillate 662–1,022 °F portion of the feed. Figure 9 shows the yields when cracking the bitumen portion of the feed. Both series of curves relate to the soaking volume factor.

The Zone of Critical Decomposition

Experimental data show that cracking and stability of the cracked product varies with the characteristics of the crude source material and boiling range. Figure 10 demonstrates this criterion as a relationship with the Watson characterization factor "*K*" of the feedstock.

The shaded area of the figure is the range in which the major portion of cracking occurs. Above this area, the cracked residue becomes unstable and precipitates sediment when stored. It is undesirable to operate above this zone in most cases where a cracked residue is required.

Discussion of the Concept

This is not a new concept for it has certainly been accepted as a basis for design since the late 1950s. To date, there are at least six visbreakers and/or thermal crackers to the author's knowledge that were designed using these parameters and are still in commercial use. In evaluating this concept, it is

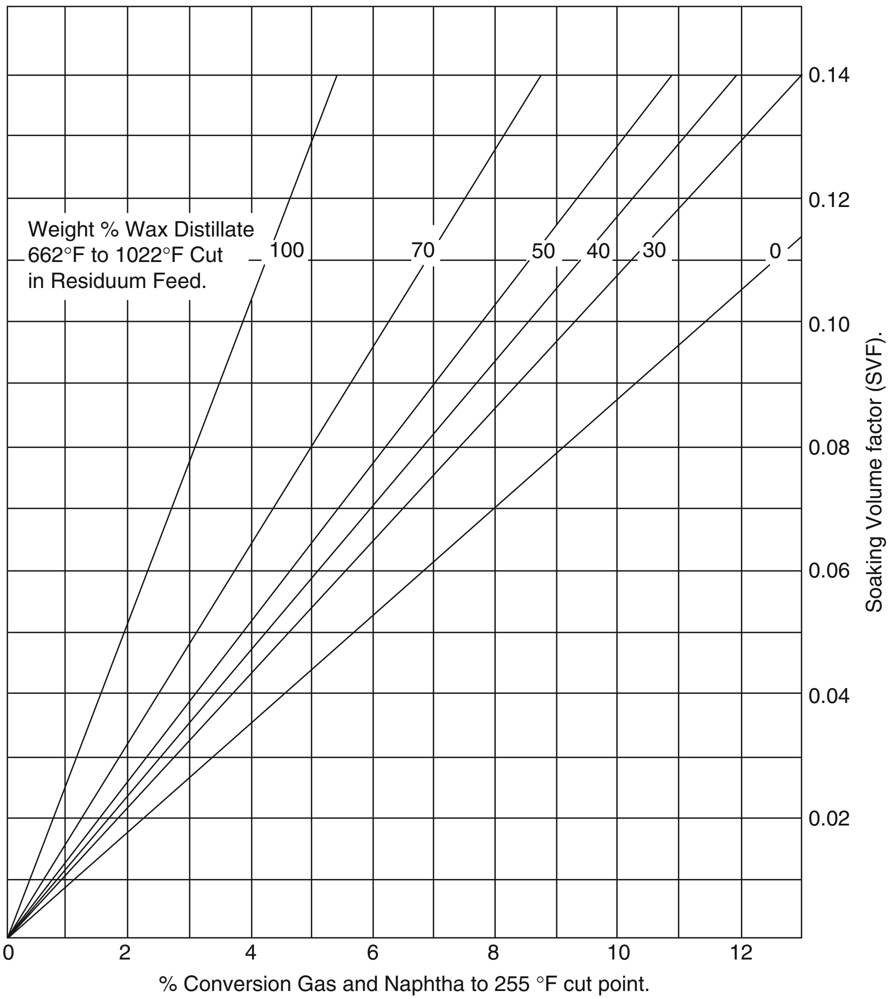


Fig. 7 Soaking volume factor (SVF) versus wt% conversion

interesting to note the following test run data compared with that calculated using SVF concept (Table 3).

It can be seen that the data calculated compare well with those actually observed under test conditions. One interesting point in the test run data is the high coil outlet temperature that was used. As this is slightly above the critical decomposition zone for this type of crude, it would lend one to suspect that the cracked residue would be unstable. There was no recorded evidence of this, however.

An example calculation using the SVF concept is given in the Appendix of this chapter.

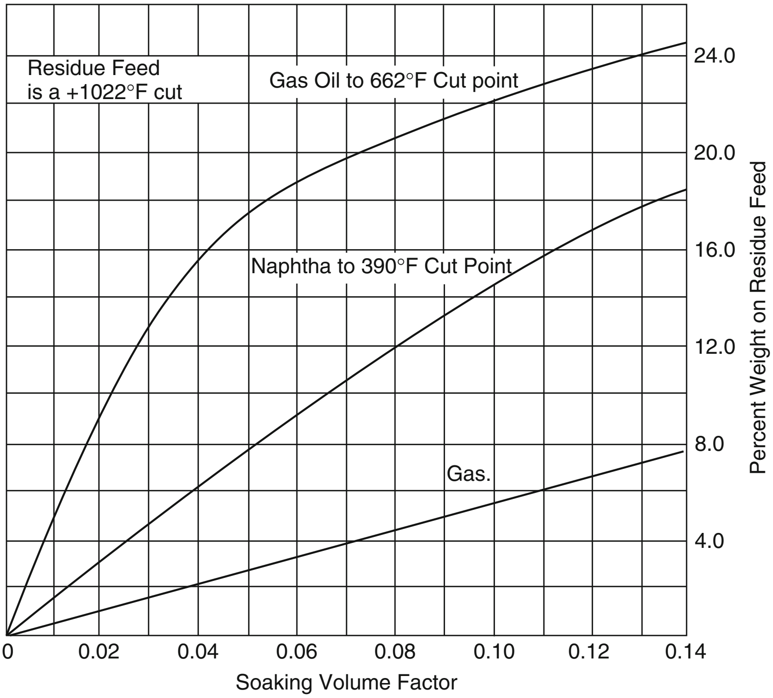


Fig. 8 Conversion yields from wax distillate versus SVF

"Deep Oil" Fluid Catalytic Cracking

Up to the late 1980s, feedstocks to FCCU were limited by characteristics such as high Conradson carbon and metals. This excluded the processing of the "bottom of the barrel" residues. Indeed, even the processing of vacuum gas oil feeds was limited to:

$$\begin{array}{l}\text{Conradson carbon} < 10\ \text{wt\%}\\ \text{Hydrogen content} > 11.2\ \text{wt\%}\\ \text{Metals Ni} + \text{V} < 50\ \text{ppmn}\end{array}$$

During the late 1980s, significant research and development breakthroughs produced a catalytic process that can handle residuum feed.

Feedstocks heavier than vacuum gas oil, when used in a conventional fluid catalytic cracking unit (FCCU), tend to increase the production of coke and this in turn deactivates the catalyst. This is mainly the result of:

- A high portion of the feed that does not vaporize. The unvaporized portion quickly cokes on the catalyst, choking its active area.

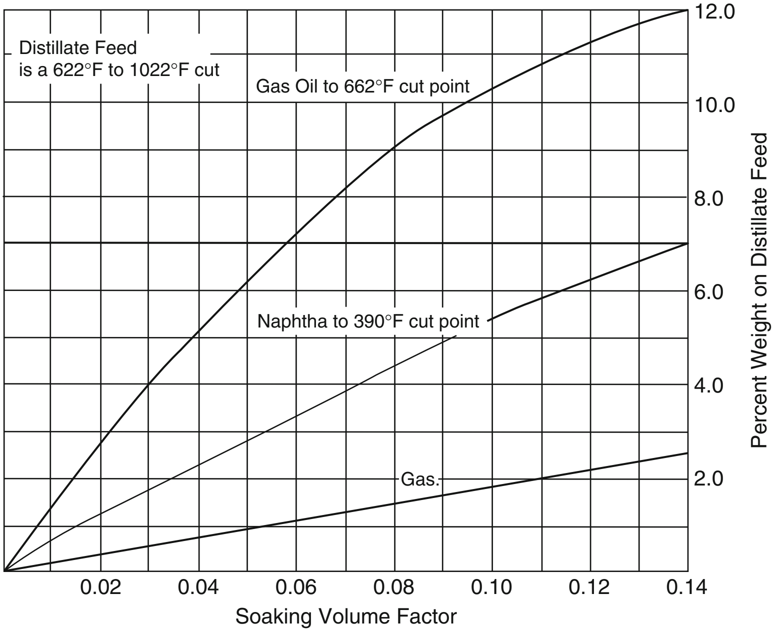


Fig. 9 Conversion yields from residuum versus SVF

- The presence of high concentrations of polar molecules such as polycyclic aromatics and nitrogen compounds. These are absorbed into the catalyst's active area causing instant (but temporary) deactivation.
- Heavy metals that poison the catalyst and affect the selectivity of the cracking process.
- High concentrations of polynaphthenes that dealkylate slowly.

In FCCUs that process conventional feedstocks, cracking temperature is controlled by the circulation of hot regenerated catalyst. With the heavier feedstocks, with an increase in Conradson carbon, there will be a larger coke formation. This in turn produces a high regenerated catalyst temperature and heat load. To maintain heat balance, therefore, catalyst circulation can be reduced, this leads to poor or unsatisfactory performance. Catalyst cooling or feed cooling is used to overcome this high catalyst heat load and to maintain proper circulation.

The extended boiling range of the feed, as in the case of residues, tends to cause an uneven cracking severity. The lighter molecules in the feed are instantly vaporized on contact with the hot catalyst, and cracking occurs. In the case of the heavier molecules, vaporization is not achieved so easily. This contributes to a higher coke deposition with a higher rate of catalyst deactivation. Ideally, the whole feed should be instantly vaporized so that uniform cracking mechanism can commence. The *mix temperature* (which is defined as the theoretical equilibrium temperature between the uncracked vaporized feed and the regenerated catalyst) should be

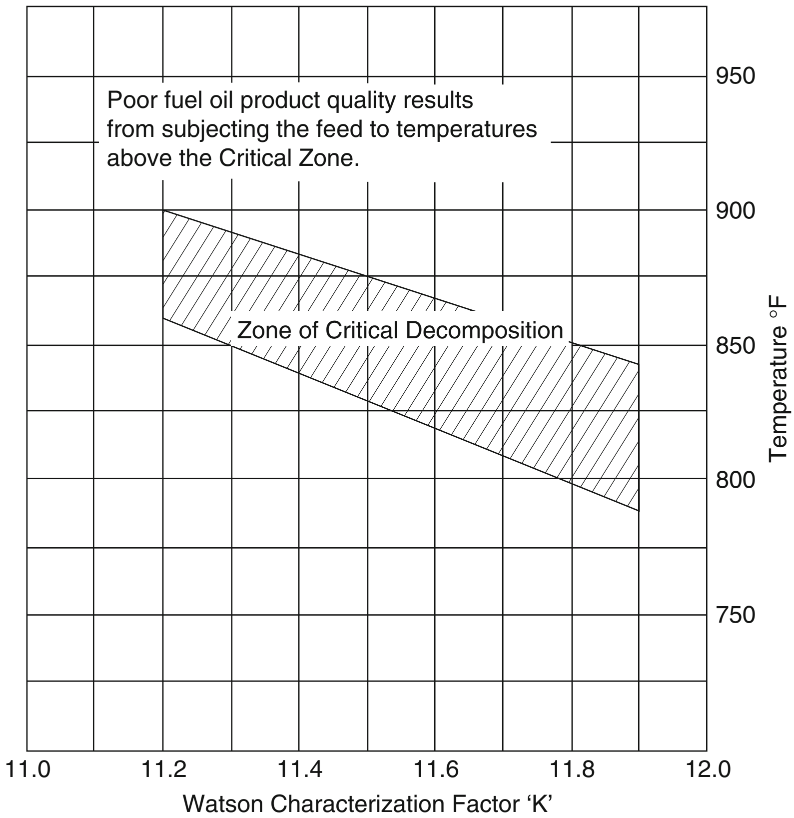


Fig. 10 Zone of critical decomposition

close to the feed dew point temperature. In conventional units, this is about 20–30 °C above the riser outlet temperature. This can be approximated by the expression

$$T_{\mathrm{M}} = T_{\mathrm{R}} + 0.1\,\Delta H_{\mathrm{C}} \tag{3}$$

where

T_{M} = the mix temperature
T_{R} = riser outlet temperature °C
ΔH_{C} = heat of cracking in kJ/kg

This mix temperature is also slightly dependent on the catalyst temperature.

Cracking severity is affected by polycyclic aromatics and nitrogen. This is so because these compounds tend to be absorbed into the catalyst. Rising the mix temperature by increasing the riser temperature reverses the absorption process. Unfortunately, a higher riser temperature leads to undesirable thermal cracking and production of dry gas.

Table 3 Comparison of test run data calculated using SVF method

	Test run	Calculated
Feedstock	Kuwait residue +350 °C	
Conversion wt%	11.07	10.5
Feed rate	11,500	12,000
Heater inlet press psig	512	Not calculated
Outlet press psig	252	Not calculated
Conversion inlet °F	548	590
Conversion outlet °F	651	655
Heater outlet °F	880	860
Soaking drum outlet press psig	242	250
Inlet temperature °F	870	850
Outlet temperature °F	849	830
Yields		
Gas wt%	4.4	4.58
Total distillate wt%[a]	33.59	32.43
Residue wt%	62.01	62.99

[a] This is total distillate C_5 to 350 °C EP

The processing of residual feedstocks therefore requires special techniques to overcome:

- Feed vaporization
- High concentration of polar molecules
- Presence of metals

Some of the techniques developed to meet heavy oil cracking processing are as follows:

- Two-stage regeneration
- Riser mixer design and mix temperature control (MTC) (for rapid vaporization)
- New riser lift technology minimizing the use of steam
- Regenerated catalyst temperature control (catalyst cooling)
- Catalyst selection for:
  - Good conversion and yield pattern
  - Metal resistance
  - Thermal and hydrothermal resistance
  - High gasoline RON

These are discussed in the following items.

Conventional fluid catalytic crackers can be revamped to incorporate the features necessary for heavy oil (residual) cracking. Worldwide, there were approximately 23 FCC residue units in operation (to the beginning of 1992), having a total processing capacity of 760,000 BD.

Two-Stage Regeneration and Regenerated Catalyst Temperature Control

An important issue in the case of deep oil (residue) cracking is the handling of the high coke laydown and the protection of the catalyst. One technique that limits the severe conditions in regeneration of the spent catalyst is the two-stage regeneration. Figure 11 shows the layout of such a regenerator.

The spent catalyst from the reactor is delivered to the first regeneration. Here the catalyst undergoes a mild oxidation with a limited amount of air. Temperatures in this regeneration remain fairly low around 700–750 °C range. From this first regeneration, the catalyst is pneumatically conveyed to a second regenerator. Here excess air is used to complete the carbon burn-off and temperatures up to 900 °C are experienced. The regenerated catalyst leaves this second regeneration to return to the reactor via the transfer line and riser.

The technology that applies to the two-stage regeneration process is innovative in that it burns off the high coke without impairing the catalyst activity. In the first stage, the conditions encourage the combustion of most of the hydrogen associated with the coke. A significant amount of the carbon is also burned off under mild conditions. These conditions inhibit catalyst deactivation.

All the residual coke is burned off in the second stage with excess air and in a dry atmosphere. All the steam associated with hydrogen combustion and carry-over from the reactor has been dispensed within the first stage. The second regenerator is

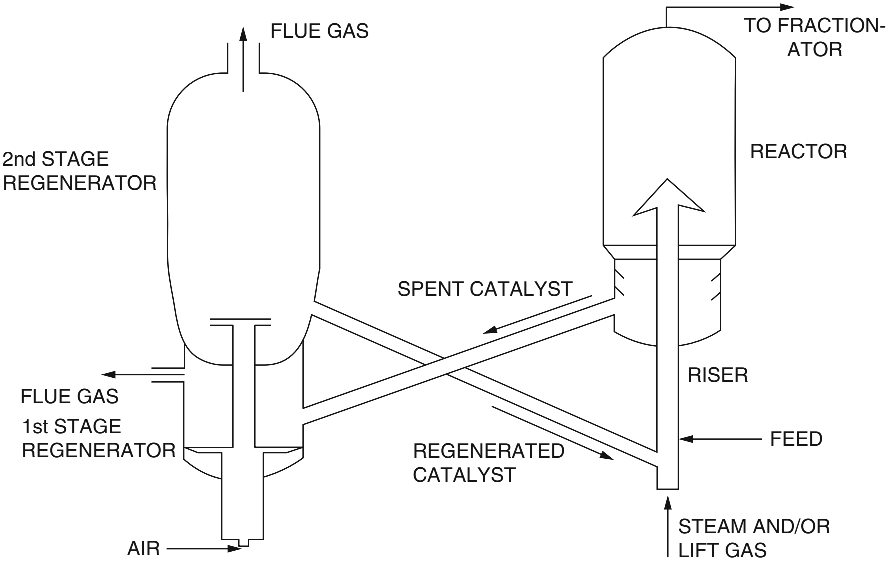


Fig. 11 Two-stage catalyst regeneration

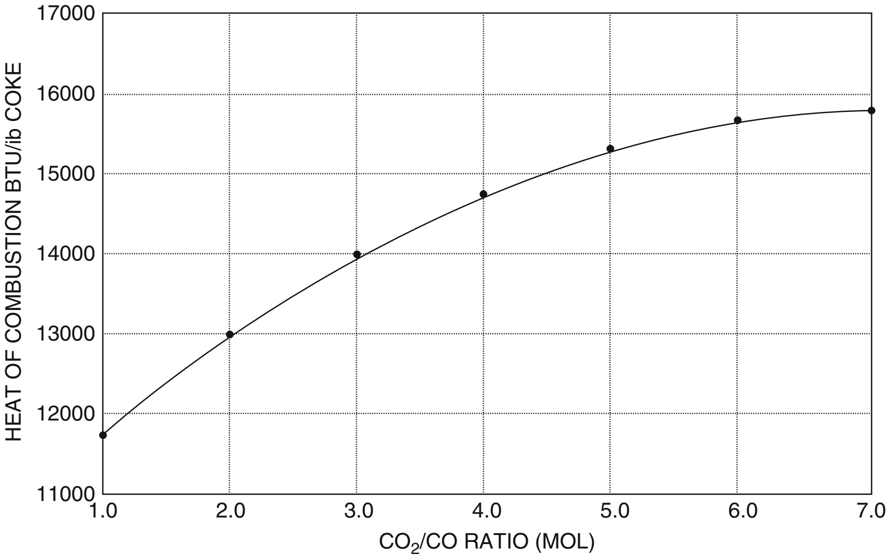


Fig. 12 Heat of combustion versus CO_2/CO ratio

refractory lined and there is no temperature constraint. The catalyst is allowed to come to equilibrium. Even at high regenerator temperatures, under these conditions lower catalyst deactivation is experienced. The two-stage regeneration technique leads to a better catalyst regeneration as well as a lower catalyst consumption. Typically, the clean catalyst contains less than 0.05 wt% carbon. This is achieved with an overall lower heat of combustion. See Figs. 12 and 13.

Since the unit remains in heat balance, coke production stays essentially the same. The circulation rate of catalyst adjusts itself to any changes in coke deposition on the catalyst according to the expressions

$$\text{Coke make} = \text{delta coke} + \text{c/o} \tag{4}$$

and

$$\text{Regenerator temperature} = \text{riser temperature} + C \times \text{delta coke} \tag{5}$$

where

$$\begin{aligned} \text{Delta coke} &= \text{difference between the weight fraction of coke} \\ &\quad \text{on the catalyst before and after regeneration} \\ C &= \text{unit constant (typically } 180 - 230) \\ \text{c/o} &= \text{catalyst} - \text{to} - \text{oil ratio} \end{aligned}$$

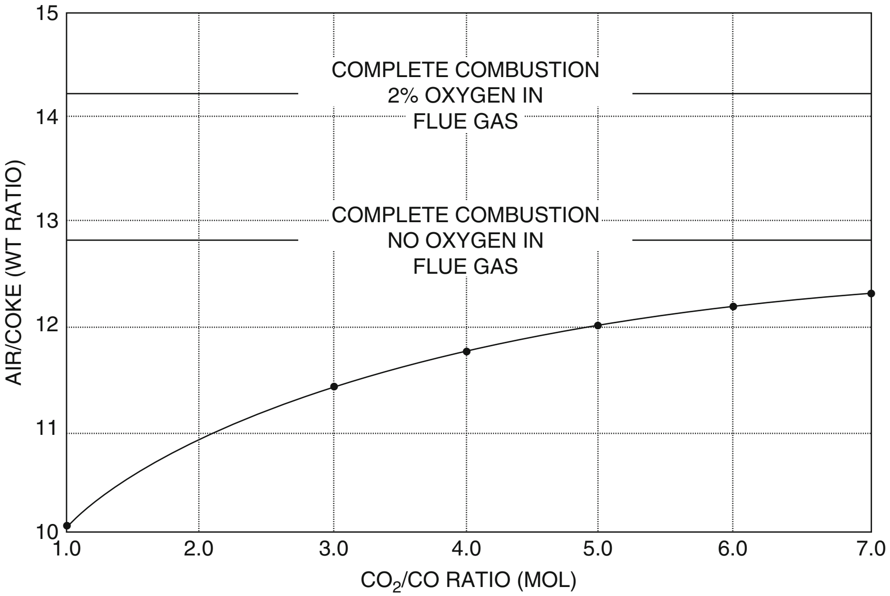


Fig. 13 Combustion air requirement versus CO_2/CO ratio in flue gas

Table 4 Enthalpy requirements for fluid cracking reactor

	Per pound of feed	
	Btu	%
Feed heating/vaporizing	530.0	69.00
Stripping steam enthalpy	5.0	0.65
Feed steam for dispersion	12.7	1.65
Feedwater for heat balance	18.4	2.40
Heat of reaction	200.0	26.04
Heat loss	2.0	0.26
Total	768.1	100.00

In this regard, a small circulation of extremely hot catalyst may not be as effective as a large circulation of cooler catalyst. It has been found that there is a specific catalyst temperature range that is desirable for a given feed and catalyst system. A unique dense phase catalyst cooling system provides a technique through which the best temperature and heat balance relationship can be maintained.

Consider the enthalpy requirements for an FCC reactor given in Table 4.

It can be seen from this table that 69 % of the enthalpy contained in the heat input to the reactor is required just to heat and vaporize the feed. The remainder is essentially available for conversion. To improve conversion, it would be very desirable to allow more of the heat available to be used for conversion. The only variable that can be changed to achieve this requirement is the feed inlet enthalpy,

Table 5 Effect of catalyst cooling on reactor yields

Feedstock		
°API	24.5	
Conradson carbon	1.6	
Yields	Without catalyst cooling	With catalyst cooling
H_2S wt%	0.1	0.19
C_2- wt%	3.4	2.00
C_3 LV%	9.9	10.34
C_4 LV%	13.9	14.51
C_5+ (430:EP) LV%	58.2	60.87
LCO (650:EP) LV%	17.1	15.54
CLO LV%	8.6	8.10
Coke wt%	5.9	6.07
Conversion LV%	74.3	76.36

that is through preheating the feed. Doing this, however, immediately reduces the catalyst circulation rate to maintain heat balance. This, of course, has an adverse effect on conversion. The preheating of the feed can, however, be compensated for by cooling the catalyst. Thus, the catalyst circulation rate can be retained and in many cases can be increased. Indeed, by careful manipulation of the heat balance, the net increase in catalyst circulation rate can be as high as 1 unit cat/oil ratio. The higher equilibrium catalyst activity possible at the lower regeneration temperature also improves the unit yield pattern. This is demonstrated in Table 5.

In summary, catalyst cooling will:

- Slightly increase unit coke
- Give a higher plant catalyst activity
- Be able to handle more contaminated feeds
- Improve conversion and unit yield
- Provide better operating flexibility

In resid cracking, commercial experience indicates that operations at regenerated catalyst temperatures above 1,350 °F result in poor yields with high gas production. Where certain operations require high regeneration temperatures, the installation of a catalyst cooler will have a substantial economic incentive. This will be due to improved yields and catalyst consumption.

There are two types of catalyst coolers available. These are:

- The back-mix type
- Flow-through type

These are shown in Fig. 14. Both coolers are installed into the dense phase section of the regenerator:

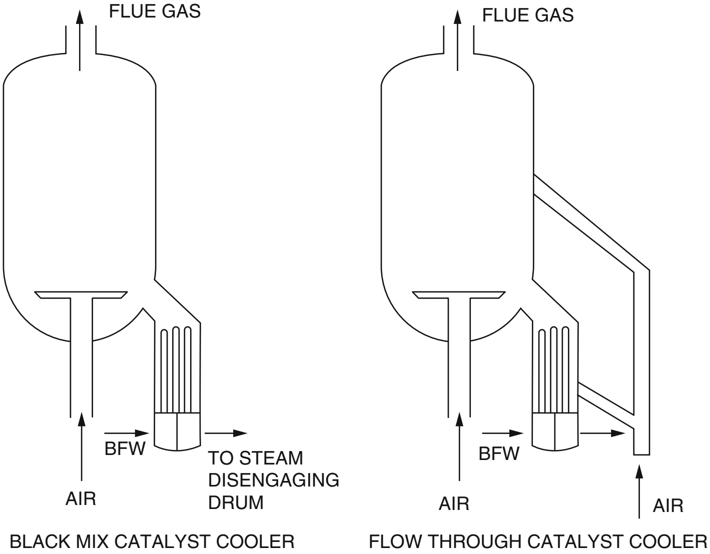


Fig. 14 Typical catalyst coolers

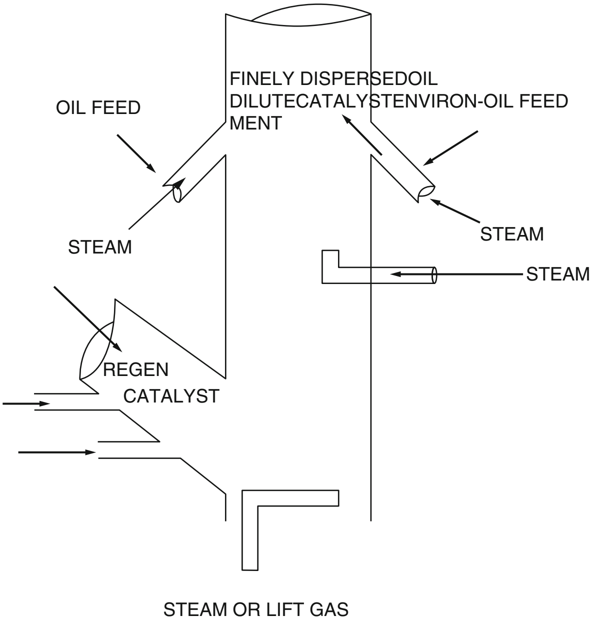
The back-mix cooler: Boiler feedwater flows on the tube side in both cooler types. The catalyst in the back-mix cooler circulates around the tube bundle on the shell side. The heat transfer takes place in a dense low-velocity region so erosion is minimized. The back-mix cooler can remove approximately 50 million Btus/h.

The flow-through cooler: As the name suggests, the catalyst flows once through on the shell side of this cooler. Again erosion is minimized by low-velocity operation in the dense phase. This type of cooler is more efficient than the back mix. This unit can achieve heat removal as high as 100 million Btus/h.

Mix Temperature Control and Lift Gas Technology

The equilibrium temperature between the oil feed and the regenerated catalyst must be reached in the shortest possible time. This is required in order to ensure the rapid and homogeneous vaporization of the feed. To ensure this, it is necessary to design and install a proper feed injection system. This system should ensure that any catalyst back mixing is eliminated. It should also ensure that all the vaporized feed components are subject to the same cracking severity.

Efficient mixing of the feed, finely atomized in small droplets, is achieved by contact with a pre-accelerated dilute suspension of the regenerated catalyst. Under these conditions, feed vaporization takes place almost instantaneously. This configuration is shown in the diagram below.



The regenerated catalyst stream from the regenerator is accelerated by steam or lift gas injection to move up the riser. The oil feed is introduced atomized by steam into the catalyst environment. The main motive steam into the riser is introduced below the feed inlet point. Good mixing occurs in this section with maximum contact between oil, catalyst, and steam.

In residue cracking, the proper selection of catalyst enables even the most bulky molecules to reach the active catalyst zone. Catalysts such as zeolites have a high silica-to-alumina ratio which cracks the heavy molecules into sizes that can enter the active zone.

Efficient mixing of the catalyst and feed together with the catalyst selection ensures:

- Rapid vaporization of the oil
- Uniform cracking severity of the oil

Another problem that is met within residue cracking is the possibility of the heavier portion of the oil being below its dew point. To ensure this is overcome, the “mix temperature” (see previous item) must be set above the dew point of the feed. As stated earlier, the presence of polycyclic aromatics also affects cracking severity. Increasing the mix temperature to raise the riser temperature reverses the effect of polycyclic aromatics. In so doing, however, thermal cracking occurs which is undesirable. To solve this problem, it is necessary to be able to control riser temperature independently of mix temperature.

Mix temperature control (MTC) is achieved by injecting a suitable heavy cycle oil stream into the riser above the oil feed injection point. This essentially separates the riser into two reaction zones. The first is between the feed injection and the cycle oil inlet. This zone is characterized by a high mix temperature, a high catalyst-to-oil ratio, and a very short contact time.

The second zone above the cycle oil inlet operates under more conventional catalytic cracking conditions. The riser temperature is maintained independently by the introduction of the regenerated catalyst. Thus an increase in cycle oil leads to a decrease in riser temperature, which introduces more catalyst; this finally increases the mix temperature and the catalyst-to-oil ratio and decreases the regenerator temperature.

The Lift Gas Technology

As described earlier, it is highly desirable to achieve good catalyst/oil mixing as early and as quickly as possible. The method described to achieve this requires the preacceleration and dilution of the catalyst stream. Traditionally, steam is the medium used to maintain catalyst bed fluidity and movement in the riser. Steam, however, has a deleterious effect on the very hot catalyst that is met in residue cracking processes. Steam under these conditions causes hydrothermal deactivation of the catalyst.

Much work has been done in reducing the use of steam in contact with the hot catalyst. Some of the results of the work showed that if the partial pressure of steam is kept low, the hydrothermal effects are greatly reduced, in the case of relatively metal-free catalyst. A more important result of the work showed that light hydrocarbons imparted favorable conditioning effects to the freshly regenerated catalyst. This was even pronounced in catalysts that were heavily contaminated with metals.

Light hydrocarbon gases have been introduced in several heavy oil crackers since 1985. They have operated either with lift gas alone or mixed with steam. The limitations to the use of lift gas rest in the ability of downstream units to handle the additional gas. Table 6 compares the effect of lift gas in residual operation with the use of steam.

Table 6 Comparison of the effect of “lift gas” versus steam; feed, atmospheric residue 4.3 wt% Conradson carbon

Product distribution	Lift gas	Steam
C_2– wt%	3.2	4.0
C_3/C_4 LV%	11.4/15.1	11.6/15.4
C_5– gasoline LV%	56.9	55.0
LCO + slurry LV%	23.9	24.4
Total C_3 + LV%	107.3	106.4
Coke wt%	8.6	8.5
H_2 scfb	70	89
H_2/C_1 mol ratio	0.74	0.85
Catalyst	Same	
SA, m^2/g[a]	91	90
Ni + V wt-ppm	7,100	7,300

[a] *SA* surface area of equilibrium FCC catalyst, m^2/g

As can be seen, the use of lift gas as an alternative to steam gives:

- Lower hydrogen production
- Lower hydrogen/methane ratio
- Increase in liquid yield

Residuum Hydrocracking

Residuum hydrocracking is often combined with a thermal cracker to upgrade the "bottom of the barrel" and provide high-quality light and middle distillates. Figure 15 shows such a configuration for a fixed-bed cracking unit (there are also fluid bed resid hydrocrackers not covered here).

Bitumen feed from the crude vacuum distillation unit enters the hydrocracker section of the plant to be preheated by hot flash vapors in shell and tube exchangers and finally in a fired heater. A recycle and makeup hydrogen stream is similarly heated by exchange with hot flash vapors. The hydrogen stream is mixed with the hot bitumen stream before entering the hydrocracker heater. The feed streams are risen to the reactor temperature in the heater and leave to enter the top of the reactor vessel. The feed streams flow downward through the catalyst beds contained in the reactor. Additional cold hydrogen is injected at various sections of the reactor to provide temperature control as the hydrocracking process is exothermal.

The reactor effluent leaves the reactor to enter a hot flash drum. Here the heavy bituminous portion of the effluent leaves from the bottom of the drum while the lighter oil and gas phase leaves as a vapor from the top of the drum. This vapor is subsequently cooled by heat exchange with the feed and further cooled and partially condensed by an air cooler. This cooled stream then enters a cold separator operating at a pressure only slightly lower than that of the reactor. A rich hydrogen gas stream is removed from this drum to be amine treated and returned as recycle gas to the process. The distillate liquid leaves from the bottom of the separator to join a vapor stream from the hot flash surge drum (thermal cracker feed surge drum). Both these streams enter the cold flash drum which operates at a much lower pressure than the upstream equipment. A gas stream is removed from the drum to be routed to an absorber unit. The liquid distillate from the drum is routed to the debutanizer in a light-ends recovery unit.

The thermal cracking section of the unit takes as feed the heavy bituminous liquid from the hot flash drum. This enters the cracker heater via a surge drum. This heater has two parallel coils. The oil feed enters these coils to be thermally cracked to form some lighter products. The stream leaving the heater is quenched before entering a flash chamber. This vessel contains some baffled trays and a light gas and oil vapor stream leaves overhead. This stream is subsequently cooled and the distillate formed routed to the cold flash drum. The bottoms from the flash chamber

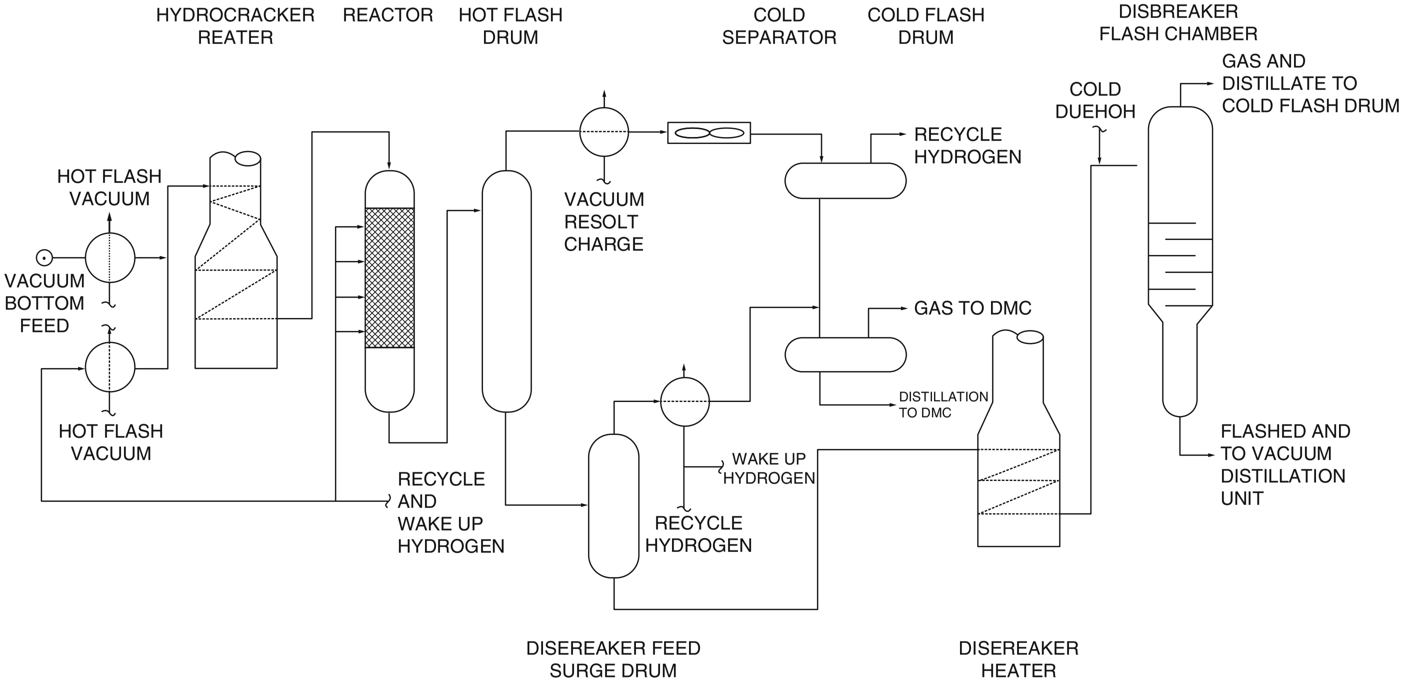


Fig. 15 Typical residuum hydrocracking configuration

Table 7 Conditions and yield data on hydrocracking Middle East residue

	SOR	EOR
Reactor conditions		
Pressure, psia	3,000	3,000
Inlet temperature, °F	700	750
Outlet temperature, °F	750	800
Space velocity, V/V/h	0.5	0.4
Feed		
Vacuum residue	+1,025 °F TBP cut point	
BPSD	13,000	13,000
lbs/h	190,266	190,266
Makeup hydrogen		
Scf/Bbl	1,290	1,875
lbs/h	4,010	5,606
Products		
Ammonia		
lbs/h	209	203
Mol weight	17	
H_2S		
lbs/h	6,964	6,680
Mol weight	34	
Net separator gas		
lbs/h	Nil	2,405
Mol weight		4.3
Cold flash gas		
lbs/h	3,772	5,569
Mol weight	9.6	
Cold flash liquid		
lbs/h	22,586	39,886
BPSD	1,852	3,321
Hot flash liquid		
lbs/h	160,744	141,129
BPSD	11,672	10,280

are fed to the thermal cracker vacuum distillation unit where vacuum gas oil is removed as feed to an FCCU or to a lube oil refining facility.

Hydrocracking Yields and Product Properties

The data in Table 7 illustrate the yield and operating conditions for a fixed-bed residue hydrocracker. Both the start-of-run (SOR) and end-of-run (EOR) data are shown. These were recorded during a test run on a Middle East vacuum residue feed. This hydrocracker contained a guard reactor which essentially converted

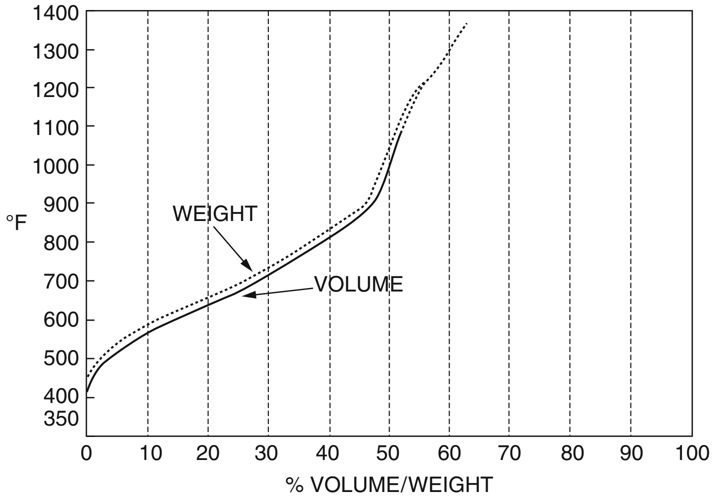


Fig. 16 A typical TBP curve for "hot flash" liquid

most of the nitrogen and sulfur content of the feed to ammonia and hydrogen sulfide, respectively.

The hot flash liquid is subsequently further cracked in a thermal cracker or can be vacuum distilled to obtain vacuum distillates to be fed to an FCCU or a distillate hydrocracker. A typical TBP curve for this liquid is given in Fig. 16.

Effect of Heavy Metals on the Catalyst

Metals such as vanadium, nickel, and sodium seriously reduce the life of the catalyst in most residue fixed-bed reactors. This fact makes the process less competitive to other residue-upgrading ones. The addition of a front-end guard reactor does help to prolong the catalyst life by removing some of these metal contaminants. The catalyst in this guard reactor does become poisoned also, but this catalyst is considerably less expensive than that used for hydrocracking.

The most effective solution to date however is to extract the very heavy ends of the residue. This is the asphalt portion and almost all the metals are contained in these asphaltene molecules. The extraction of these asphaltenes is accomplished by the countercurrent flow of propane as a liquid. The heavy asphalt is then routed to refinery fuel or blended into the asphalt pool for marketing.

Conclusion

Catalytic cracking of residues described above is a poor competitor to the other direct processes for residue upgrading. The process itself is costly to build and has relatively high operating and maintenance costs. The products however are of good quality and require much less downstream treatment. The naphtha produced is (as in the case of distillate hydrocracking) high in naphthene content ideal for gasoline production or as feed to an aromatic production process. The middle distillates also are of high quality with the kerosene fraction having very low smoke point and the gas oil fraction having a good cetane number. In the process illustration given in Fig. 15, the light distillate liquid from the cold flash drum and the associated vapor are routed to a distillate hydrocracker recovery side for further processing and fractionation. These recovery units consist of a main fractionation tower and a light-ends unit which includes an absorber column.

Appendix Sizing a Thermal Cracker Heater/Reactor

In this example, it is required to define a thermal cracker in terms of coil volume and temperature profile in processing an atmospheric residue from Sassan crude. The 25,500 BPSD of the +600 °F residue is preheated to 500 °F by heat exchange with the cracker's products and reflux stream before entering the convection side of the cracker's heater/reactor. It is required to produce a conversion (based on gas through naphtha of 260 °F cut point) of 9 wt%, and the heater will be fitted with 4″ schedule 80 tubes throughout. It will be designed to have three sections which are:

- The convection section with a heat flux of 12,000 Btu/h sq.ft.
- The radiant heater section with a heat flux of 15,000 Btu/h sq.ft.
- The soaker section with a heat flux of 10,000 Btu/h sq.ft.

The heater section and the soaker section are divided by a fire wall. A predicted temperature profile is given in Fig. 17.

The salient temperature and pressure conditions are as follows:

$$\begin{aligned}\text{Convection inlet} &= 500^\circ\text{F at } 330 \text{ psig pressure}\\ \text{Heater inlet} &= 700^\circ\text{F at } 320 \text{ psig}\\ \text{Soaker inlet} &= 820^\circ\text{F at } 290 \text{ psig}\\ \text{Soaker outlet} &= 920^\circ\text{F at } 250 \text{ psig}\end{aligned}$$

A 600 psig steam is introduced into the heater inlet coil. This will be at 10 wt% of the residue feed. Details of the residue feed are as follows (a TBP curve of the feed is given in Fig. 18):

$$\begin{aligned}\text{Feed gravity} &= 18^\circ\text{API } (7.88 \text{ lbs/gal}).\\ \text{Feed rate} &= 25,500 \text{ BPSD } = 351,645 \text{ lb/h}.\\ \text{Volume of waxy distillate in the feed to } 1,022^\circ\text{F cut point} &= 68 \text{ vol.}\%\\ &= 17,340 \text{ BPSD}\end{aligned}$$

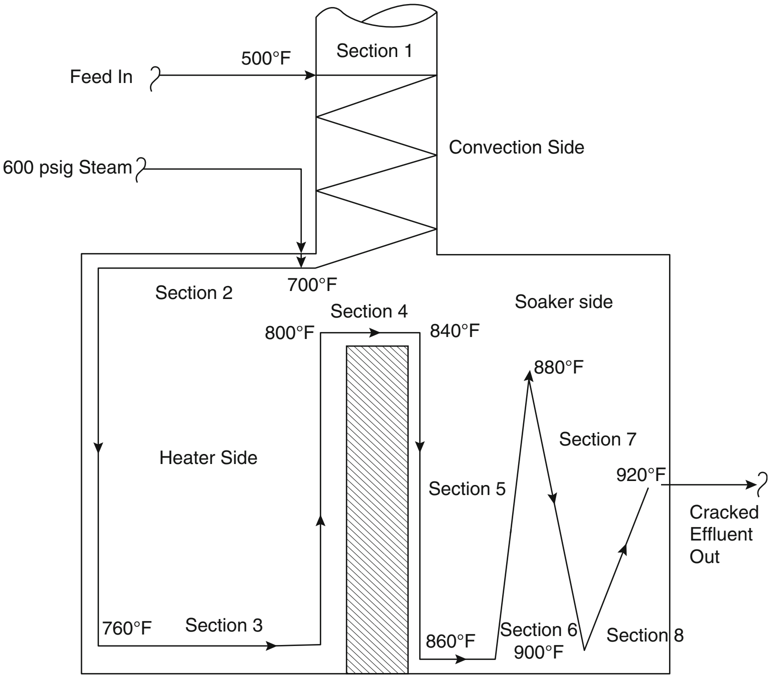


Fig. 17 Temperature profile across the thermal cracker heater

$$\begin{aligned} \text{Gravity of the distillate} &= 26^\circ\text{API}\ (7.48\ \text{lbs/gal}). \\ \text{Weight of distillate} &= 17,340 \times 7.48 \times 1.75 = 226,981\ \text{lbs/h}. \\ \text{Percent weight distillate on feed} &= 65\% \end{aligned}$$

Referring to Fig. 7 in this chapter, the soaking volume factor (SVF) corresponding to a 9 % conversion with a distillate content of 65 % is 0.135.

The heater coil is divided into the following sections:

		Temp in, °F	Temp out, °F
Section 1	Convection side	500	700
2	Heater side	700	760
3	”	760	820
4	Soaker side	820	840
5	”	840	860
6	”	860	880
7	”	880	900
8	”	900	920

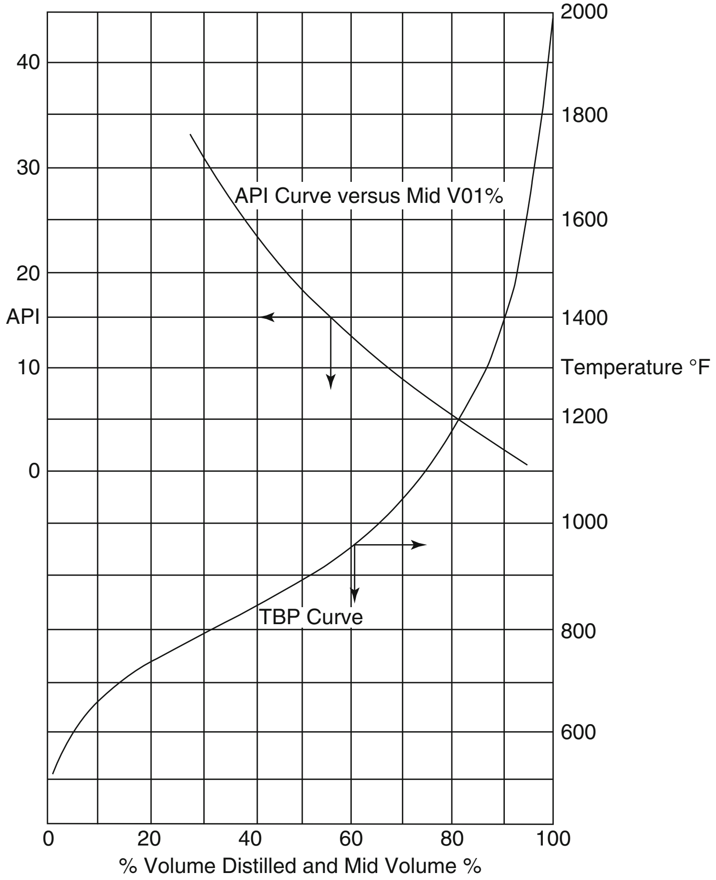


Fig. 18 The TBP curve for the Sassan crude residue feed

Heat balance over the convection side is as follows:

Section 1

Pressure = 365 psia

	V/L	°F	°API	lbs/h	Btu/lb	MMBtu/h
In						
Feed	L	500	15	351,645	250	87.911
Heater duty				By diff		47.824
Total in						135.735
Out						
Feed	L	700	15	351,645	386	135.735
Total out						135.735

$$\text{Sq.ft. of coil } = \frac{47,824,000}{12,000} = 3,985.3 \text{ sq.ft.}$$

Section 2

Pressure = 335 psia

Six hundred psig steam is introduced into this section of the furnace.

	V/L	°F	°API	lbs/h	Btu/lb	MMBtu/h
In						
Feed	L	700	15	351,645	386	135.735
Steam	V	700		35,165	1,383	48.633
Heater duty				By diff		16.652
Total in						201.020
Out						
Steam	V			35,165	1,417	49.829
Feed	L	760	15	351,645	432	151.191
Total out						201.020

Section 3

Pressure = 315 psia

	V/L	°F	°API	lbs/h	Btu/lb	MMBtu/h
In						
Feed	L	760	15	351,645	386	151.191
Steam	V	760		35,165	1,417	49.829
Heater duty				By diff		22.584
Total in						223.604
Out						
Liq feed	L	820	20	344,612	482	165.103
Vap.	V	820	73	7,033	425	2.989
Steam	V	820		35,165	1,440	50.638
Ht. of crack					547	3.874
Total out				386,810		223.604

Cracking begins at a temperature of 800 °F and the oil feed and steam enters the soaking section at 820°. The purpose of the soaking section is to provide a space for the cracking function to occur at a moderate increase in temperature. To calculate the required coil volume, the first step is to assign the degree of cracking that occurs at the end of each section. This is a trial-and-error process and provides an SVF value to each section which in turn is used to calculate the amount of cracked products leaving each section. Using these amounts, the heat balances for each section of the soaker coil are calculated. Thus:

Final Trial

Percent crack at section outlet

	% Conversion	SVF (From Fig. 7)
Section 4	3.0	0.045
Section 5	4.0	0.059
Section 6	6.0	0.090
Section 7	8.0	0.120
Section 8	10.0	0.150

Material compositions (Figs. 8 and 9)
Section 4 temp 840 ° F

	Gas		Naphtha		Gas oil		Residue	
	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h
Distillate	0.9	2,043	2.5	5,675	5.9	13,392	–	205,871
Residue	2.2	2,743	6.6	8,228	14.9	18,575	–	95,118
Total		4,786		13,903		31,967		300,989

Section 5 temp 860 °F

		Gas	Naphtha		Gas oil		Residue	
	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h
Distillate	1.1	2,497	3.3	7,490	7.3	16,570	–	200,424
Residue	5.9	3,740	8.6	10,721	17.2	21,442		88,761
Total		6,237		18,211		38,012		289,185

Section 6 temp 880 ° F

	Gas		Naphtha		Gas oil		Residue	
	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h
Distillate	1.7	3,859	5.0	11,349	9.9	22,471	–	189,302
Residue	4.4	5,785	23.2	16,456	21.2	26,429		75,994
Total		9,644		27,805		48,900		265,296

Section 7 temp 900 ° F

	Gas		Naphtha		Gas oil		Residue	
	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h
Distillate	2.1	4,767	6.4	14,527	11.5	26,103	–	181,584
Residue	5.8	7,231	16.8	20,944	23.6	29,421	–	67,068
Total		11,998		35,471		55,524		248,652

Section 8 temp 920 ° F

	Gas		Naphtha		Gas oil		Residue	
	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h	wt%	lbs/h
Distillate	2.6	5,902	7.3	16,570	12.5	28,373	–	176,136
Residue	7.2	8,976	19.0	23,686	25.4	31,665	–	60,337
Total		14,878		40,256		60,038		236,473

Heat balances over the soaker section

The heat balances for Sections 4, 5, 6, 7, and 8 can now be developed to establish the heat surface area for each of these coil sections. Only the balance for Section 4 is shown here in detail. The remaining coil sections are given in the summary table that follows.

Section 4

	V/L	°F	°API	lbs/h	Btu/lb	MMBtu/h
In						
From Section 3		820		386,810		223.604
Heater duty				By diff		12.275
Total in						235.879
Out						
Gas	V	840	73	4,786	622	2.978
Naphtha	V	840	65	13,903	616	8.564
Gas oil	V	840	38	31,967	598	19.116
Residue	L	840	17	300,989	476	143.271
Steam	V	840		35,165	1,471	51.728
Heat of cracking					547[a]	10.223
Total out				386,810		235.879

[a] Heat of cracking is 547 Btu/lb of the converted gas and naphtha

$$\text{Heater coil duty} = 12,274,500\ \text{Btu/h}$$

Heat flux is 10,000 Btu/sq.ft.:

$$\text{Sq.ft. of coil}\frac{12,274,500}{10,000} = 1,227.5\ \text{sq.ft.}$$

A summary of coil section exit temperature, surface areas, and coil volumes is given in the following table:

The volume data in the table below are based on coils constructed using 4″ schedule 80 steel pipes. The ratio of area to volume is 0.11 cuft/sq.ft.

Coil section	Exit temp °F	Duty MMBtu/h	Sq.ft. of coil	Volume of coil cuft	Cumulative volume cuft	K_T/K_{800}
1	700	47.824	3,985	438.4	438.4	–
2	760	48.633	1,110	122.1	560.5	–
3	820	22.584	1,506	165.7	726.2	1.55

(*continued*)

Coil section	Exit temp °F	Duty MMBtu/h	Sq.ft. of coil	Volume of coil cuft	Cumulative volume cuft	K_T/ K_{800}
4	840	12.275	1,227	135.0	861.2	3.02
5	860	5.682	568	62.5	923.7	5.0
6	880	21.739	2,174	239.1	1,162.8	7.3
7	900	13.855	1,386	152.5	1,315.3	9.0
8	920	11.634	1,163	127.9	1,443.2	10.2
Total		184.226		1,443.2		

Temperature versus volume of coil is plotted over each coil section and is given in Fig. 19. The plot of coil volume above 800 °F versus the K_T/K_{800} ratio is also plotted in Fig. 20. The area under the curve developed in Fig. 20 is calculated and then divided by the throughput in terms of BPSD gives the SVF for the conversion. Thus,

$$\begin{aligned}\text{Area under the curve of Fig. } 20 &= \int_{800}^{920} K_T/K_{800} \times \text{coil vol}\\ &= 3,867\\ \text{allow } 10\% \text{ for the steam} &= 3,\ 480\\ \text{then calculated SVF} &= \frac{3,\ 480}{25,500}\\ &= 0.136\end{aligned}$$

which compares well with the estimate for a 9 % conversion originally used.

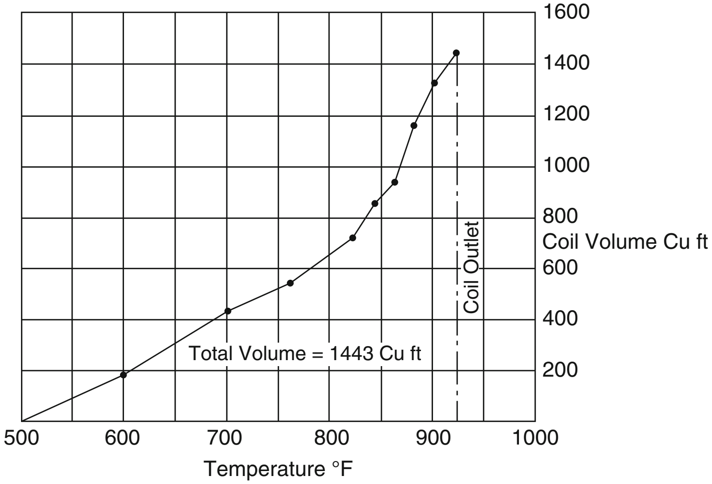


Fig. 19 Coil temperature versus coil volume

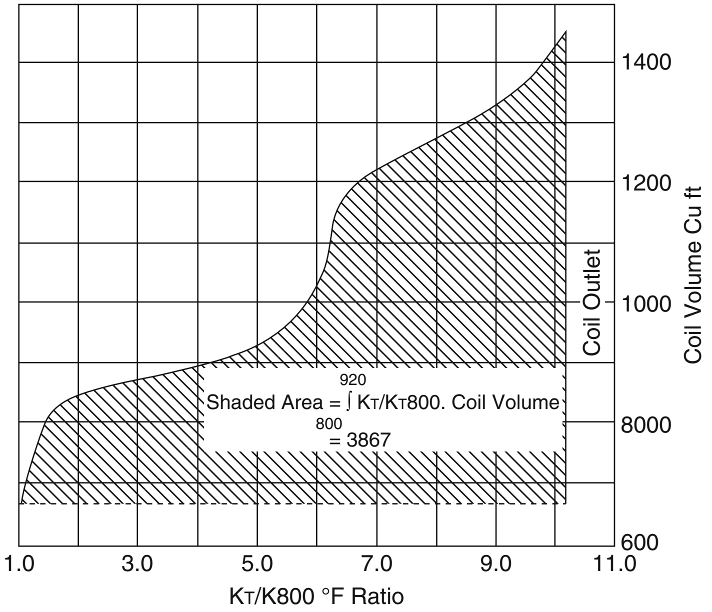


Fig. 20 Coil volume above 800 °F versus the $K_T/K_{800°F}$ ratio

The duty specification for the heater can now be developed with the coil profile and other data to meet the required conversion. The final material composition can also be used now to develop the syncrude composition for the design of the recovery side which will probably consist of a main fractionator with possibly a vacuum distillation unit for the cracked residue. The main fractionator usually produces a "wild" full-range naphtha which is routed to the naphtha product stream leaving the atmospheric crude unit. A full-range gas oil would be blended with the straight-run atmospheric light gas oil to be hydrotreated and routed to the diesel pool.

Hydrogen Production and Management for Petroleum Processing

Steven A. Treese

Contents

Steven A. Treese has retired from Phillips 66.

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_12

Abstract

As refinery product specifications become more stringent to meet environmental requirements, refinery demand for hydrogen has continually increased to supply the required hydroprocessing units. Additional improvements in burning qualities, like cetane, also require more hydrogen. This chapter addresses the processes used to make and/or recover hydrogen for petroleum processing applications. The processes described here include naphtha catalytic reforming, steam-methane reforming, hydrogen recovery, partial oxidation, gasification, olefins cracking, and electrolysis as they relate to hydrogen. Some basic methods for overall refinery hydrogen optimization and management are also described.

Keywords
Refinery • Hydrogen • Reforming • Steam methane reforming • SMR • POX • PSA • Membranes

Introduction and Scope of Discussion

Introduction

As refinery product specifications become more stringent to meet environmental requirements, refinery demand for hydrogen has continually increased to supply the required hydroprocessing units. Additional improvements in burning qualities, like cetane, also require more hydrogen.

For many refineries, the by-product hydrogen produced by naphtha reforming has been able to supply sufficient hydrogen. The drive toward ultralow sulfur diesel and near-zero gasoline sulfur has exceeded the availability of hydrogen from reforming in most cases.

Full-conversion and cracking refineries today generally need incremental hydrogen that is produced “on purpose.” A refinery with a hydrocracker will almost always need incremental hydrogen. This chapter explores the alternative methods for hydrogen production, with a focus on the most commonly applied hydrogen plant technologies.

Many refineries obtain the additional hydrogen supply “over the fence” from a second party. Several gas suppliers, like Praxair, Air Liquide, and Air Products, offer these services. They are especially common where the hydrogen can be used by several different facilities in an area. The plants used to make the hydrogen still follow the same processes discussed below. The main difference in over-the-fence supply is that the refiner is not directly responsible for the hydrogen plant operation.

Production Processes

The first source for hydrogen in a refinery is always catalytic naphtha reforming. This process is discussed in detail elsewhere in this book. We will only touch on reformer hydrogen qualities and issues in this section.

Incremental hydrogen will be our primary focus here. In order of importance to refineries, the key processes for making or recovering incremental hydrogen are:

- Steam-methane reforming
- Refinery gas recovery
- Partial oxidation/gasification
- Olefins cracking by-product recovery
- Electrolytic hydrogen
- Other processes

We will look at each of these processes in turn and provide references for additional information.

Recovery Processes

The recovery processes for hydrogen can apply to several of the production technologies. We will discuss the three most common recovery processes employed in refineries:

- Pressure swing adsorption
- Membranes
- Cryogenic recovery

Management

All the incremental hydrogen in the world is not helpful if it is poorly managed. Poorly managed hydrogen ultimately ends up getting burned in most refineries, and this is a waste. We will discuss some approaches to ensure that hydrogen is not wasted to fuel or flare.

Catalytic Reforming of Naphtha

Discussion

Production of hydrogen as a by-product of catalytic naphtha reforming is very common. This provides a large piece of the hydrogen supply in a refinery.

Semi-regenerative reformers can typically make about 1,000 scf of hydrogen per barrel of reformer charge, while continuous reformers can make around 1,700 scf of hydrogen per barrel charge. Cyclic reformers operate between.

Process details for naphtha reforming are in the chapter entitled "▶ Catalytic Reforming in Petroleum Processing" of this handbook. We will focus here on the hydrogen quality produced by the naphtha reformer and its implications in hydroprocessing.

Reformer Hydrogen Properties

Reformer hydrogen composition can vary widely as shown in Table 1. Hydrogen from a continuous reformer (CCR) will have a relatively constant composition, while hydrogen from a semi-regen unit will vary from start of run (just after regeneration) to end of run (just before regeneration). A cyclic reformer's hydrogen

Table 1 Some typical catalytic naphtha reformer hydrogen products

Type of reformer	Semi-regen	Cyclic	CCR
Hydrogen yield, scf/b charge	1,000–1,300	1,100–1,500	1,600–1,800
Typical hydrogen quality, v%			
Hydrogen	75–89	83–87	85–90
Methane	3–6	3–4	2–3
Ethane	2–5	3–4	2–3
Propane	1–5	3–4	1–2
i-Butane	0.2–2	1–2	1–2
n-Butane	0.2–2	1–2	1–2
C5-Plus	3–5	1–2	3
Chloride (as HCl)	(1–3 vppm)	(1–3 vppm)	(1–3 vppm)

composition will vary over an intermediate range, because the individual reactors are regenerated one at a time and swung back on line.

When viewing these hydrogen compositions from a user's standpoint, two items are of note:

- Methane, ethane, and propane will build up in the recycle gas system of any unit that uses the hydrogen, depressing the effective hydrogen partial pressure.
  - In many cases, the reformer hydrogen is sent initially through the naphtha hydrotreater (NHT or pretreater), sometimes once through, ahead of the naphtha reformer. The naphtha hydrotreater acts as a sponge to remove almost all the heavier impurities and some of the lighter hydrocarbons. The NHT is effectively improving the hydrogen purity before it goes to other units. There is also a benefit in recovering the yield represented by the heavier hydrocarbons.
  - Some refineries send the reformer hydrogen through a pressure swing adsorption (PSA) unit, a membrane unit, or a steam-methane reformer (SMR) to improve the purity. The impurities are rejected to fuel gas or, in the case of the SMR, used to make more hydrogen. The higher-purity product maintains high hydrogen partial pressures in the hydrogen users.
  - If the hydrogen is routed directly to a user, the impurities in the gas appear in the products from the user. When looking at net yields in a user, this needs to be factored into the balance.
- The residual chloride in reformer hydrogen presents a problem for users.
  - The chloride would normally be coming from the reforming process, but poor desalting of the crude, poor water-chloride balance control in the reformer, or organic chlorides in the crude may greatly increase the reformer hydrogen chloride contents.
  - In hydroprocessing units, the chloride, starting out as HCl, will end up forming ammonium chloride deposits in the effluent train and increasing corrosion rates.

  - Sometimes, the chloride content is tolerable, especially if the reformer hydrogen is only a minor portion of the makeup to the user.
  - See the discussion of effluent salts in the chapters on hydrocracking and hydrotreating.
- Frequently, reformer net hydrogen is sent through a low-temperature chloride absorber to remove the chloride compounds.
  - These absorbers use granular solid sorbents, like alumina, to remove the chloride to about 0.1 vppm as HCl.
  - The sorbent must be monitored and periodically changed out.
  - These beds often have issues with channeling unless the reformer hydrogen stream is kept free of liquid (Do not let it cool).
  - If there are substantial olefins in the reformer hydrogen (e.g., from running a reformer past EOR), there are significant aromatics in the gas, and/or the sorbent surface is acidic (which can be due to the being nearly spent or from presence of excessive water vapor), a chloride absorber will make "green oil." These are polymeric, chlorinated hydrocarbons. They will drop out in low spots, foul compressor valves, and move chloride into the process units. These can somewhat defeat the purpose of the absorber. Absorbents are available to reduce green oil formation through the absorbent used or alkaline additives to reduce acidification of the surface.

Further Information on Reformer Hydrogen

Please refer to the chapter on naphtha reforming for additional detail on hydrogen production from catalytic reforming.

Steam-Methane Reforming

Introduction

Steam-methane reforming (SMR) is the main process used in refineries to produce hydrogen. It should not be confused with catalytic naphtha reforming. The technology is offered by several companies on a proprietary basis, including Haldor Topsoe, Foster Wheeler, CB&I/HoweBaker, Lurgi, and KTI.

In the SMR reactions, methane is reacted with steam at very high temperatures and relatively low pressures to make hydrogen and a mixture of CO/CO_2. The process is used extensively by all industries requiring hydrogen. The largest hydrogen plants are used in the manufacture of ammonia. These are usually several times larger than the plants we use in refineries.

When a facility decides to purchase hydrogen over the fence from a gas supplier, that supplier is normally making the hydrogen using SMR.

Advantages of the SMR process are:

- High yields and efficiency – low cost of hydrogen
- High-purity hydrogen product (93–100 %)
- Feedstock flexibility (natural gas, refinery gases, refinery liquids – anything with carbon)
- Relatively easy to operate (governed by equilibrium)
- Relatively easy to monitor (you cannot ignore an SMR, however)
- Scalable – smallest units less than 1 MMscfd to more than 800 MMscfd
- Open art technology, although some equipment and design methods are proprietary
- Many design, equipment, catalyst, and sorbent suppliers, who will help train your personnel and monitor plant
- Well-established safety and support organizations (e.g., AIChE Annual Safety in Ammonia Plants and Related Facilities Symposia)

The disadvantages of the SMR process are largely manageable:

- Severe operating conditions push materials limits
- Cleanup of feedstock and products can be complex
- SMR plants work best at high loads – they do not operate well below 50 % rate
- They like stable production rates – rate changes require a lot of adjustments that are not automatic
- The plants produce CO/CO_2, NO_x, trace organic oxygenates (like methanol), and trace ammonia – all of which must be reported and managed within environmental limits
- An absolutely stable supply of boiler feedwater is required – loss of boiler feedwater for a few minutes (or sometimes seconds) can have drastic consequences

Now, we will walk through the process step by step. The process will focus primarily on making hydrogen from natural gas or refinery gases, with appropriate touches on SMR of refinery liquids.

SMR Processes: Step by Step

The steam-methane reforming process, in its most common form, can be divided into several distinct process sections, as shown in the block flow diagram of Fig. 1:

- Feed gas compression – may be required for low pressure gas feeds
- Feed liquid vaporization – required for liquid feeds
- Feedstock purification – removes all impurities to prepare the feedstock for the SMR; recycle hydrogen is needed if feed contains insufficient hydrogen

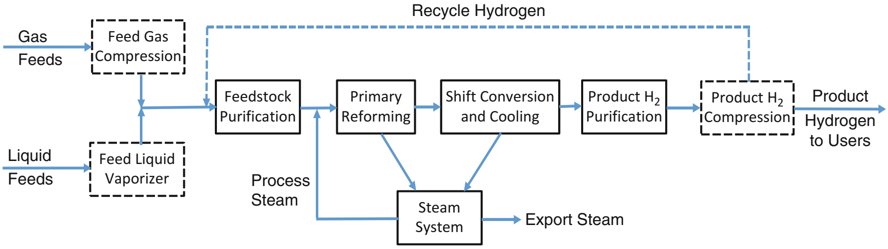


Fig. 1 Block flow diagram of typical steam-methane reforming hydrogen plant

- Primary reforming – reaction of the feedstock with steam to make hydrogen
- Shift conversion and cooling – further reaction of residual CO to make more hydrogen and cooling of raw hydrogen
- Product hydrogen purification – removing impurities from the raw hydrogen to make the high-purity hydrogen product
- Product hydrogen compression – needed at users or inside the SMR hydrogen plant, supplies any recycle hydrogen needs
- Steam system – generates steam from waste heat to supply the process steam requirements; surplus steam is exported to the refinery

We will consider the major process steps in order as the feedstock flows through the plant.

Feedstock Purification

Any feed to the primary reforming section of the plant must be very clean and must only be gaseous. It cannot have any sulfur, halides, olefins, liquids, or other less common contaminants. The function of the purification section is to remove all of the contaminants. In the process, the feedstock will be heated up toward the SMR reaction temperature.

The simplified process flow diagram for the final feedstock purification (or pretreat) steps of most SMR plants is shown in Fig. 2.

Ahead of the purification section, the feedstocks require some preparation:

- Gas feeds:
  - All liquids knocked out of the gases
  - Low pressure gases compressed to required pressure, typically around 450–500 psig
- Liquid feeds:
  - Filtered
  - Vaporized, normally in a kettle-style vaporizer

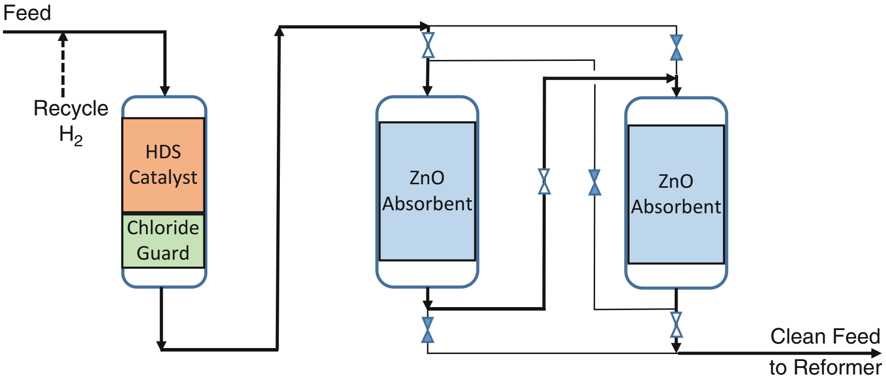


Fig. 2 Typical SMR feedstock final purification system. Note: excludes upstream preparation of feeds, such as amine scrubbing

- All feedstocks:
  - Blended together – preferably in controlled proportions
  - Final trace liquid knocked out

If the blended gas contains very high H_2S levels (more than about 10 vppm), the mixed feed will be routed through an amine scrubber to remove the bulk of the H_2S. The rich amine from the scrubber is sent to regeneration for sulfur recovery, normally out of the SMR plant. A typical reaction in the scrubber, using MEA as an example, is shown in Eq. 1:

$$HOC_2H_4-N-H_2(aq)+H_2S(g)\longleftrightarrow HOC_2H_4-N-H_3{}^+(aq)+SH^-(aq) \quad (1)$$

Depending on residual sulfur after amine scrubbing, very sour gases may also be scrubbed with caustic to remove traces of H_2S down to the sub 10 vppm H_2S range. That caustic reaction is shown in Eq. 2. The spent caustic is routed off plot for disposal:

$$H_2S(g)+NaOH(aq)\rightarrow NaHS(aq)+H_2O(l) \quad (2)$$

The somewhat cleaner feed gas is then mixed with enough hydrogen for hydrotreating and heated to about 600–750 °F. If there are significant olefins present, the preheated temperature may be lower to offset heat of reaction from olefin saturation (see below). The amount of hydrogen required depends on the feedstock but generally falls in the following ranges:

- Natural gas feed: 2–5 v%
- Refinery gases: 2–5+ v%
- Propane and butane: 12 v%
- Naphtha: 25–35 v%

The preheated feed plus hydrogen is now routed to a hydrotreating reactor to convert any residual organic sulfur compounds quantitatively to H_2S and to eliminate olefins. Organic chlorides that may be present are all converted to HCl. Equations for these reactions are below. The reactions are driven almost totally to completion and they are all exothermic:

$$\text{Sulfur}: \text{RS(g)} + \text{H}_2\text{(g)} \rightarrow \text{RH(g)} + \text{H}_2\text{S(g)} \tag{3}$$

$$\text{Olefins}: \text{R} - \text{C} = \text{C} - \text{R}'\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{R} - \text{C} - \text{C} - \text{R}'\text{(g)} \tag{4}$$

$$\text{Chlorides}: \text{R} - \text{Cl(g)} + \text{H}_2\text{(g)} \rightarrow \text{RH(g)} + \text{HCl(g)} \tag{5}$$

Because all the reactions are exothermic, the gas temperature can increase across the hydrotreating reactor. However, since the starting sulfur and chloride contents will be very low in the feeds, the main reaction generating heat is olefin saturation. Olefins can generate 40 °F rise per percent olefin in a gaseous feed, 15 °F per percent olefin in butane feed, and 10 °F per percent olefin in a naphtha feed. These rises place a limit on the amount of olefins in a feedstock. Hydrotreated product can be recycled back through the feed compressors to help moderate the reaction, but this consumes feed gas compressor capacity.

For gaseous feeds, the practical limit is about 5 % olefins in the combined feed (including any recycle). To manage this concentration of olefins, you have to lower the hydrotreater inlet temperature about 200 °F, to about 500–550 °F. If you go lower in temperature, the hydrotreater reactions may not initiate. Higher temperature may result in a hydrocracking runway.

The pretreated gases, now at about 700–750 °F, are passed through a bed of chloride trap and beds of zinc oxide (ZnO). The chloride trap, normally activated alumina ($NaAlO_2$), absorbs the chlorides quantitatively until it is nearly spent. The zinc oxide beds absorb the sulfur quantitatively (<0.01 ppm residual is possible) until the beds are nearly spent. Two ZnO beds are usually used in series with the valves and piping to change out the beds on line and swing the order of the two beds. The essential equations in the sorbent beds are below. These reactions are slightly exothermic, but do not generate significant heat at the low impurity concentrations seen in hydrogen plant feeds:

$$\text{Chlorides}: 2\text{HCl(g)} + 2\text{NaAlO}_2\text{(s)} \rightarrow \text{NaCl(s)} + \text{Al}_2\text{O}_3\text{(s)} + \text{H}_2\text{O(g)} \tag{6}$$

$$\text{Sulfur}: \text{H}_2\text{S(g)} + \text{ZnO(s)} \rightarrow \text{ZnS(s)} + \text{H}_2\text{O(g)} \tag{7}$$

Some units do not have separate hydrotreaters. This is not unusual where a plant only feeds sweet natural gas. In these cases, combined function hydrotreating/absorbing catalysts may be used. Some of the sweet feed units may also not use a hydrogen recycle, but there is some risk of thiophene sulfur getting through. Activated carbon has also been used instead of ZnO for sulfur sorption, but this is uncommon today because activated carbon has such a low capacity.

The general ranges for key operating conditions in the purification section of an SMR hydrogen plant are:

Hydrotreating	
Temperature	550–750 °F
Pressure	350–500 psig
GHSV	<3,000–4,000 h^{-1}
Catalyst	CoMo, NiMo
Absorbers (chloride and sulfur)	
Temperature	650–750 °F (from hydrotreater)
Pressure	300–500 psig
GHSV	500–3,000 h^{-1}
Catalysts	
Chlorides	Activated alumina
Sulfur	Zinc oxide
Combined function catalyst/sorbents also available	

Now, we have sweet, clean, hot gas feedstock available for the SMR reaction.

Primary Reforming

The simplified process flow diagram for the primary reforming section of most SMR plants is shown in Fig. 3. The preheat and heat recovery arrangements can vary. This is where most of the hydrogen will be made.

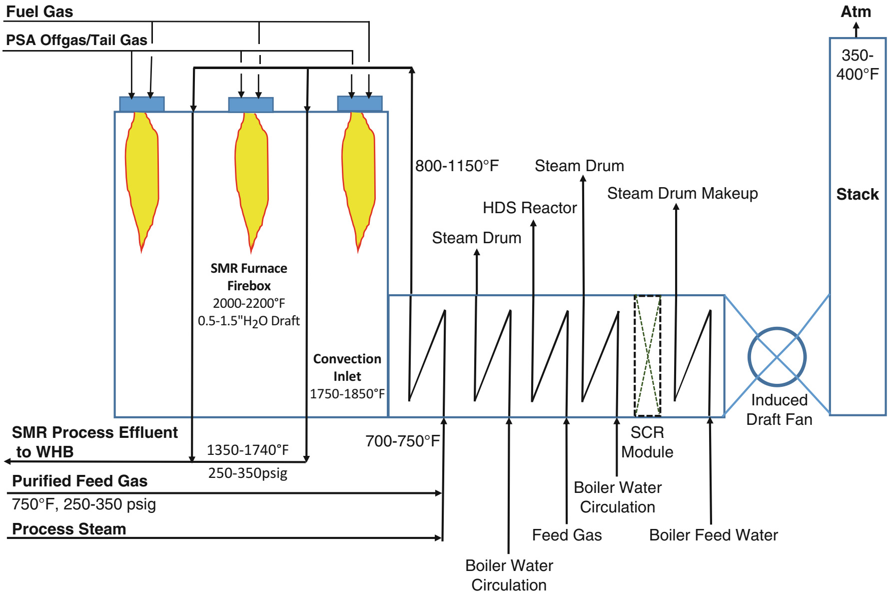


Fig. 3 Typical down-fired primary reformer simplified process flow diagram

In this section of the plant, the hot, pretreated feed is mixed with steam in a precise proportion based on the amount of carbon in the feed. This is the critical steam/carbon ratio and is based on moles of steam per mole of carbon in the feed. Steam/carbon ratio typically ranges from 2.0 to 5.0, depending on the hydrogen plant design. Most new plants in refineries run 2.5–3.0 for gaseous feeds. The ratio is increased for butane and heavier feeds and if additional heat is needed to cool the shift effluent (to be discussed later).

The combined reformer charge is preheated further to 800–1,150 °F by exchange before entering the reforming furnace radiant tubes. It is a large firebox with rows of catalyst-packed tubes surrounded by the burner flames. The SMR reactions occur in the furnace at ~1,350–1,740 °F and ~250–350 psig. There can be hundreds of tubes in a typical furnace.

Flow distribution to the tubes is by pressure drop, so the inlet and outlet header designs and catalyst loading are carefully controlled to ensure exactly the same pressure drop exists through each tube – and hence the same flow. In practice, there are some deviations and an allowable tolerance.

The reactions occurring in this section of the SMR plant are primarily:

Feed gas cracking to methane:

$$C_nH_{2n+2} + n - 1H_2 \rightarrow nCH_4 + \text{Heat} \tag{8}$$

Steam-methane reforming:

$$CH_4 + H_2O + \text{Heat} \longleftrightarrow CO + 3H_2 \tag{9}$$

Water-gas shift:

$$CO + H_2O \longleftrightarrow CO_2 + \ H_2 + \text{Heat} \tag{10}$$

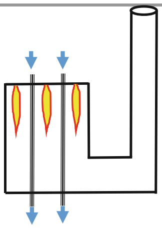
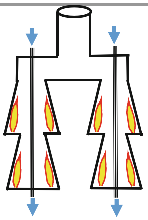
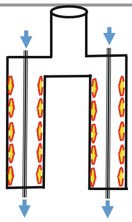
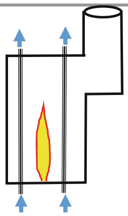
In the first reaction, which normally occurs in the catalyst near each tube inlet, all hydrocarbons coming in are cracked to methane. The catalyst used for this is an SMR catalyst that has an alkali metal component added. The alkali helps scavenge coke that may form on the catalyst from the cracking reactions.

The steam-methane reforming reaction is our primary objective in this section of the plant. Steam reacts with the methane to produce hydrogen and carbon monoxide. This reaction consumes **a lot** of heat. The heat consumed by reforming is why the primary reforming reactions are carried out in tubes within a furnace firebox.

Finally, the carbon monoxide will react further with steam to make additional hydrogen and carbon dioxide. This reaction is favored by lower temperatures, so it only goes part way to completion in the reforming furnace.

All the products are at or near equilibrium at the furnace outlet conditions when the catalyst has good activity. As the catalyst ages, the composition at the furnace outlet drifts away from equilibrium, and the outlet temperature must be raised to maintain production.

Table 2 Comparison of common steam-methane reforming furnace types

Furnace type	Down fired	Terrace-wall fired	Side fired	Bottom fired
Layout				
Advantages	Steam and feed quickly brought to reaction temperature; cheaper furnace box construction; fewer burners	Better control of heat flux; lower tube wall temperatures; moderate firebox cost	Good control of heat flux; lower tube wall temperatures	Relatively low cost; steam and feed quickly brought to reaction temperatures; fewer burners
Disadvantages	High heat flux near top = high tube wall temperatures; ID fan generally required; can have large footprint for convection section	More burners; draft balance and control with multiple cells; convection elevation high or need to use ID fan	Many (hundreds) small burners; high risk of flame impingement; draft balance and control with multiple cells; convection elevation high or need to use ID fan; High cost; Air preheat distribution cramped	Potential high tube wall temperatures near bottom; usually limited to small reformers; draft imbalance potential

The equilibrium can be calculated from the furnace inlet composition and outlet pressure and temperature using published SMR and water-gas shift K values. These data are available, for instance, in *Catalyst Handbook* (by Katalco, Springer-Verlag, NY, 1970) as Tables 2 and 3 of the Appendices to that book. Be sure you look carefully at the form of the K_{SMR} equation to get the right direction for the reaction you are calculating.

For convenience, the charts have been converted to equations relating K_{SMR} and temperatures below:

SMR reaction:

$$K_{SMR} = \left[P_{CO} \times P_{H_2}{}^{3}\right] / \left[P_{CH_4} \times P_{H_2O}\right] \tag{11}$$

where partial pressures are in atmospheres and temperature is °C.

Table 3 Common materials damage mechanisms in SMR hydrogen plants (Reference: API Recommended Practice 571)

	Damage mechanisms																	
Equipment affected	Creep/stress rupture	High temp hydrogen attack	Oxidation	Thermal fatigue	Refractory degradation	Temper embrittlement	Amine cracking	Chloride stress corr. Cracking	Steam blanketing	Thermal shock	Short-term overheading - stress rupture	Sigma-phase/chi embrittlement	Reheat cracking	Dissimilar metal weld cracking	CO_2 corrosion	Amine corrosion	Boiler water/condensate corrosion	Metal dusting	Pressure cycle fatigue
Feed gas hydrotreater		X																	
ZnO drums		X																	
Convection steam gen coils			X								X						X		
SMR furnace tubes/refractory	X		X	X						X	X	X		X				X	
SMR furnace process outlet	X	X			X							X							
Waste heat boiler/steam gen		X			X				X								X		
SMR effluent hot bypass		X	X		X					X				X				X	
HTSC inlet		X																	
HTS converter	X	X				X							X						

HTSC outlet		X																	
LTS converter		X				X							X						
Shift effluent cooling								X							X				
Shift effluent to KO drum								X							X				
Solvent CO_2 removal																			
CO_2 absorber							X								X	X			
Rich solution lines/equipment							X	X							X	X			
CO_2 stripper							X								X	X			
CO_2 stripper reboilers							X	X							X	X			
Lean solution lines/equipment							X	X							X	X			
Methanator preheat exchange		X																	
Methanator reactor		X																	
PSA purification																			
PSA vessels																			X

Correlations are valid within +/−1 °C (1.8 °F) between 200 and 1,200 °C (400–2,200 °F):

$$K_{SMR} = \exp(-4.8858E-14 * T^5 + 2.1457E-10 * T^4 \\ - 3.8682E-07 * T^3 + 3.7620E-04 * T^2 \\ - 2.2251E-01 * T + 5.8282E+01) \tag{12}$$

$$T, °C = -1.7663E-05 * \ln(K_{SMR})^5 + 1.1690E-03 * \ln(K_{SMR})^4 \\ - 3.5357E-02 * \ln(K_{SMR})^3 + 9.4694E-01 * \ln(K_{SMR})^2 \\ - 2.9272E+01 * \ln(K_{SMR}) + 6.1880E+02 \tag{13}$$

Water-gas shift reaction:

$$K_{WGS} = [P_{H_2} \times P_{CO_2}]/[P_{H_2O} \times P_{CO}] \tag{14}$$

Note that this is the reciprocal of the normal WGS K value.

Partial pressures are in atmospheres absolute and temperature is °C.

$$K_{WGS} = \exp(-7.1865E-15 * T^5 + 3.3071E-11 * T^4 \\ - 6.2984E-08 * T^3 + 6.4760E-05 * T^2 \\ - 3.9276E-02 * T + 1.1066E+01) \tag{15}$$

$$T, °C = -2.9492E-01 * \ln(K_{WGS})^5 + 4.4116E+00 * \ln(K_{WGS})^4 \\ - 2.6510E+01 * \ln(K_{WGS})^3 + 9.3947E+01 * \ln(K_{WGS})^2 \\ - 2.9167E+02 * \ln(K_{WGS}) + 8.0912E+02 \tag{16}$$

It should be noted that inerts entering the furnace will pass through unreacted and dilute the products. These inerts will affect the equilibrium by reducing the reactant and product partial pressures.

If the feedstock contains CO, CO_2, or O_2 (as some natural gas does), you have to remember to account for this in the equilibrium calculations.

Key operating conditions around the primary reforming furnace are thus:

Process-side conditions	
Steam/carbon molar ratio	2.0–5.0+
Temperatures	
Feed preheat coil inlet	700–750 °F
Preheat coil outlet	800–1,150 °F
Reforming furnace outlet	1,350–1,740 °F
Pressures	
Reforming furnace outlet	250–350 psig

(*continued*)

Tube pressure drop	15–40 psi
Catalyst volume/GHSV	By designer
Firebox-side conditions	
Firebox temperature (firing level)	2,000–2,200 °F
Draft at burners	0.5–1.5 “H_2O
Flue gas exiting firebox (bridgewall)	1,750–1,850 °F

Water-Gas Shift

The outlet from the reforming furnace consists of hydrogen, CO, CO_2, residual CH_4, a lot of steam, plus any inerts. These products are all at or close to equilibrium at the process outlet temperature from the furnace, usually in the 1,350–1,740 °F range. At these temperatures, there will still be 30–70 % of the carbon present as CO. This CO can be “shifted” to CO_2 with incremental production of hydrogen at lower temperatures using the water-gas shift reaction:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 + \text{Heat} \tag{17}$$

The simplified process flow diagram for the water-gas shift section of most SMR plants is shown in Fig. 4. The heat recovery arrangements in this section will vary, depending on the type of purification system used and the shift stages employed.

For the first shift stage, the reformer effluent is cooled, usually in a large steam generator or waste heat boiler, to about 650–700 F and enters a high-temperature shift (HTS) reactor. This fixed-bed reactor is packed with a chrome-promoted, iron oxide shift catalyst. In the reactor, most of the CO is shifted to CO_2, with additional hydrogen production. The temperature in the reactor rises 50–100 °F due to heat released by the reaction, so reactor effluent is around 700–800 °F. Pressure is low. Normally, all plants have HTS reactors. The catalyst is fairly robust and stable, resistant to poisoning.

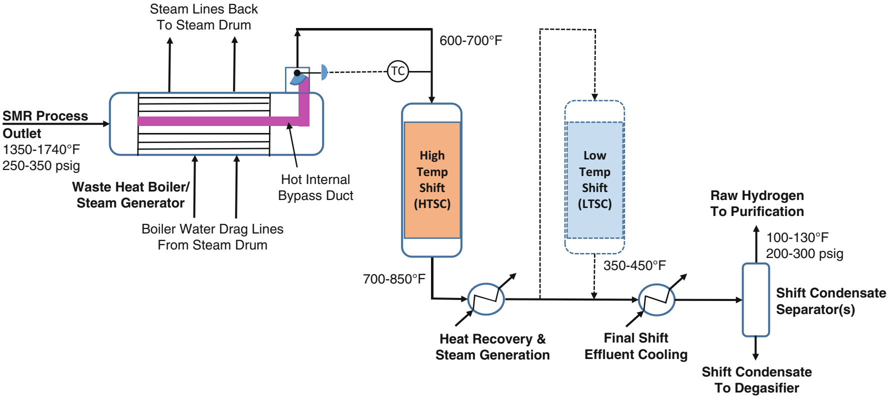


Fig. 4 Typical water-gas shift simplified process flow diagram

The HTS effluent is cooled further. In pressure swing adsorption (PSA)-based plants, the effluent is normally cooled all the way to near-ambient conditions without further shift. In plants employing a wet chemical purification system and in a few PSA plants, there is a low-temperature shift (LTS) reactor to make additional hydrogen and eliminate more CO. Some plants use medium temperature shift (MTS) reactors, but these are less common.

The LTS reactor normally uses a copper-based catalyst to reduce the residual CO to less than ~0.5 v% (can be as low as 0.1 %). This type of catalyst is not robust, so activation and management of the LTS catalyst requires special procedures. A LTS reactor tends to make methanol and ammonia, which will contribute to emissions later. This issue is exacerbated by very low steam/carbon ratios. Specific, low-methanol catalysts are available to limit these side reactions. For a unit with only HTS, the addition of LTS can increase hydrogen production 5–10 %, provided the purification system can handle the extra load. Purification may need to be debottlenecked.

In the final steps of shift effluent cooling, we condense and recover the unreacted steam (shift condensate) for reuse. The relatively dry raw hydrogen is then sent to final purification.

Shift condensate will be saturated with CO_2 and is quite corrosive. It is handled in stainless steel equipment. Direct reuse of the condensate with the dissolved CO_2 would cause high corrosion rates in the boiler system and introduce excessive amounts of CO_2 into the steam from the hydrogen plant – causing high corrosion rates in condensate systems throughout the refinery. Before reuse, the shift condensate must be "degassed" by steam stripping to remove the CO_2. This can be done separately in a dedicated stripper or degasifier or combined with deaeration of incoming boiler feedwater (BFW). Combining degassing with deaeration is generally less effective.

Because the shift condensate also contains methanol and other trace organic oxygenates plus trace ammonia, disposal of the stripper or degasifier off-gas must be considered. Environmental regulations limit the options in many areas. If a unit only has HTS, degasifier off-gas can often go to atmosphere. In other cases, the degasifier or deaerator off-gas can be routed to the reforming furnace firebox. Some units use high-pressure steam strippers to remove the dissolved gases, with the stripper off-gases routed back to feed as part of the process steam.

Typical key operating conditions in the water-gas shift section of the plant are:

Temperatures	
High-temperature shift reactor	
Inlet	600–700 °F
Outlet	700–850 °F
Low-temperature shift reactor	
Range	350–450 °F
Final shift condensate separator	100–130 °F
Pressure	
Final raw hydrogen to purification	250–350 psig

The raw hydrogen is now ready for purification to the final product.

Purification

There are two general approaches to purification of raw hydrogen which we will consider here:

1. Pressure swing adsorption
2. Wet chemical/solvent with methanation

Pressure Swing Adsorption

In modern hydrogen plants, pressure swing adsorption (PSA) is the most common method of purification. The resulting product is nearly 100 % pure hydrogen, and the off-gas can be used as fuel in the SMR furnace.

Refer to the section "Pressure Swing Adsorption" of this chapter for more detailed discussion of PSAs. The following comments address how a PSA is applied in SMR hydrogen plant service.

A PSA is typically integrated into an SMR hydrogen plant as shown in Fig. 5.

The PSA feeds the cooled, dry (<130 °F) raw hydrogen from the SMR shift effluent. The PSA beds adsorb the impurities from the raw hydrogen at inlet pressure (~250–450 psig normally). Pure, nearly 100 %, hydrogen is produced at near PSA inlet pressure.

Each bed in the PSA is periodically cycled off-line and depressured to release the adsorbed impurities. This cycle occurs a few times per hour, typically. Off-line, the pressure in the PSA bed is decreased in steps to near atmospheric pressure (say 4–6 psig). The adsorbent releases the impurities at the low pressure. The resulting tail gas or off-gas is sent to the SMR furnace as fuel.

There are normally several (4–12) PSA adsorbers that are connected together in a system. The PSA system uses control valves, headers, surge vessels, and a

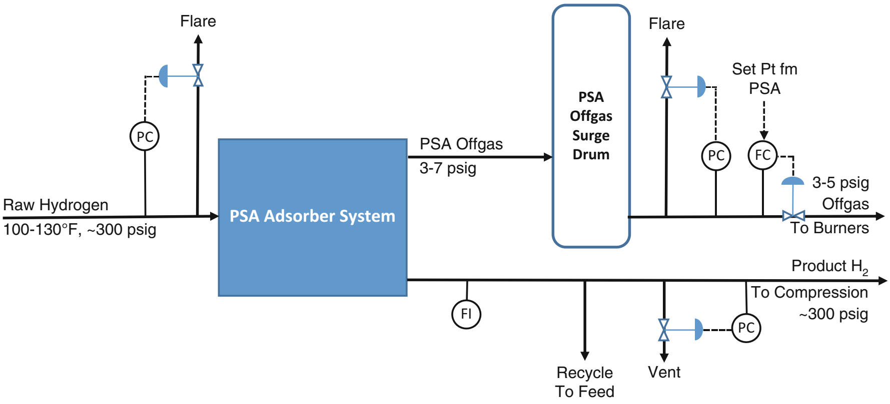


Fig. 5 Typical PSA product hydrogen purification system integration simplified process flow diagram. For details inside PSA adsorber system box, refer to more detailed PSA system process flow diagram in PSA discussion

programmable logic controller to swing each bed through the adsorption-desorption steps in sequence to provide continuous product hydrogen flow. The off-gas is collected in a surge drum to moderate pressure and composition changes before it is sent to the SMR furnace to be burned. The off-gas provides about 50–70 % of the SMR fuel requirement.

Hydrogen recovery in a PSA tied to an SMR unit typically ranges from 80 % to 92 % of the total hydrogen produced in the plant, with a good typical value of about 85 %. The multiple steps in the bed regeneration sequence help optimize hydrogen product recovery. More steps increase recovery, but can require more beds and additional complexity. There may be 50–100 individual steps in the sequence for several beds.

Hydrogen recovery can also be enhanced by online analyzers to monitor product or intermediate-pressure step gases.

One downside of a PSA tied to a continuous process is that it either works or it does not. There are several problems that can cause a PSA to trip. In a trip, your hydrogen product is immediately lost and the hydrogen plant will experience a major upset as the off-gas fuel is lost immediately – causing a major furnace firing disturbance.

The most frequent problems for PSAs are valve failures. These can be expected a few times a year. Sometimes, the PSA logic can work around a problem by removing pairs of beds from service and not interrupting the flow; but often a problem trips the unit. Operators will develop experience to manage the trips with time.

The finished PSA product is nearly 100 % hydrogen, with traces of nitrogen and CO (typically <100 ppm N_2, <10 ppm CO). N_2 and CO are the first gases that will break through a PSA. The PSA operation can be adjusted to allow more or less N_2/CO slip, depending on the hydrogen user limitations. For instance, if the hydrogen is used in an isomerization unit, you would want less than 1 ppm CO. This can be achieved by a PSA, with some loss of recovery. More typically, a CO level of <10 vppm in the product hydrogen is the target. Allowing more CO to slip into the product hydrogen does not significantly increase the amount of hydrogen recovered and, at some point, actually decreases net hydrogen recovery because methanation begins consuming the hydrogen in the users.

Wet Chemical/Solvent with Methanation

Most of the older hydrogen plants used a wet chemical/solvent approach to hydrogen purification. These systems remove nearly all the CO_2, but leave CO in the product hydrogen; hence, plants using wet chemical/solvent purification follow the CO_2 removal with a methanation step to eliminate the CO.

The chemical processes used here generally follow these equations, using DGA as an example solvent:

Absorption/desorption:

$$\text{Solvent(aq)} + \text{CO}_2\text{(g)} \longleftrightarrow \text{Solvent.CO}_2\text{(aq)} \tag{18}$$

Table 4 Typical SMR hydrogen plant CO_2 removal solvents (Reference: Benamor (2012) Carbon capture and Storage . . ., Gas Processing Center, Qatar University)

Removal system type and technology	Licensor/Supplier
Amine solvent systems	
Monoethanolamine (MEA)	Fluor (Econamine^{SM})
Diglycolamine (DGA)	Fluor (Econamine^{SM})
Methyldiethanolamine (MDEA)	
Jefftreat	Huntsman
Gas/Spec CS-2000	Ineos
BASF aMDEA (MDEA + Accel)	BASF
ADIP-X (MDEA + Accel)	Shell
Ucarsol	Dow
KM CDR (KS-1 hindered amine)	Mitsubishi Hvy Ind
Hot potassium carbonate systems	
Catacarb and LRS-10	Eickmeyer and assoc
Benfield and Benfield ACT-1	UOP
Physical solvents	
Selexol	UOP/Dow
Mixed solvents	

Methanation:

$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g) + \text{heat} \tag{19}$$

Table 4 provides a summary of the wet chemical/solvent processes that are available for hydrogen purification, along with a few comparison notes. Some of the processes employ simple chemical solvents. Some use physical solvents. Some use combined chemical and physical solvents. Some of these processes may be patented or involve proprietary information.

Most of these processes offer an option that is not readily available in a PSA system: i.e., food-grade carbon dioxide is a by-product of the process. This CO_2 product can be sold to help offset operating costs. This has some advantage in the current drive to reduce greenhouse gas emissions.

Figure 6 provides a typical flow sheet for a wet chemical/solvent system of hydrogen purification. An amine-type system is used in this example since these are the most common. Individual processes and units may deviate from this flow, but the general principles are the same.

In the wet chemical/solvent approach, cool, raw hydrogen is sent to an absorber where the CO_2 is removed by a circulating solvent. The scrubbed hydrogen, with residual CO and saturated with water, is heated and sent through a fixed-bed methanation reactor (methanator). The catalyst in the reactor is a high nickel oxide material, in a reduced form. The CO is converted almost quantitatively to methane according to Eq. 19 above, consuming some of the hydrogen. Note that methanation is really just undoing the reaction we performed in the SMR furnace, and it will release just as much heat – although from much less reactant.

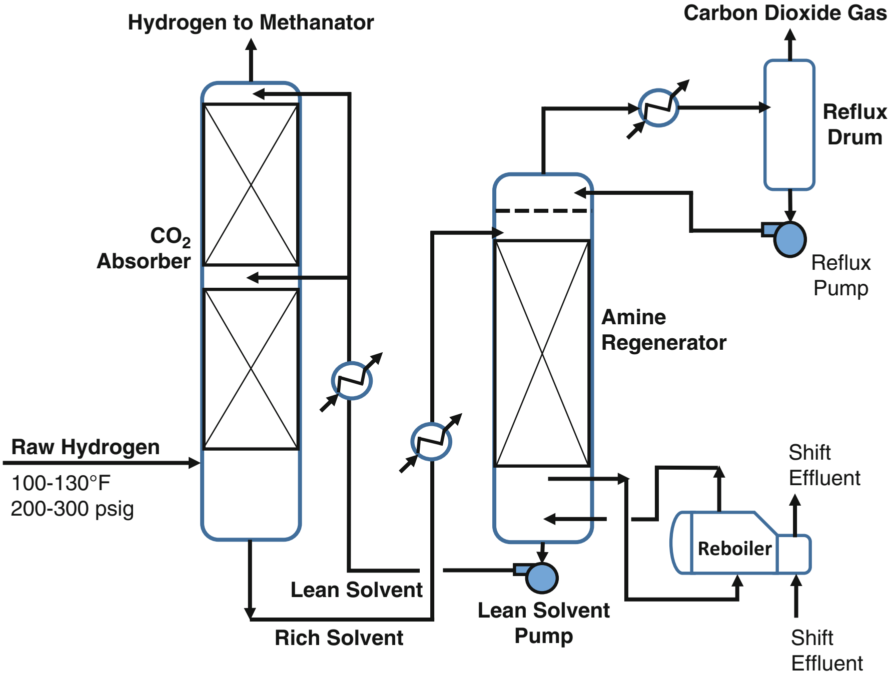


Fig. 6 Typical wet chemical/solvent CO_2 removal system for an SMR hydrogen plant

The outlet temperature of the methanator is controlled by the inlet temperature and the CO slip out of the last shift reactor. The final hydrogen from the methanator is cooled and sent to the users.

Dry hydrogen after the methanator is typically 92–96 % hydrogen, with the balance being methane. There will also normally be <10 vppm CO+CO_2 remaining plus some water from saturation of the hydrogen from the absorber and the methanation reaction.

Because the methanator is so highly exothermic, a methanator normally has an automatic emergency shutdown system, which will bypass the reactor and send the hydrogen to flare or vent on high-high temperature to avoid failing the reactor vessel or piping.

Meanwhile, our solvent containing the CO_2 (“rich” or “fat” solvent) is preheated and sent to a reboiled stripper or regenerator. In the stripper, the CO_2 is driven overhead to a condensing system. The water condensed from the overhead is refluxed to the stripper.

The overhead gas, which is nearly pure CO_2, is vented or sold as carbon dioxide product. For a CO_2 liquid product, only minor final cleanup is needed. Sales of CO_2 are typically via an over-the-fence arrangement with a gas supplier who does the final cleanup, liquefies, and ships the product.

The regenerated ("lean") solvent from the bottom of the stripper is cooled and circulated back to the CO_2 absorber for reuse. Small amounts of makeup water or solvent may be needed to cover losses or a small water purge may be necessary to avoid accumulation. Water balance and solvent purity must be controlled within limits.

Key operating conditions for a solvent CO_2 removal system depend on the solvent used, so are not listed here. A methanator will normally operate in the 200–300 psig range with temperatures from 600 to 700 °F inlet and 700–800 °F outlet. The temperature rise in the methanator will be about 130 °F per v% CO in the methanator feed and about 108 °F per v% CO_2 in the methanator feed.

Overall Hydrogen Plant Reaction

For material balance, catalyst activity monitoring, and process control purposes, it is helpful to look at the overall hydrogen plant reaction equation. The overall equation for an SMR hydrogen plant is

$$\begin{aligned} CH_{2\alpha} + XH_2O \longleftrightarrow\ & aCO + bCO_2 + (1 - a - b)CH_4 \\ & + (X - a - 2b)H_2O + (3a + 4b + \alpha - 2)H_2 \end{aligned} \tag{20}$$

where

α = factor based on feed C/H molar ratio
X = steam/carbon molar ratio
a, b = coefficients for CO and CO_2 concentrations, respectively, at any point in the process

This equation allows you to calculate the composition of the wet gas at any point in the process from the SMR furnace inlet to the final shift outlet, as well as the composition at the methanator outlet – given a few of the gas analyses in the system. You can assume equilibrium (or some temperature difference from equilibrium) and use the K_p value tables. The calculation will be iterative. There is more about this under "Operations and Monitoring."

Another useful view of steam-methane reforming is presented in Figs. 7, 8, 9, 10, 11, and 12, based on information in *Catalyst Handbook* (by Katalco, Springer-Verlag, NY, 1970). These charts show how the various reactions involved in steam-methane reforming are interrelated to reach the final product. The values from the charts are only approximate, but can be used to help calculate wet gas compositions at the reformer outlet.

There are separate charts for reformer outlet methane, CO, and CO_2 from reforming of both gases (methane) and liquids (naphtha). The methane charts would apply when 2α in Eq. 20 is greater than about 2.5 (butane and lighter). When 2α is less than 2.5 (pentane and heavier), the naphtha charts can be used.

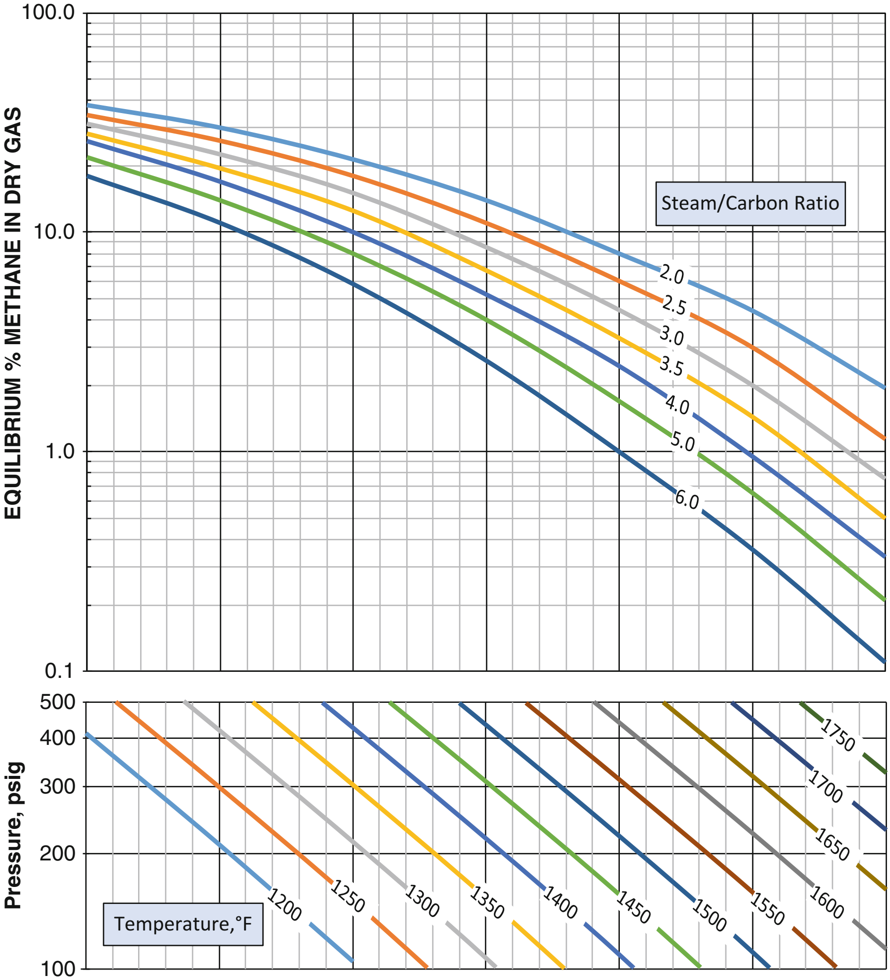


Fig. 7 CH_4 slip equilibrium chart for steam/methane reforming of methane (After: Katalco 1970)

One use of these charts is to estimate the required temperature change for the SMR reformer to target a specific methane slip. For instance, suppose you are operating a unit on natural gas (methane) at 3.0 steam/carbon ratio and 300 psig getting 7.5 % methane slip. On the upper chart for methane slip during methane reforming, find 7.5 % methane slip. Follow the methane slip horizontally to the 3.0 steam/carbon ratio line. Follow the vertical index line straight down to the bottom portion of the chart where the index crosses 300 psig. Your estimated equilibrium temperature is about 1,465 °F (you have to interpolate between the lines). This may or may not be the same as the actual process outlet temperature, but you are only going to use it as a reference in this example.

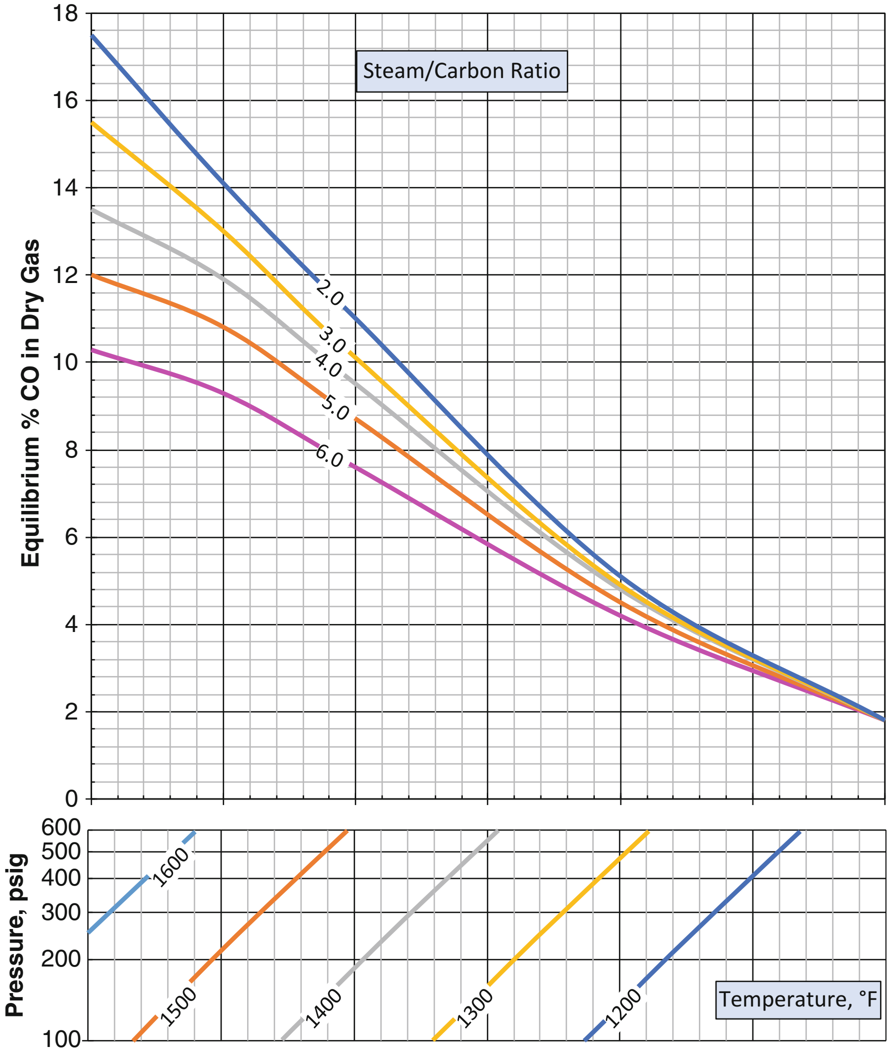


Fig. 8 CO slip equilibrium chart for steam/methane reforming of methane (After: Katalco 1970)

Now, you want to decrease the methane slip to a new target of 6.0 v% methane. You can increase steam/carbon ratio or you can change temperature. Suppose you chose to change temperature. In the upper chart, find where 3.0 steam/carbon crosses the 6.0 % methane slip line. Then, follow the index line vertically down to the 300 psig on the lower chart. The indicated equilibrium temperature is about 1,500 °F. So, increasing the reformer outlet temperature by 1,500 °F−1,465 °F = +35 °F should bring the methane slip to 6.0 v%.

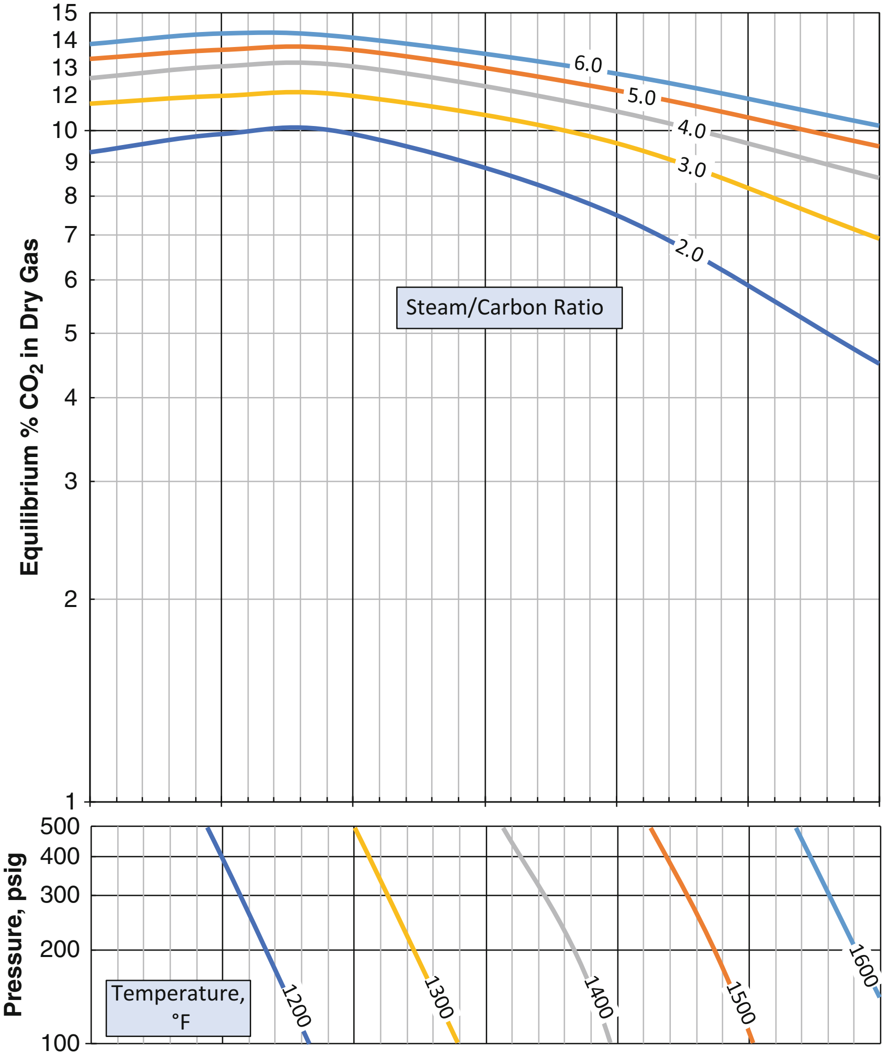


Fig. 9 CO_2 slip equilibrium chart for steam/methane reforming of methane (After: Katalco 1970)

Steam System

Intimately integrated into the SMR process is a steam system which provides process steam as well as removes the large amount of waste heat required to cool the furnace process outlet, shift outlet, and flue. The steam system allows a hydrogen plant to be nearly self-sufficient. Many hydrogen plants generate surplus, high-pressure steam that is exported to the refinery. They can be major steam

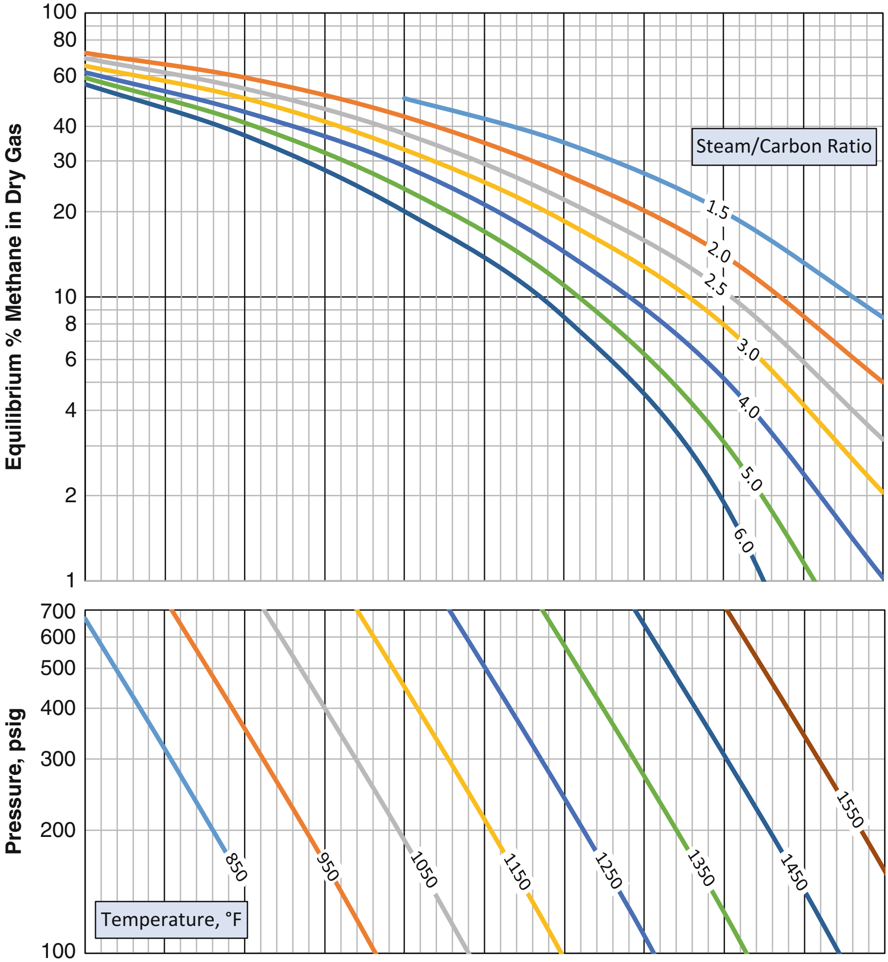


Fig. 10 CH_4 slip equilibrium chart for steam/methane reforming of naphtha (After: Katalco 1970)

generators, replacing boilers. When properly designed and spared, hydrogen plants can supply steam in an emergency, such as the loss of other boilers.

A typical steam system for an SMR hydrogen plant is illustrated in Fig. 13. Many configurations are used for these systems, however.

There are three areas where most steam is generated in a hydrogen plant:

- Reforming furnace process outlet. Here, a steam generator/waste heat boiler (WHB) is installed. The WHB cools the process gases from their exit temperature of 1,350–1,740 °F down to the HTS converter inlet temperature of about 700 °F. The final temperature is controlled by bypassing hot gas around

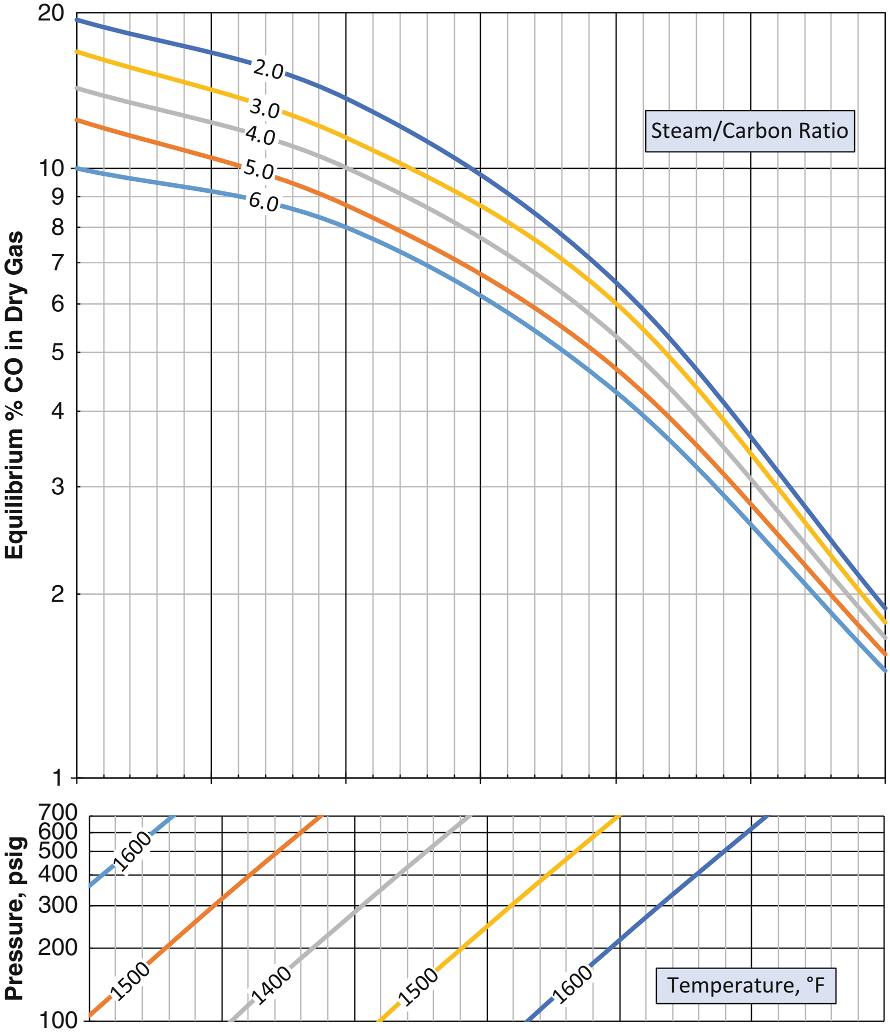


Fig. 11 CO slip equilibrium chart for steam/methane reforming of naphtha (After: Katalco 1970)

(or through) the steam generator using a damper system. Water supply to the WHB is normally by thermosiphon from a steam drum located somewhat above the WHB. Vaporization is typically 10–20 % in the WHB.

- Reforming furnace flue gas. One or more steam generation coils plus an economizer to preheat boiler feedwater are normally included in the flue gas ducting. These are usually thermosiphon or forced circulation steam generators tied to the main steam drum.
- High-temperature shift reactor effluent. Many plants employ a separate steam generator(s), sometimes kettle style, on the shift reactor effluent to recover

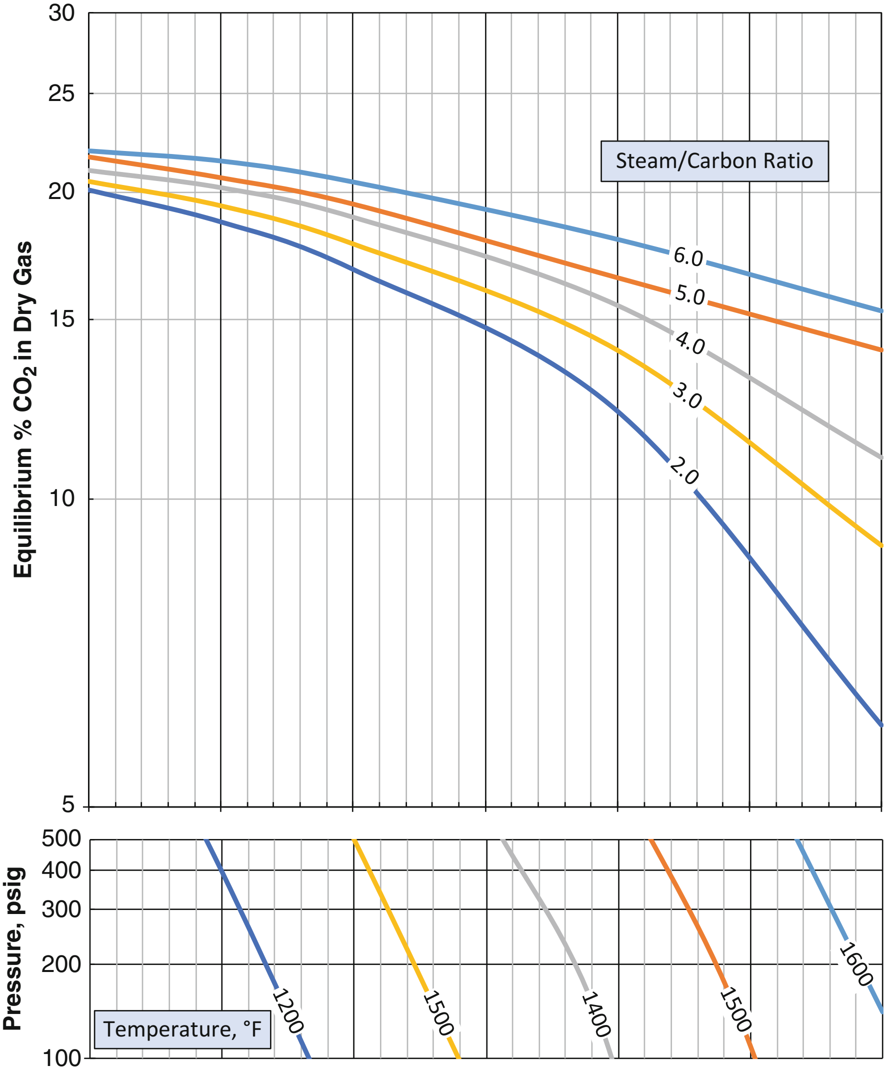


Fig. 12 CO_2 slip equilibrium chart for steam/methane reforming of naphtha (After: Katalco 1970)

additional high-level heat. In plants that use wet chemical/solvent CO_2 recovery, this heat is normally used to drive the solvent system, so the steam generator may be omitted in these plants.

Treatment of the boiler feedwater (BFW) for the steam generator systems and steam from hydrogen plants is critical. Table 5 summarizes the typical BFW treatment requirements.

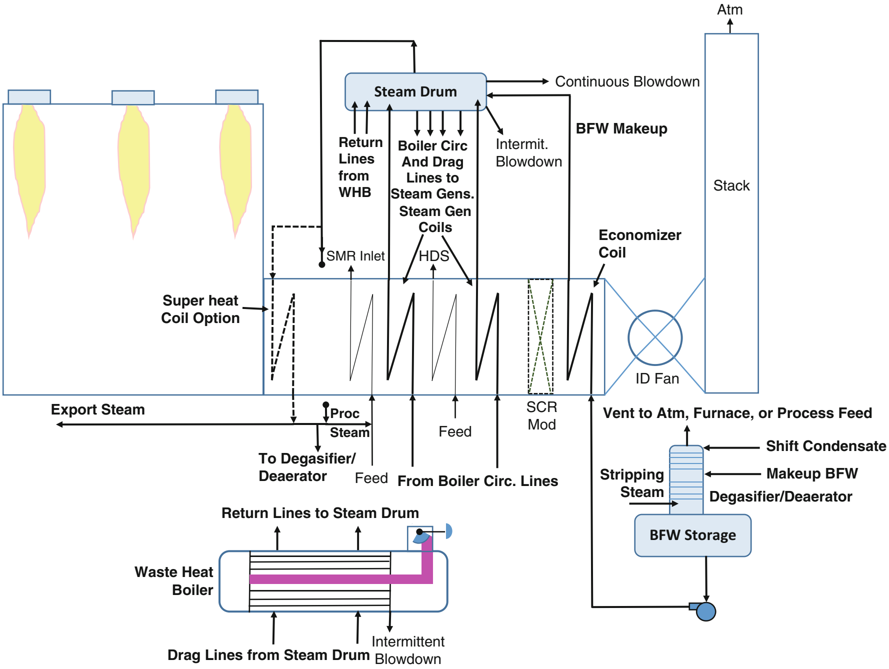


Fig. 13 Typical SMR steam system simplified process flow diagram. Note: This is only one possible configuration presented, for example. Other steam generators may also be installed in the shift effluent

Table 5 Typical SMR hydrogen plant boiler chemical treatment (Reference: Nalco)

Function	Chemical	Feed point	Notes and comments
Oxygen scavenger	Passivating scavenger	Deaerator/degasified storage tank	No sulfur compounds
Boiler pH control	High-purity caustic	BFW to pump suction	Depends on makeup water; avoid ammonia and amines
Boiler internal treatment	Polymer system	BFW to pump suction	Avoid ammonia generation; need iron dispersant capability; analytical capability to track chemicals; maximize cleanliness of boilers
Supplemental iron dispersant	Polymer system	BFW to pump suction	Needed if chelant or phosphate internal treatment is used
Condensate treatment	Mixed amines	Export steam line only	Amine boiling points should match condensate system pressures; H_2 plant condensate system should be stainless steel; amine in H_2 plant will convert to ammonia in process

Hydrogen plant steam systems are highly stressed and require higher treatment levels than normal boilers. In the WHB on the furnace outlet, for instance, the tube walls will be over 1,000 °F. When working with a boiler chemical vendor, you need to be sure the vendor is experienced in hydrogen plant chemical treatment. One specific caution is that BFW for a hydrogen plant should not use sulfite as an oxygen scavenger. The small amount of residual sulfur that ends up in the steam will poison the reforming catalyst.

Recycle of shift condensate can introduce higher levels of CO_2 into the steam generated. The CO_2 becomes a corrosion problem in condensate systems using the steam. Critical factors in preventing this corrosion are:

- Proper stripping of the shift condensate, as noted in the discussion of the water-gas shift section above
- Injection of amine corrosion inhibitors into the export steam that will drop out into the condensate headers at the correct pressures/temperatures

Unique Equipment Design and Metallurgy Considerations

In this section, we will review a few of the unique considerations in hydrogen plant equipment design. Properly addressing these factors is critical to building and operating a hydrogen plant.

SMR Furnace

Here, we will highlight only some of the more important considerations around an SMR furnace. These furnaces are not “run-of-the-mill” units. They require design experience. For very large furnaces, computational fluid dynamics (CFD) may be employed to ensure heat release and flow in the firebox are properly designed.

- *Style of furnace* – The SMR furnaces are generally some of the largest, if not the largest, fired heaters in a refinery. Several furnace types have been used, as shown in Table 2. The table enumerates some of the key advantages and disadvantages of each style of heater. Today, most hydrogen plants are either down fired or terrace-wall fired.
- *Radiant tubes* – Some typical hydrogen plant tube configurations are depicted in Fig. 14.

  The tubes are made of high nickel alloys (HK-40, Manurite, etc.). Tube IDs range from 1.5 to 5.5 in.. The tube design temperature is chosen based on the calculated maximum expected end-of-run wall temperature. The design margin today is about 50 °F higher than the maximum expected wall temperature. This can be very tight. Our ability to monitor tube temperatures is about +/− 100 °F. Monitoring will be discussed later.
- *Burners* – SMR furnaces use large numbers of burners to distribute heat evenly to all the tubes. Because the firebox operates over 2,000 °F, the burners used

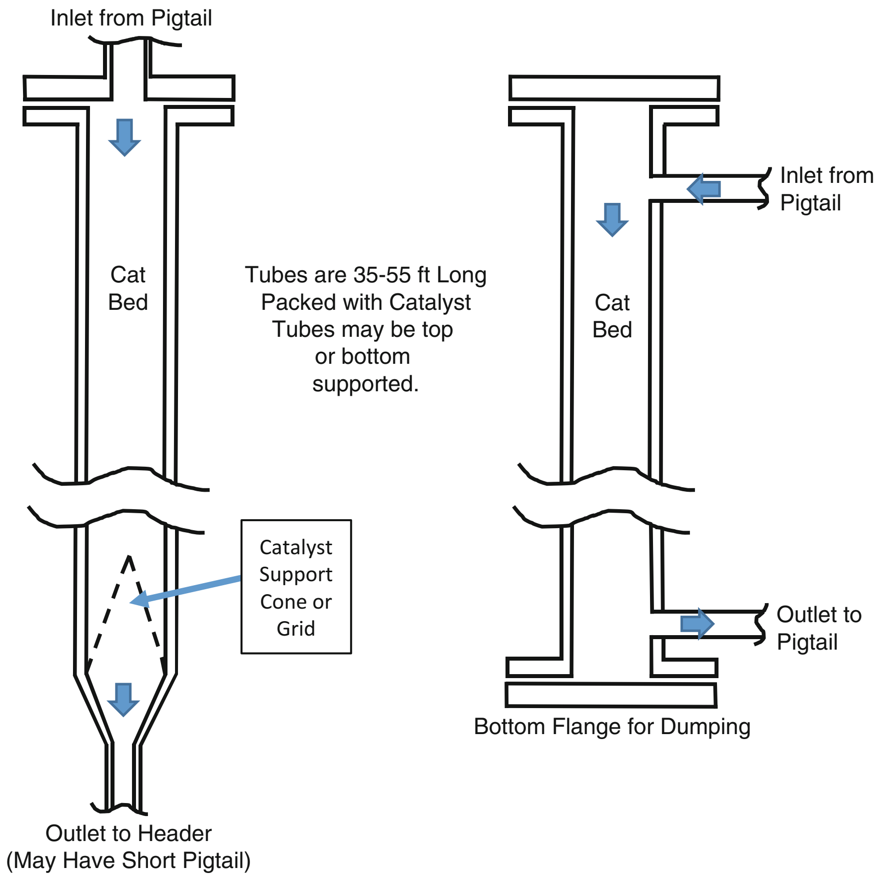


Fig. 14 Some typical SMR tube arrangements. Note: These are examples only. There are many styles in use

today are generally special low-NOx styles. In PSA hydrogen plants, the burners have an extra, low-pressure-drop nozzle for PSA off-gas.

Arrangement or design of the burners must avoid flame impingement on the tubes. All burners may not be the same size, as dictated by the heat input requirements in a given section of the heater.

- *Convection section* – The convection sections of hydrogen plant furnaces generally have a series of services. Typically, you will see coils for:
  - Steam superheat
  - Mixed steam/feed preheat
  - Steam generation (one or more levels)
  - BFW economizer/preheat
  - Combustion air preheat

In some areas, selective catalytic reduction (SCR) units may be installed in the flue to reduce NO_x. These systems employ a catalyst matrix with very low pressure drop (inches of water). Ammonia is injected into the flue ahead of the catalyst through a grid of nozzles. The ammonia is vaporized outside the flue and diluted into hot air to improve distribution. The SCR must be located in an exact temperature range (depending on the catalyst chosen). Sometimes, these are retrofitted to existing hydrogen plants, with the convection coils rearranged to ensure the correct temperature range.

- *Furnace draft control* – SMR furnaces may be natural draft, induced draft, or forced/induced draft. You seldom see forced draft-only furnaces in this service. Older units tend to be natural draft. For down-fired furnaces or where an SCR is required, induced draft is used. If a furnace has air preheat, it will generally have both forced and induced draft fans.

  The burner registers provide additional draft control. The registers must be open enough to allow the control system to work.

  PSA off-gas combustion introduces a swing into the fuel gas controls that will affect draft. The draft will vary slightly every couple of minutes as the PSA cycles. Controls around the PSA attempt to moderate the swing, but generally cannot eliminate it. With careful tuning of controllers, the swing can generally be managed. Keep in mind that swinging draft also means swinging excess oxygen levels.
- *SMR process outlet header* – The high process outlet header temperatures from an SMR furnace give rise to special problems when transferring the effluent to the waste heat boiler. The outlet headers inside the firebox are generally high alloy (e.g., Incoloy). The high alloy is transitioned to a lower alloy header, normally something like 1¼ Cr steel, that is lined with a refractory system. Figure 15 illustrates the types of refractory arrangements normally seen in this service.

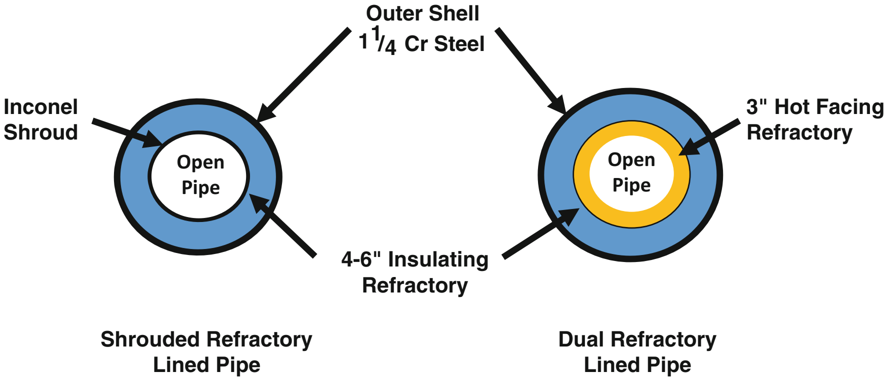


Fig. 15 Typical refractory systems for SMR furnace process outlet

The refractory-lined effluent piping needs to be monitored to ensure that an internal refractory failure does not lead to a pipe wall failure. Even a small crack in the refractory will increase wall temperature. A major refractory loss will rapidly heat the wall above its allowable maximum. To monitor for this, the outside wall of the transfer line is painted with temperature-indicating paint, normally changing color if the pipe wall exceeds about 500 °F. This provides a margin between maximum allowable temperature and actual.

Conversely, it is important that the steel wall of the refractory-lined header be maintained above the water condensation temperature. The SMR effluent, if condensed, will form carbonic acid. That acid will corrode the low-alloy steel. The outside wall of the refractory lined pipe normally runs about 250–350 °F to meet all the requirements.

- *Safety* – Any fired heater needs a safety system, and an SMR furnace is not an exception. The complexity of the SMR means that the safety systems around these units are correspondingly more complex. These systems will not be comprehensively covered, but a few specific considerations in SMR furnaces are highlighted:
  - *Loss of draft control* – Because an SMR fires at such high rates, loss of draft control in the firebox creates a potentially hazardous situation. This can occur with loss of the forced or induced draft fans, damper or register control issues, PSA trips, excessive changes in fuel gas rates, high or low fuel pressures, and many other causes. Safety systems for these furnaces generally trip on high or low draft. These systems are backed up by excess oxygen monitoring at the firebox outlet.
  - *SCR problems* – Where a furnace has an SCR, the SCR may be tripped on high or low flue gas temperature or on loss of ratio control in the vaporizer skid. These trips are intended to avoid potentially explosive mixtures or deposits in the vaporizer and/or flue.
  - *Fuel gas, pilot gas, or PSA off-gas high/low pressures* – Depending on the type of failure, there will generally be trips on several fuel stream pressures because these can cause other issues. Fuels are tripped out of the furnace to avoid accumulating an explosive mixture. Generally, pilot gas is maintained unless draft is lost.
  - *Firing protection* – In modern reformers, the safety systems contain a number of interlocks to ensure the heater is fired safely. Typical interlocks include verifying that all fuels are isolated before allowing a purge, ensuring that a purge is completed, verifying that pilots are lit before allowing main fuel to be admitted, and verifying that the main fuel is on before allowing PSA off-gas. Factory Mutual (FM) cock valves and nitrogen pressurization of fuel headers have both been used to verify fuel isolation before allowing a purge to start.
  - *Process trip* – If the process side of the furnace trips for any reason, the heat load on the furnace is drastically and immediately reduced. The furnace must be cut back very quickly, and this can lead to the furnace tripping on draft or fuel pressure. Generally, however, a process trip does not require a furnace trip if the furnace can be reduced back to pilots with control.

Waste Heat Boiler

- *General design* – The SMR effluent steam generator or waste heat boiler is normally a large, horizontal heat exchanger. See Fig. 16 for a sketch of a typical WHB exchanger.

  The inlet to the process side of the exchanger is connected to the SMR furnace with the refractory-line transition header. The WHB inlet is normally refractory lined also, with high alloy inserts into each of the boiler tubes.

  There is normally a single, larger, lined tube that passes through the boiler to act as a hot gas bypass duct. In some units, this may be an actual bypass around the WHB, rather than through it.

  The hot gas bypass is equipped with a damper to control the final process outlet temperature from the WHB. The damper is generally arranged to act like a three-way valve – restricting the flow through the boiler tubes as it opens to allow hot gas bypassing. Sometimes, the bypass is automatically controlled, but manual control is also used.

  On the water side of the exchanger, the flow is generally by thermosiphon, so water from the overhead steam drum is distributed to the WHB at several points along the bottom of the shell. Mixed steam/BFW returns to the steam drum from outlets distributed along the top of the shell. Intermittent blowdown is taken from the bottom of the shell. The steam side of the WHB is hard to inspect normally.
- *Metal dusting* – The process conditions in the WHB can result in metal dusting. This is where the process gases cause migration of carbon to the grain boundary metals, and the metal crystallites essentially turn to dust. It is promoted by reducing gases (H_2, CO, methane) in the 900–1,500 °F range. While a hydrogen plant normally has an oxidizing atmosphere, the reformer outlet is much closer to reducing conditions. Metal dusting is seen more at low steam/carbon ratios. The metal tubes and the hot gas bypass in a waste heat boiler are especially susceptible to this damage. The inserts on the tube inlets and selection of metallurgy help control this phenomenon.

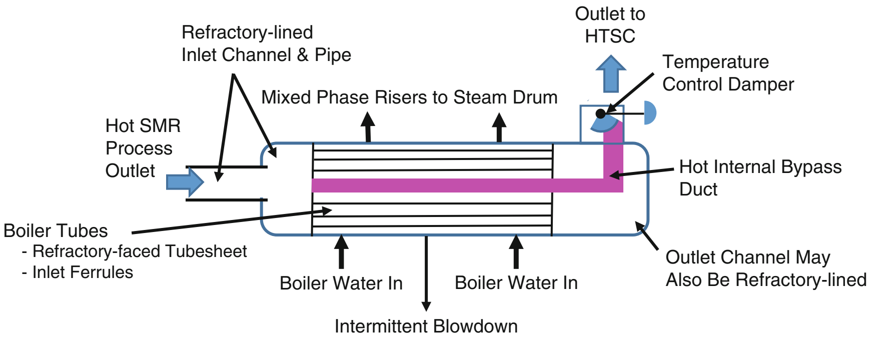


Fig. 16 Sketch of a typical SMR furnace process outlet waste heat boiler or steam generator

PSA Systems

Most modern hydrogen plants use pressure swing adsorption (PSA) systems. Refer to the detailed PSA discussion in the section "Pressure Swing Adsorption" of this chapter for information on critical aspects of PSAs.

Some specific areas to note about PSAs in the discussion are:

- Valves and sequence steps
- PSA adsorbers
- Off-gas/tail-gas drum
- Control system

Wet Chemical/Solvent Systems

Wet chemical or solvent CO_2 removal systems present their own challenges in design. We will focus on amine solvent systems here, since they are most common. Hot carbonate and other systems have some of the same issues, with slightly different flavors.

A couple of the challenges considered here are:

- *Corrosion management*

  As with most acid gas removal systems, metallurgy of the system needs to consider the materials handled. Some specific considerations with hydrogen plant systems are:
  - Amine scrubbing solutions subject equipment to potential amine cracking. Post-weld heat treatment of amine handling systems is advisable.
  - The amine regenerator/CO_2 stripper tower and overhead are subject to carbonic acid attack. Stainless steel piping is needed.
  - Carbonic acid attack is also seen in some unexpected places around the stripper: shell near the reboiler return line and the piping and shell around the stripper inlet line. It is advisable to consider alloying these areas and watching the maximum velocities.
  - In MEA amine systems, arsenic compounds may be used for corrosion inhibitors. These are effective, but introduce an additional hazard during operation and maintenance.
  - Solvents tend to build heat-stable salts. These need to be eliminated to keep the solution healthy. Some systems employ side-stream reclaimers to remove the salts. They can also be removed by ion exchange using an outside service company.
- *Filtration*

  The circulating solvent streams will build up corrosion products and other solids, in spite of corrosion inhibitors. These materials need to be removed from the stream. This is normally accomplished by side-stream filtration of a slipstream off the main circulating flow. The slipstream usually passes through a cartridge filter and may also go through an activated carbon filter to remove potential foaming materials or trace organics that you do not want in the solvent.

Materials Damage Mechanisms

There are a number of mechanisms that can cause damage to materials in a hydrogen plant. Some of these have been alluded to in the above discussion. For a complete review of the damage mechanisms and management practices, please refer to API RP-571. This is an excellent resource for any type of system.

For general reference, the mechanisms highlighted in RP-571 for hydrogen plants are summarized in Table 3.

Operations and Monitoring

Operations

The following discussion will briefly describe the main operating phases of an SMR hydrogen plant from start-up through shutdown. Initial commissioning of a hydrogen plant is beyond the scope of this discussion. For additional detail, consult the references listed at the end of this chapter.

- *Start-up*

  Start-up of a hydrogen plant follows this general outline:
  - Inventory water in the steam system. If the unit has solvent CO_2 purification, the solvents are inventoried in parallel.
  - Air-free the process system with nitrogen.
  - Pressure and circulate the process system with a noncondensable gas.

    This is often nitrogen, but pure hydrogen or natural gas can also be used. Do not use reformer hydrogen.

    It is also possible to heat the furnace to 800 F in the flue without circulation. The downside of this approach is that the high-temperature shift converter is not heated up, so it must be bypassed when steam is introduced and then heated later with process flow.

    If the system uses a LTS converter, this converter should be bypassed. It will be activated later.
  - Fire the reforming furnace and heat to about 800 °F in the *furnace outlet flue gas* (convection inlet) at 50–100 °F per hour.

    When the flue gas reaches the required conditions, the SCR (if applicable) can be started.

    Initially, you would use only a few burners evenly distributed in the furnace. As the furnace heats up, add more burners and ensure they are evenly distributed in the firebox to avoid tube failures from flame impingement. These comments apply throughout the start-up procedure.
  - Slowly start process steam and increase steam rate to at least 50 % of design with continued heating to 1,000 °F in the *process outlet* temperature from the furnace.

    Inert circulation can be discontinued at this point since the main flow is now steam.

  There may be condensation of steam in the HTS converter initially, but the converter will dry out. Do not heat the shift converter too fast to avoid catalyst damage.
  If the initial heat up to 800 °F did not use inert gas flow, then the HTS converter should be bypassed and heated up with steam at a controlled rate once the main flow is stable.
- Continue increasing temperature and steam rate to feed gas inlet conditions at no more than 100 °F per hour – normally about 1,200–1,300 °F on the *process outlet* from the SMR furnace.
- Start clean feed gas.
  If the system has a low-temperature shift converter, the converter is bypassed.
  Adjust the feed gas purification conditions to clean up the feed gas. You should have no detectable H_2S in the reformer feed gas (<0.01 ppm).
- Maintain a high steam/carbon ratio (>~6.0) in the reformer as the reforming catalyst and HTS converter catalyst are activated over a few hours.
- Continue heating to 1,350–1,550 °F *process outlet* temperature from the SMR furnace with the high steam/carbon ratio. Adjust the SMR and HTS temperatures to your start-of-run targets.
- If the hydrogen plant uses PSA purification, the PSA can be purged out with nitrogen and then started up, initially taking no product.
  Once the product hydrogen is on spec, the product can be sent to the users.
  The PSA off-gas can be sent to the SMR furnace for firing once the PSA is stable.
- If the hydrogen plant uses wet chemical purification, the absorber system can be started and stabilized.
  The methanator can be heated up before being brought on line at the initial target temperature. Nickel carbonyl formation is a potential concern here. The methanator temperature must be over 400–450 °F before introducing gases containing CO.
  CO_2 production can start when the system is stable.
- Once the main process is stable, the low-temperature shift converter is normally activated and brought on line. This may be a couple of days after the main process.
- Finally, move the steam/carbon ratio to the target level and begin adjusting operating conditions to targets.
  Adjust the SMR furnace to achieve the desired methane slip.
  Adjust the HTS and LTS converters to obtain the target CO slip.
  Adjust the PSA cycle or the solvent system conditions to obtain and maintain targets.
  Export surplus steam.

- *Routine operations*
  There are not a lot of major adjustments required for hydrogen plant operating conditions normally. The rate may be increased or decreased with corresponding adjustments, but certain targets stay the same. Note that hydrogen plants operate

best at a steady, stable rate. They do not respond well to frequent rate changes. Daily rate changes are usually tolerable; hourly changes make operation difficult.

The most common adjustments to operating conditions are listed below. This is, by no means, a comprehensive listing.

– *Feed purification*

Adjust temperatures and/or absorber flows and loadings to maintain non-detectable H_2S in the reformer feed.

– *Reforming furnace*

Maintain steam/carbon ratio at design. Slight changes may be needed, depending on the feedstock.

Pressure is not normally changed.

Reformer process outlet temperature is controlled to maintain the target methane slip.

Firebox-side control of the reforming furnace is similar to other furnaces, with appropriate safety interlocks. The PSA gas may introduce fluctuations that must be managed by the controls.

Adjustments to manage methane slip can be estimated from the figures included in the overall process discussion section. These figures relate methane slip, steam/carbon ratio, temperature and pressure for methane, and naphtha feedstocks. Essentially, they are graphical representations of the SMR equilibrium with parameters in the normal operating ranges.

If the furnace has an SCR, the vaporizer and ammonia flows will be automatically controlled. They just need to be monitored.

– *Shift conversion*

Adjust the shift converter inlet temperature to obtain the target outlet CO slip. For quick estimates relating CO slip, temperature, and steam/carbon ratio, the following equation can be used:

$$\ln(\mathrm{CO}) = 3.5514 * \ln(\mathrm{T}) - 1.6775 * \ln(\mathrm{S/C}) - 20.338 \tag{21}$$

where:

CO = v% CO in dry gas

T = Temperature at reactor outlet, °F

S/C = Initial steam/carbon molar ratio to SMR

Note that, because the reaction does not change the number of moles in the vapor, there is negligible pressure effect in this range.

– *Product purification*

For a PSA system, the time on adsorption for a single bed is adjusted to maintain purity. Sometimes, this is part of the “capacity” factor. The control system makes the other necessary adjustments. Routinely check the PSA valves for leakage around the packings and smooth action.

For a solvent purification system, the absorption and regeneration flows, temperatures, pressures, and solvent loadings need to be kept within the design limits.

  - *Steam systems*

    Adjust blowdown rates to target conductivities. This may be automatic.

    Adjust BFW preheat conditions. This must be coordinated with other conditions.

    The steam system controls will normally handle changes in the plant.

    Stripping conditions in the shift condensate degassing system need some attention to ensure the CO_2 is removed. Use the system design as a guideline to what conditions to expect.

- Shutdown

  Shutdown of a hydrogen plant generally follows the same sequence, regardless of the type of unit. The primary steps are:

  - Cool reforming furnace to 1,200–1,300 °F process outlet temperature.
  - Stop feed, but continue steam. Stop the PSA, if present.
  - Steam the catalysts for 2–6 h at 1,200 °F in the reformer.

    The LTS converter may be bypassed and shut down separately.
  - Cool the reforming furnace with steam flow at no more than 100 °F per hour to about 800 °F at the flue gas outlet from the radiant box.

    During this time, inert gas flow can be reintroduced to the process, if desired. Inert flow will help cool the HTS converter and other equipment.

    If the unit has a methanator, it should be removed from the flowing system and separately purged at least five times with nitrogen before cooling below 400–450 °F to prevent nickel carbonyl formation.
  - Stop steam flow. If using inert flow, continue cooling with the inert gas. The SMR furnace can be shut down when firing reaches minimum.
  - Purge the entire system with nitrogen to eliminate hydrogen and hydrocarbons. Test for CO in the gas. The concern is that nickel carbonyl may form at low temperatures ($<\sim$450 °F). CO must be less than 10 vppm in the system if you are below this temperature. The methanator is especially susceptible to nickel carbonyl and should be managed separately as noted above.

Monitoring

Table 6 provides a list of the key variables to monitor in an SMR hydrogen plant, along with the frequency. The following discussion describes calculation of some of these key variables. Issues around tube wall temperature monitoring in reforming furnaces are also discussed.

Most catalyst suppliers for hydrogen plants will provide a detailed material balance and analysis of your unit's performance if you provide them with operating data. Table 7 indicates the information needed to obtain a detailed performance analysis from a supplier. You should be continually monitoring the unit yourself; but, it is still a good idea to have a third party evaluation periodically (say quarterly). This service is usually provided at no cost.

- *Material balance*

  Successful monitoring of an SMR hydrogen plant process starts with a good material balance for the plant at a point in time. The flow, composition,

Table 6 Typical key SMR hydrogen plant monitoring parameters

Monitored variable	Frequency	Basis
Overall unit		
Feed rate(s)	Daily	Trend meters
Production rate(s)	Daily	Trend meters
Material balance	Weekly/monthly	Detailed calculation
Feed pretreat process		
Hydrogen recycle rate	Daily	Trend meter
Hydrotreater temperatures	Weekly	Review data
Zinc oxide bed outlet H_2S	Weekly	Look for breakthrough
SMR and shift processes		
Steam/carbon ratio	Daily	Trend, verify weekly
Reformer outlet temperature	Daily	Trend
Reformer outlet pressure	Daily	Trend
Reformer tube pressure drop	Weekly	Trend normalized dP – watch for jumps
Reformer max tube wall temp	Weekly	Trend, watch for hot spots
Methane slip	Daily	Trend, adjust
Reformer ATE	Weekly/monthly	Calculate, trend – watch for deactivation
Shift converter outlet temps	Daily	Trend
Shift converter rises	Daily	Trend
CO slip	Daily	Trend, adjust
HTSC ATE	Weekly/monthly	Calculate, trend – watch for deactivation
LTSC temp front location	Weekly/monthly	Calculate, trend – watch for deactivation
Boiler water chemistry	Weekly	pH, conductivity, hardness – adjust
Steam production/ distribution	Weekly	Trend – watch for loss in rates
SCR performance	Weekly/monthly	Watch for increasing NH_3 rqmt => deactivation
Product purification		
Overall purification		
Product purity, % H_2	Weekly	Watch for loss of purity, ethane
Product H_2/unit feed	Weekly	Watch for loss of efficiency, trends
Solvent/wet chemical		
Lean and rich loadings	Weekly	Keep within design limits
Methanator rise	Daily	Trend, watch for increases => CO_2 removal problem
Methanator temp front location	Weekly/monthly	Trend location in bed => deactivation
CO_2 production rate	Daily	Trend
Pressure swing adsorption		
Recovery, v% raw H_2	Weekly	Calculate and trend => efficiency loss, optimization

Table 7 Example of data needed by third party to analyze hydrogen plant performance

Date:	
Unit:	
Location:	

Notes:

1. Provide as much actual data as possible.
2. Use only measured values.
3. Provide process PFD.

SMR Design Data		
Number of tubes		
Tube ID/OD	inches	
Fired/loaded height	feet	
Tube material		
Type of furnace		
Key Flow Rates		
Design feed rate	MMscfd	
Feed rate	MMscfd	
Recycle H2	MMscfd	
Raw H2 to purification	MMscfd	
Total product	MMscfd	
PSA offgas	MMscfd	
Process steam	lbs/hr	

Gas Analyses		**Feed**	**Reformer**	**HTS**	**LTS**	**Meth In**	**Meth Out**
H_2	v%						
N_2	v%						
Ar + He	v%						
CO	v%						
CO_2	v%						
CH_4	v%						
C_2	v%						
C_3	v%						
C_4s	v%						
C_5s	v%						
C_6-Plus	v%						
Sulfur	ppm						

Reactor Data		**Hydrotreater**	**Cl-guard**	**ZnO**	**Reformer**	**HTS**	**LTS**	**Methanator**
Catalyst type								
Bed diameter	feet							
Bed height	feet							
Catalyst volume	cubic feet							
Inlet Pressure	psig							
Outlet pressure	psig							
Inlet temperature	°F							
Outlet temperature	°F							
Other bed temperatures	°F & Location							
					Provide IR Survey			

pressure, and temperature for the process streams at the following points are required for the best results. The minimum data required are indicated by asterisks below:

- Feed gas ahead of pretreat system
  Gas chromatograph (GC) analysis* – note that even natural gas feed will have variable composition
  You especially need the moles of carbon per mole of feed*
  Flow rate*
- Feed pretreat system inlet
  Feed gas analysis from above
  Flow rate of feed and recycle hydrogen
- Reforming furnace inlet
  Composition calculated from pretreat system inlet after reactions plus process steam flow
  Flows for feed gas and steam*

- Reforming furnace outlet/HTS inlet

  Ideally, you want a GC of the reformer outlet gas, but this is a hard sample to take.

  You can back calculate the composition from the methane contents in the raw hydrogen to purification*.

  Total flow will be the same as the reformer inlet.
- LTS inlet (if applicable)

  Need a GC of the HTS converter outlet

  Total flow is normally the same as the HTS outlet.
- Raw hydrogen before purification

  Need a GC of this dry gas going to the purification system*

  Assume the gas is saturated with water

  Need the total gas rate*
- Product hydrogen to methanator (if applicable)

  A GC of this is nice, but it can be estimated from the raw hydrogen by removing the CO_2.

  The stream will be saturated with water at absorber overhead conditions.
- Product hydrogen

  Need a GC of this stream*

  Need flow rate*
- Product CO_2 (if applicable)

  This stream will be mostly CO_2, so it mainly needs the temperature and pressure.

  It will be saturated with water at production conditions.
- PSA off-gas (if applicable)

  GC of the gas*

  Flow rate*
- Shift condensate

  This stream is normally not metered, so the flow must normally be calculated or estimated from the other streams.

  It may be sampled; the CO_2 content can be estimated assuming the water is saturated with CO_2 at production conditions.

  If there are hot and cold shift effluent separators, you need to estimate the flows and CO_2 contents for each separator.

Using the available data, a component-by-component material balance can be constructed, along with the pressure and temperature for each stream. An example of how to do this is in the Appendix of this chapter.

Where data are not available (especially GCs), the data can be calculated assuming equilibria and using the overall equation for SMR reforming (Eq. 20). Remember that you want the *wet* compositions at each point because water is a major participant in many of the reactions.

Usually, this can all be built into a spreadsheet that will reconcile all the data. This takes an initial effort to set up; but once the spreadsheet is built, it greatly improves your ability to analyze the hydrogen plant operation.

Once you have a reasonable material balance, catalyst activity tracking and other analyses are possible.

- *Steam/carbon ratio*

  The molar ratio of steam to carbon is one of the most critical parameters to monitor in an SMR. To calculate the steam/carbon ratio (sometimes abbreviated S/C):

  - Use the feed detailed analysis to calculate the moles of carbon per mole of feed. Include any CO or CO_2 in the feed as part of the calculation.
  - Calculate the total moles of feed using the feed flow meter, with corrections. Normally, this will be moles per hour of feed.
  - Calculate the molar rate of carbon in the feed from the moles carbon per mole feed times the feed rate. This will normally be moles carbon per hour.
  - From the process steam flow meter, calculate the moles of steam per hour.
  - Divide the moles steam per hour by the moles carbon per hour to get the steam/carbon ratio.

  For liquid feedstocks where composition is not necessarily available, the carbon in the feed can be estimated using C/H ratio correlations from API based on boiling range and specific or API gravity.

  The S/C must be maintained within a specified range. A high ratio will make more hydrogen, but loses some efficiency in the process. A low ratio leads to coking and deactivation of the reforming catalyst, as well as making less hydrogen.

  Note that you do not need the whole material balance to calculate the steam/carbon ratio. Often, the ratio is calculated online with sufficient accuracy using average compositions to allow the direct control of the ratio by the basic process control system.

  See the Appendix for a sample calculation of the corrected steam/carbon ratio.

- *Reforming catalyst approach to equilibrium*

  Using the reformer outlet composition from the material balance and the equilibrium K values, the equivalent reformer outlet temperature that the equilibrium corresponds to can be calculated. This calculated temperature is subtracted from the actual temperature to obtain the "approach to equilibrium" (ATE) temperature. This is a way to track reforming catalyst activity.

  Note that an equation for calculating the equilibrium temperature from the calculated K value is included in the overall reforming process discussion in section "Primary Reforming" of this chapter (Eq. 13).

  The ATE value is normally negative with fresh catalyst. The actual approach is zero, but heat loss from the actual catalyst outlet to the reformer outlet temperature measuring point results in the negative value. This is not really a problem, because you will track catalyst activity by relative changes in the ATE.

  Over time, the reformer ATE trends upward as the furnace eventually cannot reach equilibrium. At some point, you decide to replace the catalyst. Reformer catalyst can typically operate over 5 years, unless it is poisoned or coked. However, even a few minutes with very low or no steam in the feed may dictate an immediate end of run.

The ATE value calculated will bounce around significantly, so you are really looking for a trend. Another hint that the catalyst is spent is if you detect any ethane above ~0.05 v% in the product hydrogen.

See the Appendix for a sample calculation of the reformer approach to equilibrium.

- *HTS catalyst approach to equilibrium*

  Similar to the reforming furnace, you can calculate the approach to equilibrium from HTS using your material balance compositions and the previously provided equilibrium information.

  Note that an equation for calculating the equilibrium temperature from the calculated K value is included in the overall reforming process discussion in section "Primary Reforming" of this chapter (Eq. 16).

  The HTS will not completely reach equilibrium, normally. A plot of the ATE in the HTS will trend upward with catalyst deactivation. You will need to decide at what point you want to replace the HTS catalyst. Usually, this will be determined by the amount of CO slipping and your ability to handle it downstream. The ATE plot does allow early identification of major problems.

  See Appendix for a sample calculation of the HTS converter approach to equilibrium.

- *PSA recovery*

  For units with PSAs, it is important to track the hydrogen recovery in the PSA. Poor recovery may indicate problems with the valves as well as potential adsorbent issues.

  Using the material balance, you can determine the hydrogen recovery in several ways. The most straightforward approach is to determine the percentage of the incoming hydrogen that exits in the product hydrogen stream. Since the product hydrogen is essentially 100 % hydrogen, the recovery is just the product hydrogen flow rate divided by the PSA feed gas % hydrogen times feed gas rate, all times 100 %.

  This recovery should be around 85–87 %. If it is lower, the PSA is not performing and needs to be further investigated. If it is above about 92 %, there is probably a metering or analysis error.

  See the Appendix for a sample calculation of PSA recovery.

- *Reforming furnace tube wall temperature monitoring*

  One of the trickiest aspects of SMR furnace operation seems to be obtaining accurate tube wall temperatures. When you "shoot the tubes" with an infrared thermometer, there are a number of interferences:

  - You are looking through hot combustion gases that have some luminosity.
  - You are getting reflections from the very hot furnace refractory walls.
  - You may be seeing part of the furnace refractory in the background.
  - The emissivity of the tube walls may be different or the tube wall may have a deposit on it.

  To manage some of these interferences, IR thermometers for hydrogen plants look at a relatively narrow frequency of IR radiation that minimizes the gas interference. The measuring zone on an IR thermometer is usually a small spot focused on the tube. A laser sight may be used. Equations are used to correct the reading for background and reflected radiation. Still, the resulting tube wall temperature measurements are probably not accurate to more than +/− 50–100 °F. There are techniques available, such as the "gold cup measurement method," which directly measure tube wall temperature by contact. These can be used to verify other readings or to calibrate readings.

Some refiners routinely take infrared photos of their tubes to monitor issues and trends. This is a good approach for trending, but, from experience, these photos seem to indicate higher temperatures than other methods.

- *Reformer pressure drop*

  Pressure drop in the reformer tubes is one of the best and simplest methods to track catalyst coke buildup and catalyst crushing. The pressure drop needs to be normalized for rate.

  To normalize the pressure drop in a furnace, you can use Eq. 22. The flow factor is usually the volumetric flow of steam plus feed gas. You could refine the factor further, but the simple volumetric flows at STP seem to work fine. The exponent, n, is determined by trial and error to minimize scatter of the normalized dPs. Once set, the same value of n is used consistently for a given plant, and it is usually between 1 and 2:

  $$\mathrm{dP_{norm}} = \mathrm{dP_{act}} \times (\mathrm{F_{norm}}/\mathrm{F_{act}})^{\mathrm{n}} \tag{22}$$

  where
  $\mathrm{dP_{norm}}$ = normalized pressure drop
  $\mathrm{dP_{act}}$ = measured pressure drop
  $\mathrm{F_{norm}}$ = flow factor at normalized condition
  $\mathrm{F_{act}}$ = flow factor at measured conditions
  n = scaling exponent, determined by best fit

  The normalized pressure drop is trended with time. When excessive coking incidents or shutdowns occur, you will see step increases in the normalized pressure drop. The maximum allowable pressure drop will normally be set by either (1) the ability to get feed gas into the plant or (2) the ability of the purification system to deliver product at the required pressure. Once the maximum dP is reached, the reformer catalyst has to be replaced.

  See the Appendix for a sample calculation of normalized reformer pressure drop.

- *LTS converter activity*

  Tracking of catalyst activity in a low-temperature shift converter is accomplished by tracking the position of the temperature rise front (as a percentage of the total bed depth) as it moves through the catalyst bed. The catalyst is poisoned slowly in service by both sulfur and chloride in a plug-flow manner. It is much more sensitive to these poisons than reforming or HTS catalysts.

  Replacement of the LTS catalyst should be planned when the deactivated catalyst reaches about 70–80 % of the bed depth. The position of the deactivated catalyst front can be plotted with time to project end of run.

Note that if there is a sulfur slip problem in the feed gas pretreatment system, the LTS catalyst will take a large hit and may need to be replaced immediately. Activity of this catalyst cannot be recovered in service.

- *Methanator activity*

  Similar to a LTS catalyst, methanator catalyst will deactivate in a plug-flow manner. The methanation reaction occurs quickly, producing a sharp temperature rise in the catalyst bed. The position of this sharp rise can be trended using the available temperature points at different elevations in the bed. The bed should be replaced when the rise is about 70–80 % of the way through the bed.

  Fortunately, methanator catalyst is fairly robust, so it does not deactivate quickly.

Catalyst Changeout

Fixed-Bed Reactors

Changeout of the fixed-bed catalysts and sorbents in a hydrogen plant is similar to changeout of fixed beds in any other process units. There are a few specific points highlighted below.

- Methanator and hydrotreating catalysts contain nickel and may generate nickel carbonyl if any CO is present.
  - In the methanator, CO may be left by inadequate purging during shutdown. Refer to comments in the generic shutdown procedure.
  - Hydrotreating catalyst that has coke on it can begin low-level combustion and generate CO. The CO may react with nickel on the catalyst to release nickel carbonyl.
  - In both cases, the reactors should be routinely monitored for CO whenever work is occurring in or around the reactors.
- PSA adsorbents are normally dense loaded using a method specified by the technology provider. The pressure drop through each vessel must be as close as possible to the same value, so care must be taken during the dense loading process.
- PSA adsorbents generate a large amount of heat if they are exposed to water, even atmospheric moisture. Do not let these materials get wet and do not unload or load adsorbents in rain.
- Shift catalysts, both HTS and LTS, will probably be self-heating if they contact air. Monitor the unloading atmosphere to keep them blanketed with inert gas.
- Zinc oxide, carbon adsorbents, and certain other solids used in a hydrogen plant reactor do not hold up well during handling. They will generate a lot of dust. Respiratory protection and dust management practices should be employed by anyone near these materials.
- Because of the high nickel content of methanator catalyst, respiratory protection must be used by anyone handling either fresh or used methanator catalyst.

- Get samples of all your spent materials for postmortem analysis. Your catalyst supplier will generally be willing to provide some analyses of the spent catalysts to identify poisoning mechanisms and other potential issues.

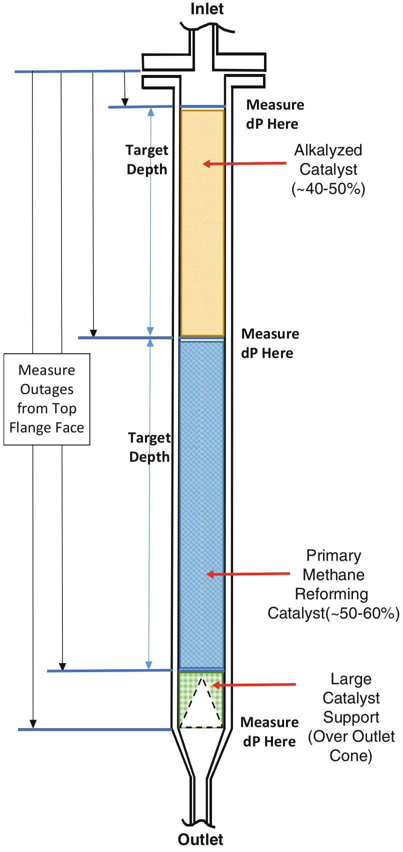
Work with your catalyst and adsorbent suppliers and the catalyst handling personnel to ensure the materials are loaded and unloaded safely and correctly. This will provide the best performance from the fixed-bed reactors and absorbers/adsorbers.

SMR Reformer Tubes

Unloading and loading of reformer tubes presents some special challenges. Each tube is a small, fixed-bed reactor. A few of the critical items are noted below.

- The reforming catalyst contains high levels of nickel, which is a known carcinogen. Anyone handling the catalyst or around catalyst dust should be wearing respiratory protection. Vacuum systems and dust suppression measures should be used.
- Catalyst is unloaded from the reformer furnace tubes by vacuuming. It may be necessary to break the catalyst up to get it out. Contractors experienced in hydrogen plant catalyst replacement are accustomed to the procedures.
- Reloading of catalyst is best accomplished with one of several available dense loading methods (Unidense, Spiraload, Catcade, etc.). Sock loading can be done, but is not as effective (i.e., you will probably have to vacuum out and reload more tubes to meet pressure-drop constraints).
- A typical catalyst tube loading and loading data sheet are shown in Table 8.
- Every tube in the reforming furnace must have as close to the same pressure drop as possible because flow to the tubes is distributed by pressure drop. The dPs of all tubes will be measured (1) empty, (2) after loading each layer of catalyst, and (3) after all the tubes are completely loaded. When measuring the dP on each layer, load all the tubes before taking the measurements and do not load tubes while you are taking measurements. Each dP should be within +/− 10 % of the average dP using a pressure-drop measurement apparatus like that shown in Fig. 17. An experienced hydrogen plant catalyst loading company will have their own pressure-drop apparatus. Dense loading techniques generally are able to achieve +/− 5 %.
- Sample the spent SMR catalyst from each catalyst layer at several points in the furnace. Composite these samples by layer for analysis. Your catalyst supplier will generally provide a postmortem analysis of the catalyst to identify poisoning mechanisms and enable him to advise you on future operations. This is especially important if you experience a rapid, unexpected poisoning event for which you could not identify a cause.
- When loading, make sure you get the right catalysts in the right order in the tubes. This is most easily accomplished by only loading one type of catalyst at a time throughout the entire furnace.

Table 8 Typical SMR furnace tube loading and data record sheet

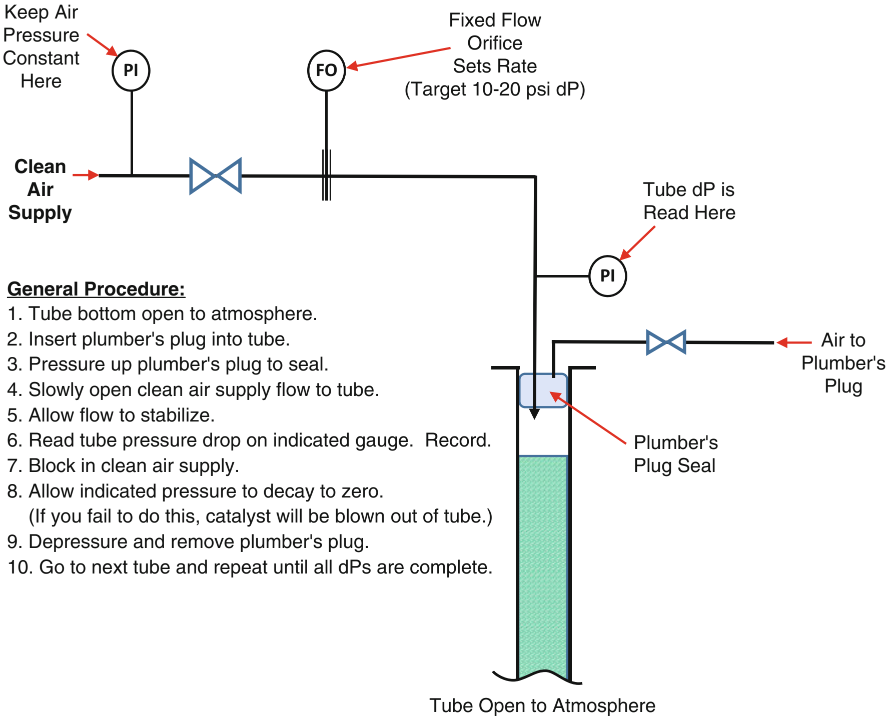


Loading Date:

Unit/Equipment:

Page ______ **of** ______

Loading Measurements													
	Bottom Support			**Primary Reforming**			**Alkayzed (Top) Catalyst**			**Video**	**Pressure Drops**		
	Outage	**Volume**	**Weight**	**Outage**	**Volume**	**Weight**	**Outage**	**Volume**	**Weight**	**Check**	psi		
Tube No	ft-in	cft	lbs	ft-in	cft	lbs	ft-in	cft	lbs	Empty	Empty	Middle	Full



General Procedure:

1. Tube bottom open to atmosphere.
2. Insert plumber's plug into tube.
3. Pressure up plumber's plug to seal.
4. Slowly open clean air supply flow to tube.
5. Allow flow to stabilize.
6. Read tube pressure drop on indicated gauge. Record.
7. Block in clean air supply.
8. Allow indicated pressure to decay to zero.
   (If you fail to do this, catalyst will be blown out of tube.)
9. Depressure and remove plumber's plug.
10. Go to next tube and repeat until all dPs are complete.

Fig. 17 Procedure for measuring SMR furnace tube pressure drops

- It is a good practice to select a few tubes in different sections of the furnace to load as "test tubes" before beginning to load the entire furnace. Usually, you pick about 1–3 % of the furnace tubes as test tubes. Load this subset of tubes just like you load the rest of the furnace: (1) take empty dPs, (2) load each layer and then measure dPs, and (3) take final dPs after loading. Track the weight of catalyst in each layer of the test "tubes" (and how many buckets or socks are required for each layer). The resulting data will act as a check on loading the balance of the furnace.
- After a tube is loaded, cover the tube opening to ensure nothing gets accidently dropped into the tube before closure.

Loading the SMR furnace sounds more difficult than it is. An experienced hydrogen plant loading contractor will be able to perform the work adequately.

Troubleshooting

As alluded to in the foregoing discussion, there are several things that can result in problems when operating a hydrogen plant. Table 9 provides a matrix of the most common symptoms and related problems in the SMR process, along with potential

Table 9 Common SMR process problems troubleshooting chart

Type of symptom	Observation	Possible problem	Possible remedies
Uneven SMR tube temperatures	Discolored lower half of tubes	Catalyst ≥ 5 years old	
		Settling	Plan catalyst reload
		Crushing	Plan catalyst reload
		Catalyst 2–5 years old	
		Settling	Track, potential reload
		Crushing due to shutdowns	Plan catalyst reload
		Catalyst ≤ 2 years old	
		Poisoning	Steam catalyst, potential reload if not recovered
		Coking	Immediately steam catalyst, potential reload
		Bad load	Reload catalyst if too severe
		Unstable operation	Check feed analysis, instruments, stabilize process
	Discolored upper half of tubes	Whole tube hot	
		Plugged tube	Pinch or cap tube before failure, reload if widespread hot tubes
		Maldistribution	Check steam rate, increase steam/carbon
		Boiler carryover	Check boiler chemistry, level instruments
		Very top of tube hot	
		Crushing (empty tube zone)	Plan catalyst reload if widespread
		Hot middle of tube	
		Flame impingement	Adjust burners and draft
		Wrong catalyst loaded	Reload catalyst if not tolerable
		Sulfur poisoning	Check ZnO slip, potential upstream upsets
		Giraffe-necking (spotty tubes)	
		Isolated poisoning	Look for poisoning source, increase steam/carbon, potential to steam catalyst
		Low steam/carbon	Increase/correct steam/carbon, check feed, check flow
		Random hot spots, stripes	
		Voids in catalyst load	May be able to vibrate tube, otherwise reload is widespread, may cap/pinch individual tubes

(*continued*)

Table 9 (continued)

Type of symptom	Observation	Possible problem	Possible remedies
Increased SMR pressure drop	Gradual increase in dP	Tube color even	
		Slow sulfur or other poisoning	Check ZnO outlet H_2S, check upstream sources
		Tube color uneven	
		Feed too heavy	Check feed analysis, increase steam/carbon
		Boiler carryover	Check boiler chemistry, level instruments
		Low steam/carbon	Check feed analysis, increase steam/carbon
	Rapid increase in dP	After upset	
		Bad sulfur or other poisoning	Steam catalyst, potential reload if not recovered
		Catalyst damage	Probable reload, unknown problem
		Heavy feed during upset	Immediately steam catalyst, run high S/C for extended period,
		Compaction	Reload catalyst
		No upset	
		Bad dP instrument	Check instrument
		Bad metering	Check meters
		Low steam/carbon	Check feed analysis, increase steam/carbon
		Heavier feed than known	Check feed analysis, increase steam/carbon
High methanator temperature	High rise	High Inlet CO2	
		CO2 removal system failure	Correct CO_2 removal system problem, bypass methanator or shutdown to fix
		Low reformer outlet temperature	Check feed, S/C, adjust SMR temperature
		Poor shift converter operation	Check feed, S/C, adjust HTS/LTS temperatures
		Low steam/carbon ratio	Check feed analysis, increase steam/carbon
		High feed carbon content	Check feed analysis, increase steam/carbon
		Sulfur poisoning of reformer or shift	Steam reformer catalyst, replace shift catalyst
PSA system problems	PSA system problems are beyond the scope of this chart. Work with your PSA vendor to troubleshoot PSA problems		

remedies. This table is by no means all-inclusive, but can be used as a starting point for troubleshooting.

SMR Process Flow Sheet Variations

The foregoing section described the most common, and simplest, process flow sheet for carrying out steam-methane reforming with a couple of minor variations in the product hydrogen purification system. There are other process variations in commercial operation. These are less common, but may be encountered or considered for a specific plant. Some variations may be helpful in debottlenecking or production rate increases. The three most common variations are briefly described below.

Pre-reforming

A pre-reformer is a fixed-bed reactor installed upstream of the main SMR reforming furnace. The pre-reformer performs the cracking part of the reactions (Eq. 8) and does some minor reforming. At the pre-reformer outlet, the feedstock has been converted to essentially all methane for the SMR furnace. This enables the furnace tube volume to be devoted to the SMR reaction.

A pre-reformer also acts as a guard bed for the main reforming catalyst; it takes any impacts from poisoning and protects the furnace catalyst. Pre-reformers can often be taken off-line and changed out, while the main process continues, albeit with an easier feed during the changeout. Pre-reformer catalyst is permanently deactivated by sulfur, chlorine, and other poisons. The pre-reformer helps open up the possible feedstocks for a hydrogen plant and levels out feedstock variations.

Heat is supplied to the pre-reformer by replacing one of the convection steam generation coils with a pre-reformer preheat coil. This means less steam generation from the plant, but improves hydrogen production efficiency.

Some process designers like to always include a pre-reformer in their flow sheet. Others offer pre-reforming as an option or for increasing rate. Addition of a pre-reformer to an existing hydrogen plant can enable it to make about 10–20 % more hydrogen and use a lower steam/carbon ratio. The shift cooling and product purification systems still need to have enough capacity to handle the incremental raw hydrogen produced, so some additional debottlenecking may be required.

This technology is offered by Haldor Topsoe, ThyssenKrupp Uhde (Uhde), CB&I/HoweBaker, Technip, Kellogg Brown & Root (KBR), and others.

Exchanger Reforming/Post-Reforming

An exchanger reformer uses waste heat from the SMR furnace to reform additional feed and make more hydrogen. The post-reformer is usually an exchanger with catalyst-packed tubes. Heat is supplied by waste heat in the SMR furnace effluent or convection section at the expense of steam generation.

This type of reformer can also be used in place of a primary reformer with tight heat integration.

Additional feed gas and steam may be introduced ahead of the post-reformer to provide incremental production. About 35–40 % additional hydrogen can be made by post-reforming. As with the pre-reformer, the shift cooling and product purification systems may have to be debottlenecked to take advantage of post-reforming.

This technology is offered by Haldor Topsoe, KBR, Uhde, and others.

Autothermal Reforming

Autothermal reforming (ATR) can be added in parallel to a standard SMR furnace to significantly increase hydrogen production or it can be used in place of the conventional SMR furnace. In autothermal reforming, feed gas is partially burned using pure oxygen. Steam may be injected along with the feed. The CO_2 produced is recycled to moderate the combustion temperatures. The heat from burning is used to drive the reforming reactions in the balance of the feed. You make CO directly in the combustion process and then shift it to hydrogen. No catalyst is required; however, some systems do incorporate reforming catalyst. The ATR effluent joins the main hydrogen plant gases going to the HTS converter and flows through the rest of the plant.

An ATR can also be used in series as a post-reformer. You find ATRs more commonly in ammonia or methanol manufacture than refinery hydrogen production, since ATRs can easily make the necessary synthesis gas.

This approach to reforming is related to gasification, although gasification usually refers to making hydrogen from residuum/pitch or solids by partial oxidation followed by a sour shift reactor and product cleanup.

As with the other variations, if an ATR is added, the cooling and purification system capacities may need to be debottlenecked. This type of reformer also requires availability of pure oxygen, which usually means proximity to an air separation plant.

This technology is offered by several suppliers, including Haldor Topsoe, KBR, Süd Chemie, Lurgi, Imperial Chemical Industries, and Johnson Matthey.

Partial Oxidation

Introduction

Partial oxidation (POX) has been used commercially to produce hydrogen from very heavy liquid feedstocks (resid, asphalt, tar) and solids (coal, petroleum coke). Essentially, this is a gasification process. More commonly, the technology is used to generate synthesis gas for other products, however. Texaco had several POX hydrogen plants at one time, but these have been largely replaced by the more reliable and easier to operate SMR furnace plants. Still you will occasionally find POX plants associated with refineries.

POX is essentially the same as autothermal reforming discussed above. The distinction drawn here is between the types of feedstocks. In autothermal

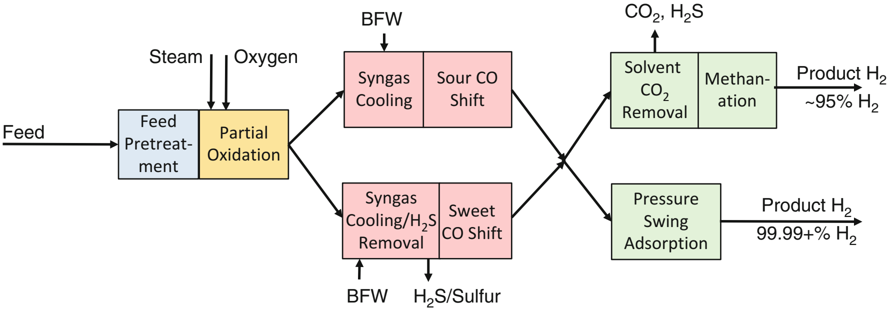


Fig. 18 Block flow diagram of partial oxidation hydrogen plant options

reforming, we have focused on gases through naphtha. There are several of that type of plant in operation. The autothermal reformer feedstock has generally been cleaned to SMR reformer standards, so sulfur in minimal.

For a POX unit, the feedstock generally still contains sulfur, ash, and other contaminants. This has equipment, catalyst, and reliability implications.

Process: Step by Step

A POX hydrogen plant process can be broken into three primary steps, as illustrated in Fig. 18:

- Gasification of the feedstock by partial oxidation
- Shift reaction to increase hydrogen generation
- Product purification and recovery

Along with these sections, there is a major boiler feedwater and steam generation system, much like for an SMR plant.

We will consider each of these systems in turn.

Gasification/Partial Oxidation

The POX process starts with a gasifier or combustor. In the gasifier, the feedstock that has been slurried and/or heated is introduced into a combustor. In the combustor, the feed is burned with pure oxygen, in an oxygen-deficient atmosphere, according to Eqs. 23 through 27. Steam is injected with the feed for reaction and atomization:

$$C_xH_y(l,s) + {}^x/_2O_2(g) \rightarrow xCO(g) + {}^y/_2H_2(g) + \text{Heat} \tag{23}$$

$$CO(g) + {}^1/_2O_2(g) \longleftrightarrow CO_2(g) + \text{Heat} \tag{24}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) + \text{Heat} \tag{25}$$

$$CH_4(g) + H_2O + \text{Heat} \longleftrightarrow CO(g) + 3H_2(g) \tag{26}$$

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g) \tag{27}$$

Because the sulfur and other contaminants have not been removed from the feed, the sulfur will be converted to H_2S and some SOx. Nitrogen compounds will similarly be converted to NH_3 and oxides.

The products equilibrate at the combustor outlet conditions. The products will include CO, CO_2, H_2O, H_2, H_2S, SO_2, NO_x, inerts, etc. These will exit the combustor as gases. Some of the ash, soot, and other solids in the feed will leave the combustor with the gases as fines. The remaining ash, solids, and soot will deposit in the combustor. Some combustors are followed by water quench on the outlet, which collects soot and ash for removal.

Shift Conversion

The products in the combustor effluent are similar to those from an SMR. The gases differ from SMR effluents primarily because they are sour (H_2S present), contain entrained solids, and have different ratios of the shift reactants.

Further, shift conversion is necessary to make a practical amount of hydrogen. The shift reaction itself proceeds via Eq. 28 below:

$$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g) \tag{28}$$

There are two general approaches to shift conversion in POX plants, as illustrated in Fig. 18.

- The H_2S can be removed, along with soot and other solids and the resulting gases sent to conventional shift converters – a process tolerant of impurities is used for this, such as Rectisol (cold methanol).
- The soot and solids can be removed and the product sent to a sour shift converter before final cooling. The availability of sour shift catalysts is fairly recent.

Product Purification and Recovery

The raw hydrogen is finally purified. If the raw hydrogen is sour, the purification system will need to remove both H_2S and CO_2. This would entail a system like a CO_2 Rectisol (cold methanol), which may be followed by PSA. If the sour components have been removed ahead of the shift reactor (or after shifting), then the purification system can be either wet chemical/solvent or PSA.

Equipment Design and Metallurgy

The key to the POX process is the combustor/gasifier design and the quench immediately downstream.

Several combustor system designs have been used. There are many combustor variations offered by Linde, Shell, Lurgi, and others. Because this is a very severe service, more than one combustor is normally installed to permit servicing of the equipment.

These systems will not be discussed in further detail here. The POX system suppliers are the best references.

Concluding Remarks on POX

POX hydrogen plants are not common, but this is a viable option to make hydrogen and it has been used on a commercial scale. The costs are high compared to making hydrogen in an SMR. Still, POX units can feed solids and residual materials that are not feasible to run in an SMR. There are times POX may be favored.

We will not go into further discussion of POX at this time. Several vendors offer this technology, including Linde, Lurgi, and Shell.

Electrolytic Hydrogen

Introduction

Hydrogen can be made by electrolysis of water. There are packaged units available for this service. These are generally limited in size, so they are not commonly used in refineries. They are being considered for renewable energy applications.

The following discussion provides only a broad brush background for this type of unit. Contact the suppliers of these units for additional information.

Process

Electrolytic production of hydrogen occurs in an electrolytic cell. The overall process is simple, as described in Eq. 29:

$$H_2O(l) + \text{power} \rightarrow H_2(g) + {}^{1}/{}_{2}O_2(g) \tag{29}$$

The reaction requires an electrolyte. Normally, potassium hydroxide is used, as noted in the flow diagram below.

There are three types of cells available, as summarized in Table 10.

The general flow sheet for an electrolysis hydrogen plant is shown in Fig. 19.

Concluding Remarks on Electrolytic Hydrogen

No further details about electrolytic hydrogen production are offered here, because of the limited opportunities for refinery application at this time. Future renewable

Table 10 Types of electrolytic cells for making hydrogen

Type of technology	Key elements
Solid oxide electrolysis cell (SOEC)	Operate at high temperatures (~800 °C); outside heat sources (waste heat) can reduce electrical requirement, long start-up times, and material differential expansion issues
Polymer electrolyte membrane cell (PEM)	Operate at low temperatures (<100 °C), simple, commercially available, variable voltage input capabilities, no KOH required, high pressures
Alkaline electrolysis cell (AEM)	Operate at intermediate temperatures (~200 °C), high electrolyte (20–30 % KOH or K_2CO_3) concentrations

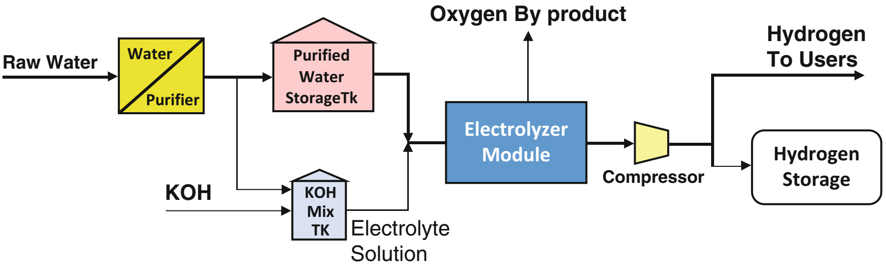


Fig. 19 Simplified typical electrolysis flow sheet for low-pressure electrolyzer (Source: Ivy 2004)

developments may change this picture, but widespread use of electrolytic hydrogen in refineries is not likely in the near future.

Manufacturers of commercially available units include:

- Avalence LLC – high-pressure and ultrahigh-pressure hydrogen, small units; brand name: "Hydrofiller," focus on hydrogen fueling (www.avalence.com)
- Proton Onsite – fuel hydrogen and renewable focus, backup power systems integrated with fuel cells; brand name: "HOGEN RE" (www.protononsite.com)
- Teledyne Energy Systems – PEM units to 150 Nm^3/h (134,000 scfd); brand name: "TITAN" (www.teledynees.com)
- NEL Hydrogen AS (Norsk Hydro) – atmospheric pressure units, 50–485 NM3/h (45,000–434,000 scfd); brand name: NEL-A (www.NEL-hydrogen.com)
- Hydrogenics – alkaline and PEM cells; brand name: "HySTAT" (www.hydrogenics.com)

Olefin Cracking By-Product Recovery

The furnaces that make olefins from refinery feedstocks like ethane, propane, and naphthas make hydrogen as a by-product according to Eq. 30, using ethane cracking as an example:

$$C_2H_6(g) + \text{Heat} \rightarrow C_2H_4(g) + H_2(g) \tag{30}$$

The hydrogen by-product from this reaction can be recovered as part of ethylene recovery and separation. Recovery of the hydrogen can be accomplished cryogenically or using membranes.

This is a source of hydrogen in some refineries that are tied to chemical plants. The product hydrogen will contain some contaminants (like CO, N_2, CH_4), but will generally be about 90–98 % pure.

Refinery Gas Recovery

Introduction

A lot of hydrogen made in a refinery finds its way into the fuel gas and other systems. Eventually, much of this hydrogen gets into fuel gas, if it is not recovered. Burning the hydrogen can be wasteful. Ideally, you want to prevent the hydrogen from getting into the fuel gas in the first place. That discussion will be covered under hydrogen management.

Many refiners chose to recover hydrogen from the various refinery off-gases for reuse. Membrane and PSA units are normally used for this service. Cryogenic recovery is also feasible, but the increased complexity in operating cryogenic units makes them less desirable, unless recovery of light hydrocarbons (ethane, ethylene) is also desired.

Process Discussion

Membrane Recovery

Membrane technology can be applied to several refinery gases:

- Catalytic reformer off-gas
- Hydrotreater off-gas and purge
- Hydrocracker off-gas and purge
- Fuel gas
- FCC off-gases
- PSA off-gases

Table 11 indicates how membranes can be used to recover the hydrogen from a few of these gases and their effectiveness.

Figure 20 illustrates the key process steps in using membranes for hydrogen recovery in a possible application. The pressures and purities are for illustration only.

Note that the feed gas to a membrane must be clean (no solids, low sulfur, etc.), free of liquids (both aqueous and hydrocarbon), and at elevated pressure

Table 11 Some typical refinery hydrogen recovery membrane applications (Source: Fleming 2006)

Refinery gas source	Typical source purity Mole % H_2	Membrane product purity Mole % H_2	Hydrogen recovery %
Catalytic naphtha reformer	70–80	90–97	75–95+
FCC off-gas	15–20	80–90	70–80
Hydroprocessing purges and off-gas	60–80	85–95	80–95
PSA off-gas	50–60	80–90	65–85

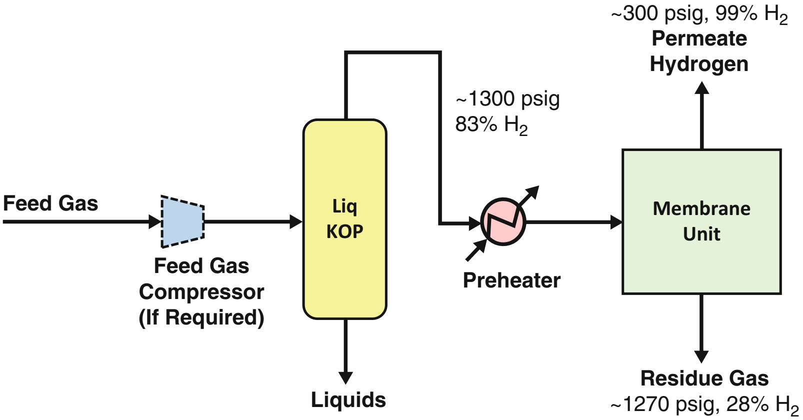


Fig. 20 An example of a hydrogen recovery membrane application (Reference: Fleming 2006)

(prefer >1,000 psig, but can be used at less than 1,000 psig). The final hydrogen from a membrane unit will be at low pressure and the impurities are rejected at high pressure. The product hydrogen must be recompressed for use.

Additional discussion of membranes follows later in this chapter.

Pressure Swing Adsorption Recovery

PSAs can be used to recover hydrogen from refinery gases in essentially the same services as membranes. PSA recovery will be 60–90 % of the contained hydrogen and product purity can be nearly 100 %.

Figure 21 illustrates how a PSA can be integrated into a recovery scheme.

The feed gas for a PSA unit must be of similar quality to that for a membrane unit – clean, no liquids, and high pressure. The pressures used for PSAs can be somewhat lower than for a membrane (~300 psig is alright), with some loss of recovery or increase in size. The product hydrogen from a PSA will be available at essentially feed pressure, but the purge gases containing the impurities are at low pressure.

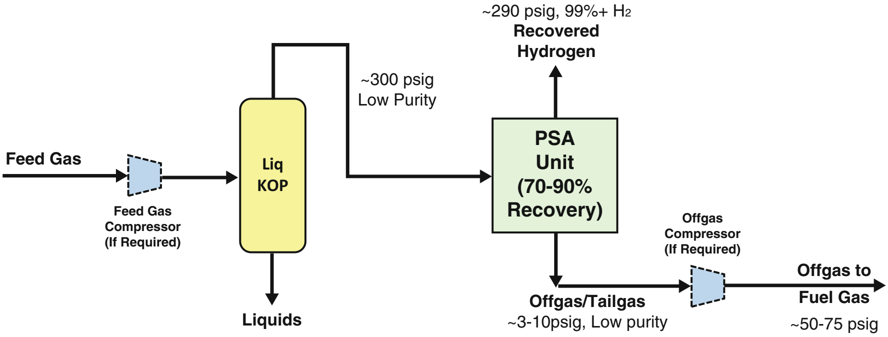


Fig. 21 An example of a hydrogen recovery PSA application

Additional discussion of PSAs follows later in this chapter.

Other Options

Over the Fence

A refiner does not necessarily have to operate his own hydrogen plant, or even hydrogen recovery units. Several industrial gas supply companies will build and operate facilities to make or recover hydrogen for a refinery. This service can be provided onsite or offsite. Here, this arrangement is referred to as “over-the-fence” supply. The supplier will charge for the hydrogen. The charge includes cost of operation, cost of the facilities he needs to build (amortized over time), and a profit margin. There is usually a take-or-pay arrangement for a minimum volume of hydrogen. Handling of emissions impacts can be negotiated.

This type of arrangement is especially advantageous where several facilities in an area need hydrogen. An industrial gas supplier can build a pipeline connecting the facilities, along with one or more hydrogen production or recovery units to supply the pipeline. The supplier may take refinery off-gases to make the hydrogen and return steam as well as hydrogen. The potential for multiple sources of hydrogen producing into the pipeline improves the reliability of hydrogen supply.

Involvement over the fence can also be as simple as the gas supplier installing a membrane unit inside the refinery to recover hydrogen from off-gas from a catalytic reformer, for instance. The supplier operates and maintains the membrane unit for a fee.

Industrial gas companies often are better (i.e., more reliable) at operating hydrogen plants and recovery facilities than a refiner, since this is their main business. The resulting reliable hydrogen supply means fewer production problems in the refinery.

This type of service is well established by companies like Air Products, Air Liquide, Praxair, and others.

Tube Trailers

Sometimes, you need only a small amount of hydrogen of high purity. This is common for semi-regeneration naphtha reformer start-ups. In these cases, hydrogen is often supplied at high pressures in tube trailers. These are available from many industrial gas suppliers. The high pressure eliminates the need for compression by the user.

A typical, large tube trailer from Air Products, for example, holds about 126,000 scf (3,570 Nm^3) of hydrogen at 2,640 psig (83 barg).

Pressure Swing Adsorption

Introduction

Throughout the discussion of hydrogen production, we have referred to pressure swing adsorption (PSA) units. In this section, we will go a little deeper into the design and operation of these units. The discussion will be limited to nonproprietary information and available public literature. There is a great deal of proprietary knowledge needed to design an effective and reliable PSA unit. Detailed design is best accomplished by one of the PSA suppliers – such as UOP, Air Liquide, Linde, Air Products, or CB&I. Industrial gas suppliers will also install and operate recovery PSA systems at a refinery in an over-the-fence arrangement.

Also, note that hydrogen PSAs are not the same as PSAs for other purposes (like instrument air drying or air separation). They require specific knowledge of the hydrogen applications.

Process: Step by Step

A simplified process flow diagram for the business end of a generic 5-bed PSA is illustrated in Fig. 22. To mimic a continuous process, a PSA unit consists of a series of identical vessels filled with adsorbents. There are typically 4–12 beds.

The vessels are connected by several headers that carry the feed gas, product hydrogen, purge and equalization gases, and off-gas or tail gas. The final off-gas passes through a large surge drum that moderates pressure and composition surges for the off-gas and minimizes the pressure swing impacts on the system receiving the off-gas – normally an SMR furnace or fuel gas header/compressor.

Adsorbents in the vessels are selected based on the impurities in the feed gas. For instance, in a typical SMR hydrogen plant, the bottom portion of the PSA bed will contain activated carbon and the upper portion will contain molecular sieve. The activated carbon can easily adsorb methane, CO_2, water vapor, some CO, and other trace compounds. The mole sieve adsorbs nitrogen and the balance of the CO.

It is critical that the feed gas be as dry as possible. If the gas has a high moisture content, water adsorption may reach the molecular sieve where it will permanently attach, reducing adsorption capacity. SMR hydrogen plant raw hydrogen feed is limited to about 130 °F to avoid this problem.

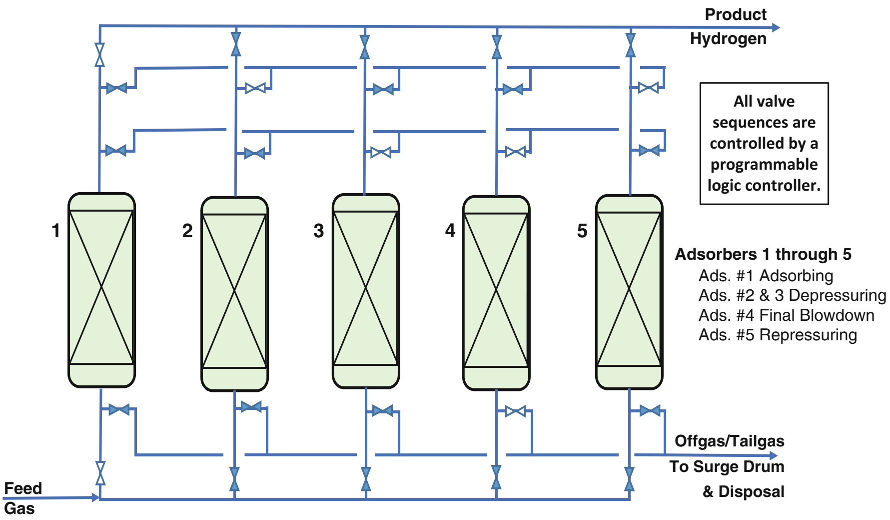
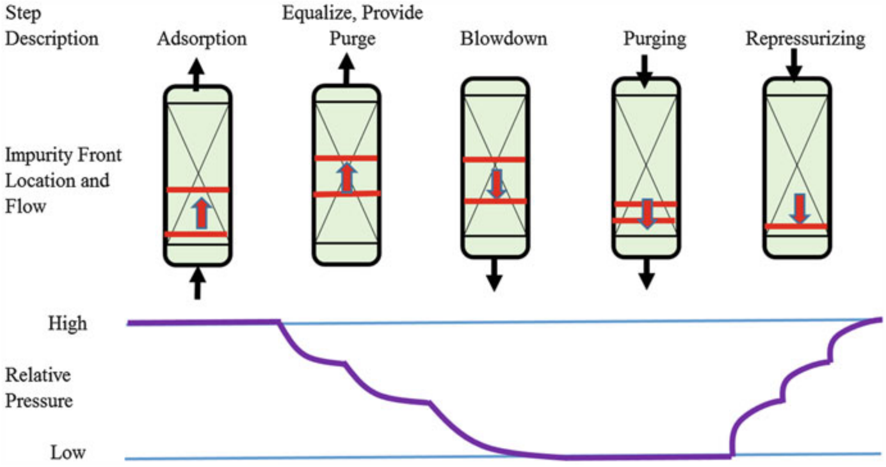


Fig. 22 Simplified process flow diagram of a 5-bed PSA unit

Table 12 Example PSA bed cycle steps



Step Description	Adsorption	Equalize, Provide Purge	Blowdown	Purging	Repressurizing
Impurity Front Location and Flow					
Relative Pressure					

Adsorption releases heat. The temperature of a PSA bed rises slightly (5–20 °F) during the adsorption steps and drops back down as the bed is depressured. If any liquids reach the bed, the adsorption heat rise will be very high, so liquids are strictly excluded.

The steps in a typical PSA cycle applied to one bed are shown in Table 12. There are several sub-steps in the actual control software, but the cycle will generally follow the pattern in the table. The table also illustrates the pressure steps a single adsorption bed progresses through during a cycle.

Let us start with a single target adsorber at full pressure being brought on line and follow the steps:

- *Adsorption* – Raw feed is brought into the pressured vessel, normally in upflow. Impurities in the feed adhere to the adsorbents from the bottom up, with hydrogen adhering the least. Hence, hydrogen passes mostly through the bed and onto production at nearly full pressure. The bed stays on line for a set time, determined by the amount of impurities in the feed and the flow rate. This adsorption time can be fine-tuned based on the product hydrogen purity. Nitrogen and CO will be the first impurities to begin slipping out of the bed – normally setting the maximum adsorption time. During this time, another adsorber bed is being brought up to pressure using a little of the product hydrogen so it can be swung on line when our current bed is taken off-line, without any pressure bumps.
- *First equalization* – At the end of the adsorption time, the feed and product valves are closed on the vessel of interest, and the other vessel that was being pressured up with product hydrogen goes on line. Then, the first equalization valve opens on our target adsorber. This is the first of several depressurization steps. The initially purged gases are fairly pure hydrogen, so flow in this first step is upward and the hydrogen leaving is used to pressure up another adsorber bed that will be brought on line next. There is no gas coming into the vessel. This is called an equalization because at the end of the step, the pressure of our target vessel and the pressure of the vessel it is repressuring are both about equal.
- *Additional equalizations and providing purges* – There are typically two more equalization steps with other PSA vessels. In these steps, gas from our target vessel is dropped in pressure. Flow out of the vessel is still upward. There is no incoming flow. Flow from the current vessel, which is reasonably pure, is used to push the impurities out of other, lower-pressure vessels. During these steps, the actual impurities front in the target bed is continuing to rise.
- *Blowdown* – Now, we begin rejecting the impurities from the bottom of our target vessel using downward flow. The vessel pressure is dropped to the low tail-gas or off-gas drum pressure. This is where the impurities are largely desorbed. Some hydrogen is unfortunately lost in the process. At this point, there is no incoming gas, just depressurization out the bottom of the vessel.
- *Purge* – Now, the vessel is purged to blowdown using gas from one of the other PSA vessels in the "provide purge" step. This is downflow at low pressure. The impurities are reduced to their minimum in the bed.
- *Equalization steps* – The vessel is now repressured using equalization step gases from other vessels that are being depressured. As the pressure is increased, the purity of the repressuring gases increases. Flow is downward to avoid fluffing the bed and there is no outgoing flow at this time.
- *Repressurization* – There is a final repressurization step using product hydrogen in downflow to bring the bed pressure up to the product header pressure and avoid a pressure bump when the vessel comes on line. There is no outflow.

- *Adsorption* – The vessel is brought back on line in upflow to start the next cycle by opening the feed and product valves.

  There are pressure and time criteria for completion of each step before the sequence will advance. If these are failed, the control system can adjust or, if the failure is serious enough, it can shut down the PSA and block in the vessels.

Equipment Design and Metallurgy

Valves

PSA systems depend heavily on control valves to accomplish their function. Each PSA vessel has four to six valves associated with it, depending on the number of steps in the cycle. Each PSA vessel valve will go through around 35,000 cycles per year on average. In addition, there are other valves that control surge pressures and compositions of the off-gas or tail gas.

All of these valves must be routinely and regularly checked and serviced to ensure reliability of the PSA system. Valve failure is the number one problem in low PSA reliability.

PSA designers have specific valves they recommend for their units based on extensive experience. It is wise to take advantage of their expertise. These are not normal control valves. The valves have specific features tailored to the PSA service.

PSA Adsorbers and Cyclic Service

Just as each PSA vessel valve will go through about 35,000 cycles per year, each vessel is pressurized and depressurized about 35,000 times per year. This cyclic stress on a vessel can exacerbate small defects in construction of the vessel, resulting in cracking of vessel.

This cyclic loading has to be recognized in specifying and monitoring the vessels. Normally, there are periodic inspections for cracks growing from the cyclic stresses. Inspection methods continue to develop for this service.

Off-Gas/Tail-Gas Surge Drum

The off-gas or tail-gas surge drum is a large vessel designed to moderate the pressure and composition changes that come from the PSA vessel cycles. This is required to provide a relatively stable fuel supply to the SMR furnace or other fuel gas users.

At one time, there were two surge drums employed – one to moderate the pressure cycles and a second drum to even out the compositions. This two-drum system resulted in very stable off-gas flow and composition.

Recent practice for PSAs uses a single surge drum combined with improved control valve logic and tuning to provide stable off-gas flow. This has not been quite as effective as the two-drum system, but works well enough and significantly reduces capital cost and footprint.

The surge drum is mostly just an empty space, but the inlet lines from the PSA usually terminate inside the surge drum with elbows or distribution headers. These improve mixing and reduce composition variations. Pressure surge may be managed with control valves (in and/or out) of the surge drum.

Control System

The PSA cycles are controlled by a programmable logic controller (PLC). In some cases, this logic has been incorporated into the plant's distributed control system (DCS), but more often the logic is housed in a dedicated PLC, with interfaces to the DCS.

The control system will normally match the capacity of the PSA to the plant rate and handle rate changes. The system can manage some types of valve failures by switching between operation modes (number of beds on line), with minimal upset. Many systems have built-in diagnostics to help analyze problems. The systems can also be combined with online gas analyzers to optimize recoveries.

Operations

Start-Up

From a routine standpoint, the start-up of a PSA is relatively simple:

- The PSA system is air-freed.
- Feed gas is lined up to the unit. Off-gas is lined up to the surge drum and, usually, flare. The vessel block valves are all opened, with the control valves still closed.
- The adsorber pressures are set to the required starting pressure profile for a desired start-up step using available gases. This may also be automatic.
- The PLC is started at the desired step and the PSA valves begin cycling. All the incoming feed gas goes out through the surge drum to flare initially for a few cycles to establish the correct impurity profiles.
- Once the system is operating reliably and smoothly, hydrogen production to users can begin.
- Once the system is stable, the off-gas can be routed to either the SMR or fuel gas.

Shutdown

Shutdown of a PSA unit is accomplished by stopping the PSA cycle. The control logic in the PLC will automatically block in the vessels and freeze the cycle and pressures in the current step. Incoming feed gas will go to flare or its alternative destination. The off-gas/tail gas will stop immediately.

Adjustments will need to be made to downstream, and possibly upstream, units that feed the PSA or use the off-gas.

Routine Operation

Once in service, the PLC controlling the PSA will operate the unit and continuously monitor for problems. The operator may need to adjust the adsorption cycle time periodically to fine-tune the cycle or for major rate changes. Generally, the PSA system will take care of itself.

Table 13 Key routine monitoring parameters for a PSA unit

Parameter	Basis	Frequency	Criteria
Hydrogen recovery	% Recovery $= (\text{mols or scf } H_2 \text{ in product}) / (\text{mols or scf } H_2 \text{in feed gas}) \times 100\%$	Weekly	Trend and watch for loss of recovery with time
Feed and off-gas pressures	Review pressure trends	Daily	Ensure pressures stay within allowable ranges
Feed gas temperature	Review data	Daily	Ensure temperature stays within allowable range
Feed gas composition	Review data	Weekly	Watch for excessive ethane or heavier components
Adsorption time	Review adsorption time for each bed in seconds	Weekly	Trend and watch for increasing requirement at the same feed rate
Product purity	ppm CO in product hydrogen – this will need to be by detector tube or other sensitive means, GC will not be adequate	Weekly	Trend and watch for increases in CO with time. Do not run for extended periods with low purity
Valve packing leakage	Physical inspection	Weekly	Should not be able to feel gases coming from any packings
Cycle diagnostics	Review PLC exception logs or pressure graphs for each vessel	Weekly	Look for anomalies in the cycles like extended repressurization times or changes to patterns

Once a unit is operating, it is worthwhile to have your PSA vendor periodically review the operation and fine-tune it (say, annually). They can help spot potential issues that may not be obvious.

Monitoring

Table 13 provides a summary of the important parameters and equipment to monitor on a PSA during operation. Early detection of problems provides an opportunity to make a controlled switch to an alternate operation without the PSA control system making a radical move on its own and causing an upset.

Troubleshooting PSAs

Table 14 provides a summary of the more common PSA problems and hints at possible causes. This is a starting point. The control software error logs and information will often provide a good starting point for troubleshooting.

Table 14 Some common PSA problem symptoms and possible causes

Symptom	Possible causes/remedies
Repressurization	PLC or other instrument problem
Too long or slow	PLC or other instrument problem
	Repressurization valve/instrumentation problem
	Low product header pressure (look at users)
Too short or fast	PLC or other instrument problem
	Associated control valves or instrument problems
Blowdown	
Too long or slow	PLC or other instrument problem
	Blowdown valve/instrumentation problem
	High blowdown header backpressure (look downstream)
	Valves leaking into header from other vessels
Too short or fast	PLC or other instrument problem
	Blowdown valve/instrumentation problem
Purge	
Too long, slow, incomplete	Associated control valves or instrument problems
	Valve leakage from another vessel
	Low product purity
Too short or fast	PLC or other instrument problem
	Instruments/valves on vessel providing purge gas
Pressure/flow bumps/variations	
Feed/product headers	See repressurization symptoms
Off-gas/tail-gas header	See blowdown or purge symptoms
	Problems with off-gas or purge control system
	Valve leaks or instrument problems in associated valves
	Controls/instrumentation problem around off-gas surge drum
	Tail-gas compressor problem (if applicable)
Feed or product flow fluctuations	See repressurization symptoms
	Feed flow varying (check upstream)
	See purge and blowdown symptoms
Low product purity	PLC or other instrument problem
	Adsorption time set too long
	Adsorbent damage or loss (from another problem)
	See repressurization, blowdown, and purge symptoms
	Wet or hot feed gas – possible carryover
	High feed flow rate
	High off-gas/tail-gas pressure (look for downstream problem)
	Bad analytical data

(*continued*)

Table 14 (continued)

General PSA problems causing shutdown or alarm	Low-low product pressure (causes high feed flow capable of lifting bed)
	High/low feed temperature (instrument or upstream cooling problem)
	Low instrument air pressure (instrument air supply problem)
	Long cycle times (see repressurization, blowdown, and purge symptoms)
	PLC or other instrument problem
Dust in outlet header or other PSA headers on inspection	Excessive feed flow rate causing adsorbent milling/carryover
	PLC cycle sequence or other instrument problem

Detailed discussion on troubleshooting more complex issues is beyond the scope of this book. PSA unit vendors are usually more than happy to help in troubleshooting. As noted above, a periodic (annual) review of the unit operation by the PSA vendor is advisable to identify problems that are not obvious.

Membranes

Advances in technology have made membranes a viable hydrogen recovery option for several types of systems. The discussion of the applications for membranes and the typical process flow in hydrogen recovery service is in the section "Refinery Gas Recovery." Membrane capacities over 60 MMscfd of feed are possible because of the modular nature of the process. These units are, in fact, usually supplied as prefabricated modules.

Reviewing the flow sheet in Fig. 20 above, compressed, high-pressure raw gas (preferably >1,000 psig) passes through a knockout drum or coalescer to eliminate any possible liquids in the feed. The clean raw gas is then fed to a bank of several membranes housed in tubes, all operating in parallel. Hydrogen diffuses through the membranes to the low-pressure side and exits (permeate). The impurities remain on the high-pressure side and exit (residue).

Product hydrogen permeate from a membrane will range from 80 % to 98 % purity, with 65–95 % recovery. Feed hydrogen for a membrane unit can range from 15 % to 80 % hydrogen purity, although purity greater than 70 % is best.

The most common membranes for hydrogen are hollow fibers or wound sheets of thin polyaramide or polyimide on a support material. The membrane selectively allows the smallest molecules to pass; so hydrogen gets through preferentially. The membrane materials are fairly resistant to damage from most chemicals they may encounter, but eventually are damaged to the point of requiring replacement.

Other membrane materials, including inorganics, are in development.

Basic monitoring of a membrane unit would consist of periodically calculating the hydrogen recovery percentage and trending the product hydrogen contaminants. Feed composition and potential carryover should also be tracked routinely. Membrane system vendors would provide additional support for analyzing system performance.

Membrane systems for hydrogen recovery are offered by several suppliers, including Air Liquide (MEDAL™), Air Products (PRIZM™), and UOP (Polysep™). Industrial gas suppliers will also install and operate membrane systems at a refinery in something akin to an over-the-fence arrangement.

Cryogenic Recovery

Hydrogen can be recovered cryogenically from various refinery gases and olefins cracking gases. It is normally a by-product of recovering other, more valuable materials, such as ethylene. Industrial gas suppliers and others will install, own, and operate cryogenic recovery units in an over-the-fence arrangement.

Figure 23 illustrates application of a cryogenic unit to recover hydrogen from refinery fuel gas. The gas must first be compressed to about 200–500 psig and cooled. It is pretreated to remove moisture, CO_2, and other impurities before chilling in a multiservice, plate exchanger from −60 to −120 °F. The fluid is flashed and the vapor sent to a second stage of cooling in a plate exchanger to much lower temperatures followed by separation. The gas from the second stage flash drum is expanded across a valve and provides cooling to the two plate exchangers. Final product hydrogen from the cryogenic system is about 65 % hydrogen starting with a stream at, perhaps, 30 % hydrogen. By-products include

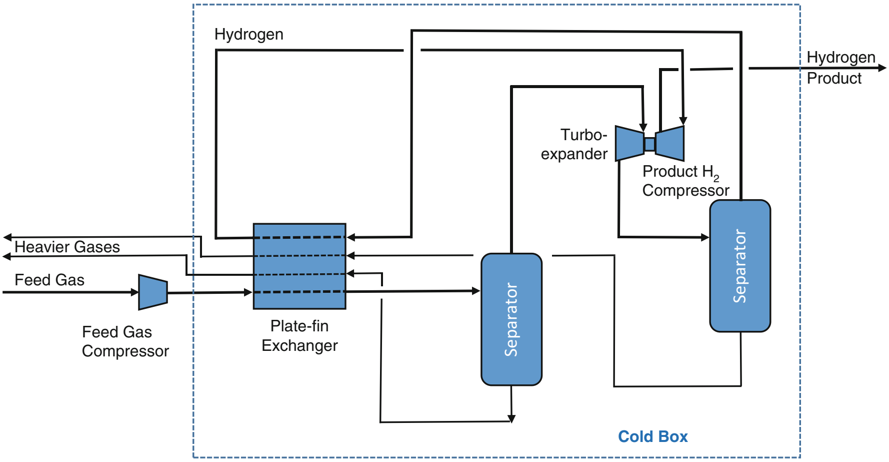


Fig. 23 Simplified flow diagram of one type of cryogenic hydrogen recovery process (Reference: Faraji et al. 2005)

LPG and fuel gas. The product hydrogen can be further upgraded by PSA or membrane. Cryogenic product hydrogen purities of 95–99 % and recoveries of 90–98 % of hydrogen are possible with appropriate process changes.

Cryogenic units are somewhat more difficult to operate and more expensive than the alternative technologies if your primary objective is hydrogen recovery. These units may be justified by the value of the other products recovered in some cases.

Because these are not common in refinery hydrogen systems, they are not discussed further here. Refer to the available references for suppliers of these systems.

Refinery Hydrogen Management

Ideally, all the hydrogen produced in a refinery would be used in upgrading the refined products to more and cleaner fuels. In reality, some of the hydrogen is inevitably lost to fuel or flare.

General Management Concepts

The purpose of hydrogen management is to minimize these losses through design, monitoring, and allocation of hydrogen to the users.

There are a few principles that guide hydrogen management:

- Treat the hydrogen system like any other process system – have a process flow diagram with critical controls shown and a material balance for the system.
- Meter all the hydrogen streams to and from units.
- Know the compositions of the hydrogen streams to and from units.
- Make or buy the lowest amount of “on-purpose” hydrogen possible.
- Preferentially use hydrogen in the highest value units.
- Minimize the need to recompress hydrogen by cascading from high to low pressure where possible.
- Keep hydrogen out of the fuel gas system and flare.
- Recover hydrogen where feasible.
- In refinery planning, the refinery LP should consider hydrogen.
- With good practices, a refinery should be able to use more than 90 % of the hydrogen generated.
- A periodic review by a company experienced in hydrogen system studies is advisable (e.g., Air Liquide, UOP, Air Products, etc.).

An example of a hydrogen system in a full-conversion refinery is illustrated in Fig. 24. There are a series of hydrogen generators (naphtha reformers, SMR plants) connected to hydrogen headers. The headers distribute the hydrogen to the users. There may also be intermediate hydrogen headers at different pressures and purities. Headers may be sweet or sour, depending on the design choices made

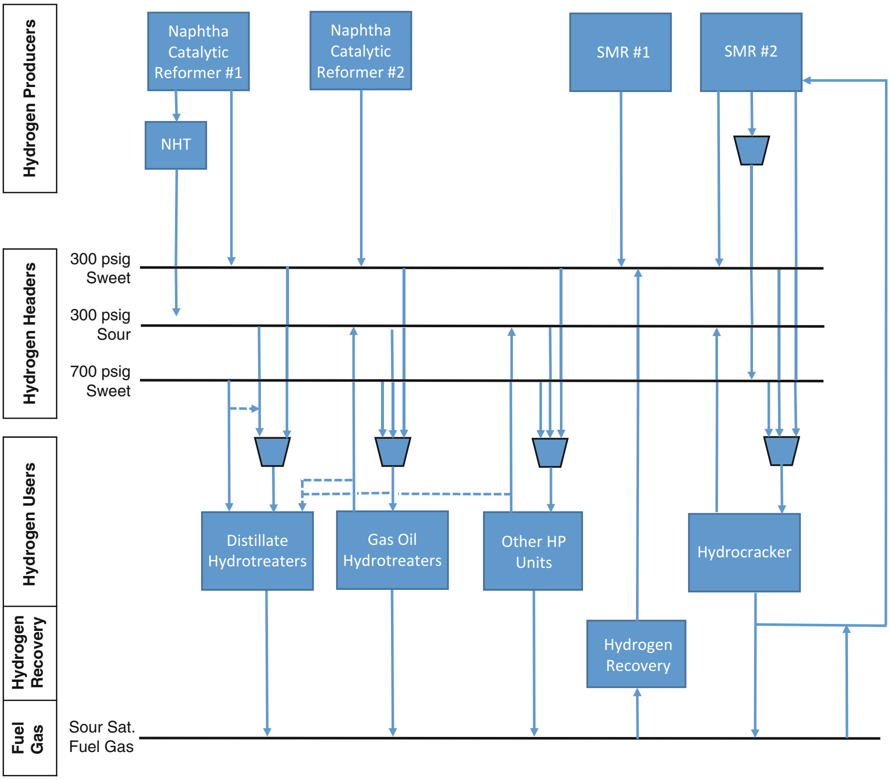


Fig. 24 Typical full-conversion refinery hydrogen management approach

for a facility. There may also be hydrogen recovery systems from fuel gas, refinery or petrochemical gases, and purge gases that make up into the headers.

Along with the process flow diagram, there should be a spreadsheet and/or simulation model that provides material balance calculations for the system. The model can use typical hydrogen consumptions and production for users based on feed rates or can be more sophisticated and account for feed quality as well as rates. Having these tools available will allow more intelligent use of hydrogen in a refinery, especially by operations personnel.

Hydrogen Headers

Fresh Hydrogen

The fresh hydrogen header takes hydrogen from the producers and distributes it to the initial users. Incoming hydrogen may originate from the SMR hydrogen plant (s), over-the-fence supply, or catalytic naphtha reformer(s). Incoming hydrogen may also be supplied by recovery unit(s).

One of the suppliers must be used as the swing unit to control the header pressure. The other suppliers should then be base loaded or may have rates that are set by other factors. For example, a naphtha reformer's hydrogen production will more often be set by the required naphtha octane and the catalyst age. You would not normally set naphtha reformer rate just to supply hydrogen, although that is an option.

The swing unit is usually an SMR unit that is large enough to control the fresh hydrogen header pressure. The SMR is able to react more quickly than many other units. An SMR does not like to be swung around too frequently, however; so, a swing SMR may end up producing a small excess of hydrogen that is lost. One objective is to minimize that loss.

Sour Hydrogen

Often, hydrogen is cascaded from high-pressure to low-pressure units for conservation and reuse. The hydrogen picks up H_2S the first time it is used. Some refineries scrub the H_2S out of purged gases from the higher-pressure units, but others purge sour gases.

The sour hydrogen is normally handled in a separate header. The gas from this header can be used in lower-pressure or less severe units. It can also be used for presulfiding or activation of hydrotreating catalysts.

Surplus hydrogen on the sour header may be cascaded to fuel gas.

Header Pressures

There are a number of strategies used to determine where to set hydrogen header pressures during design. The philosophy described here is one of the more common approaches.

The pressure for the fresh hydrogen header could be set at the maximum makeup pressure required for the highest pressure user (hydrocracker or gas oil hydrotreater), but this would mean compressing all the gas to the highest pressure all the time. That would be wasteful.

It is similarly not optimum to just supply hydrogen at low pressure, like naphtha reformer outlet pressure of 200–300 psig. That would mean installing compressors at many different users or creating another header for higher pressures.

A compromise that works well is to compress and distribute the fresh hydrogen supply at the makeup pressure required by the diesel hydrotreater (DHT). This usually means the fresh header runs 700–1,000 psig. This eliminates the need to compress within the DHT and most other units. It allows the DHT purge to be cascaded to lower-pressure services. If a refinery has a hydrocracker or high-pressure gas oil hydrotreater, the hydrogen for those services still requires additional compression.

In any event, the best practice for a given refinery is to select header pressures that result in the best economics, including the cost of compression.

Managing Hydrogen Users

Allocation of Hydrogen

Someone needs to "own" the hydrogen system in a refinery and that person has to be able to make decisions about the system. Short-term, on-shift decisions are normally made by someone in the shift operations organization. Overall decisions day-to-day are usually a joint effort of the operations and planning staffs. Longer-term planning and improvements are the purview of engineering staff.

Allocation of hydrogen is especially important when a facility is tight or short of hydrogen. To maximize the refinery profitability, hydrogen needs to go to the units that will make the most value per cubic foot (or cubic meter) of hydrogen used. All impacts need to be considered however. For instance, allocation of hydrogen to a high value unit that could force a cut in crude rate to the refinery because another unit was starved for hydrogen would not be wise.

Factors Affecting Usage and Generation

Hydrogen is primarily used to:

- Eliminate sulfur, nitrogen, and other impurities from products or feedstocks.
- Upgrade product values (ULSD, dewaxing, isomerization).
- Crack heavier hydrocarbons (gas oils) to lighter hydrocarbon products (naphtha, distillates).
- Supply reducing gas to sulfur plants (in some cases).

Changes in crude slate and rates impact all these factors. A heavy, sour crude will require more hydrogen to refine than a light, sweet crude. Higher rates in a hydrocracker or gas oil unit (possible due to crude changes) will require more hydrogen. Deeper HDS or increasing conversion will increase consumption.

On the supply side, lower reformer severity, increasing catalyst age, or less naphtha available to reform will all reduce cat reformer hydrogen makes. Changes in SMR hydrogen plant feedstocks, catalyst age, capacity, or firing/recovery limits may reduce the amount of hydrogen an SMR can make.

It is advisable to have a simple model that predicts hydrogen consumption or production for each unit based on feed rate and quality to estimate changes. These models would be incorporated into the material balance model for the system overall.

Overall Planning

Good, active hydrogen management practices will ensure that the least amount of valuable hydrogen is wasted in a refinery. The operations organization can manage the day-to-day hydrogen system, but the planning organization should include the hydrogen system in their process using the refinery LP or another model to avoid arriving at an infeasible plan.

Concluding Remarks

The production and use of hydrogen in a refinery is becoming increasingly important as refined product specifications drive toward zero sulfur, high H/C ratio fuels of all boiling ranges. There are several options for providing hydrogen to a refinery. Many of these have been discussed in this section. This is, by no means, all inclusive, however. Many variations exist among facilities and new options for production or recovery of hydrogen continue to grow.

Appendix Example SMR Hydrogen Plant Material Balance and Monitoring Parameters Development

To calculate the key monitoring parameters for an SMR plant, consider the following example that is typical of the sort of calculations needed. This example is for an SMR feeding natural gas plus refinery saturated off-gas that has been scrubbed free of sulfur (for simplicity). Hydrogen purification is by PSA unit. The plant only has high-temperature shift.

The objectives are to calculate:

- Material balance around the reforming furnace, shift converter, and PSA
- Approach to equilibrium in reformer
- Approach to equilibrium in shift converter
- PSA recovery efficiency
- Shift condensate rate
- Normalized reformer pressure drop
- Actual steam/carbon ratio

The following data are given:

Flow rates
  - Sweet feed gas = 6.87 MMscfd
  - Product hydrogen (99.9999 % H2) = 20.6 MMscfd
  - Raw hydrogen to the PSA = 31.8 MMscfd
  - Process steam rate = 66,500 lbs/h

Temperatures
  - Reformer outlet temperature = 1,500 °F
  - HTSC outlet temperature = 810 °F

Pressures
  - Reformer inlet = 315 psig

- Reformer outlet = 290 psig
- Shift converter outlet = 280 psig
- Product hydrogen from PSA = 260 psig

Dry gas analyses, vol % by GC

Component	Feed gas	PSA inlet
Hydrogen	9.3	69.5
Methane	79.7	2.3
Ethane	3.4	0.0
Propane	1.9	0.0
Mixed butanes	1.6	0.0
Mixed pentanes	1.3	0.0
Hexane and heavier	0.2	0.0
CO	0.3	3.0
CO_2	0.6	15.7
N_2	0.7	7.3
O_2	0.0	1.9

Solution

1. Normalize the dry gas analyses to 100 %. Notice that the analysis of the raw gas to the PSA inlet contains a lot of oxygen and nitrogen. This indicates air contamination and is typical of GC results. The air has to be backed out of the analysis. So remove the 1.9 % oxygen and 7.1 % nitrogen (79/21 × 1.9). This leaves 0.2 % nitrogen in the PSA inlet. Normalize the PSA inlet gas to 100 % without the air. The final normalized PSA Inlet gas is:
    - Hydrogen = 76.7 %
    - Methane = 2.5 %
    - CO = 3.3 %
    - CO_2 = 17.3 %
    - N_2 = 0.2 %
2. Set up a material balance spreadsheet for the composition, molar flow rate, mass flow rate, pressure, and temperature at each key location in the unit:
    - Feed gas
    - Reformer inlet feed gas
    - Process steam
    - Reformer outlet
    - HTSC outlet
    - Process condensate (shift condensate)
    - PSA inlet gas
    - PSA product hydrogen
    - PSA off-gas
3. Assume the feed gas flow rate is correct and use the feed gas analysis to calculate the moles of carbon and hydrogen per hour in the feed. Do not forget to include any CO and CO_2 in the carbon. We are assuming no

moisture in the feed. Use these values to calculate alpha (α) for use in Eq. 20. In this case, we have 816.2 mols of carbon per hour and 3,105.5 mols hydrogen per hour:

$$2\alpha = 3,105.5/816.2 = 3.80$$
$$\alpha = 3.80/2 = 1.90$$

4. Calculate the steam/carbon ratio (X) at the reformer inlet by converting the steam rate to moles per hour and dividing it by the moles per hour of carbon:
   66,500 lb/h steam/18 = 3694.4 mols/h steam
   Steam/Carbon = 3694.4/816.2 = 4.53 S/C Ratio = X
5. Calculate the wet shift converter outlet composition using the following equation and knowing α and X from above. The methane, CO, and CO_2 proportions (1-a-b, a, and b) come from the PSA inlet dry gas. The steam portion is calculated from the equation. Hydrogen falls out in the calculation. Remember that the nitrogen will come through as an inert:

$$\begin{aligned} CH_2\alpha + XH_2O \longleftrightarrow\ & aCO + bCO_2 + (1-a-b)CH_4 \\ & + (X-a-2b)H_2O + (3a+4b+\alpha-2)H_2 \end{aligned} \tag{31}$$

   where
   α = factor based on feed C/H molar ratio
   X = steam/carbon molar ratio
   a, b = coefficients for CO and CO_2 concentrations, respectively, at any point in the process
6. The shift or process condensate should be the residual water from the reaction. Use this as the process condensate flow rate. You can include dissolved CO_2, but the amount of dissolved CO_2 is not significant in the overall process.
7. Now check the overall balance in the unit by adding the feeds (feed gas plus steam plus any recycle hydrogen) and comparing to the HTSC outlet (PSA inlet gas plus calculated process condensate). Check the carbon and hydrogen balances also. Make adjustments to flow rates until you closed the balance. This sometimes means compromising on rates or slight adjustments to compositions. There are many sources of possible error in these calculations so flexibility is needed. If the balance can be closed to +/−2 %, that is good enough for the analysis.
8. Now estimate the reformer outlet composition.
   - Assume the HTSC outlet (in moles) is the correct methane slip from the reforming furnace. Here the slip is 2.5 v% of the dry gas or about 87 mols/h.
   - Calculate the CO and CO_2 proportions by assuming the gas is at water-gas shift equilibrium at the reformer outlet. The CO and CO_2 proportions can be derived by iteration until the calculated K_{WGS} at the reformer

outlet matches the K_{WGS} at the reformer outlet temperature of 1,500 °F. Use the definition:

$$K_{WGS} = (P_{H_2} \times \ P_{CO_2})/P_{H_2O} \times P_{CO})$$

where the partial pressures are in atmospheres in the *wet* gas.
Use the equation for K_{WGS} for the SMR process discussion.
An easier approach with sufficient accuracy is to use the equilibrium charts provided in the SMR monitoring discussion for methane to estimate the % CO and CO_2 in the dry gas at the reformer outlet. From the chart, the CO at the reformer outlet should be about 11.5 v% and CO_2 would also be about 11.5 v%. We brought in 816.2 mols/h carbon. 87 mols/h stayed in methane as methane slip. The remaining 729 mols per hour is roughly split evenly between CO and CO_2 at the reformer outlet (about 365 mols/h each). Iterative calculations give values of about 359 mols/h for CO and 370 mols/h for CO_2.
Check to be sure the reformer outlet mass balances, including C and H.

9. Calculate the partial pressures of methane, CO, CO_2, hydrogen, and water in the wet gases at the outlet of the reforming furnace and shift converter. The partial pressures must be in atmospheres absolute.
10. Calculate K_{SMR} at the reformer outlet and K_{WGS} at the shift converter outlet using the definitions in the SMR process discussion.

Reformer outlet actual $K_{SMR} = \sim 298$ (Table is reciprocal of this)
Shift converter outlet actual $K_{WGS} = \sim 6.23$

11. Calculate the equivalent equilibrium temperatures using the equations in the SMR process discussion or use the charts in that section.

Reformer actual equilibrium temperature $= \sim 1,515$ °F
Shift converter actual equilibrium temperature = 878 °F

12. Finish the material balance streams and check the overall, carbon, and hydrogen balances.
13. The key monitoring parameters can now be calculated:
    - *Overall material balance* was derived as part of the calculations. See Table 15 for the basic material balance.
    - *Approach to equilibrium (ATE) in the reformer*

$$\text{Reformer ATE} = \text{actual} - \text{calculated} = 1,500 - 1,515°\text{F} = -15°\text{F}$$

- *Approach to equilibrium (ATE) in the shift converter*

$$\text{Shift ATE} = \text{actual} - \text{calculated} = 878 - 810\ °\text{F} = +68\ °\text{F}$$

- *PSA recovery efficiency*

$$\text{Recovery} = (\text{mols } H_2 \text{in product} * 100\%)/\text{mols } H_2 \text{in feed}$$

$$\text{Product } H_2 = 20.6 \text{ MMscfd} \rightarrow \ 2,262.0 \text{ mols/h}$$

$$\text{PSA inlet } H_2 = 76.8\% \text{ of } 31.8 \text{ MMscfd} \rightarrow 2,721 \text{ mols } H_2/\text{h}$$

$$\text{Recovery} = 100\% * 2,262/2,721 = 83.1\%$$

- *Shift condensate rate*

This falls out of the material balances as 2, 378 mols/h (leftover process steam) = 42.3 Mlb/h or ~85 gpm.

- *Actual steam/carbon ratio*

This also fell out of the calculations as X = 4.53.

- *Normalized pressure drop*

For normalizing the pressure drop, prior history and a normalization basis (reference conditions) are required. Here, from prior development work, the equation for normalization of dP was found to be

$$dP_{norm} = dP_{meas} \times \left[(Q_{feed} + Q_{steam})_{norm} / (Q_{feed} + Q_{steam})_{meas}\right]^{1.6}$$

where:
dP_{norm} = normalized dP at reference conditions
dP_{meas} = measured dP at actual conditions
Q_{feed} = inlet volumetric flow of feed, reference or actual
Q_{steam} = inlet volumetric flow of steam, reference or actual
Here:

$$dP_{meas} = 315 - 290 \text{ psig} = 25 \text{ psig}$$

$$Q_{feed,\,meas} = 6.87 \text{ MMscfd}$$

$$Q_{steam,\,meas} = 66{,}500 \text{ lb/h} \times 24 \text{ h/day} \times 379.45 \text{ scf/18 lbs} \rightarrow 33.6 \text{ MMscfd}$$

$(Q_{feed} + Q_{steam})_{norm} = 51.9$ MMscfd (for normalization reference case)
So

$$dP_{norm} = 25 \times [51.9/(6.9 + 33.6)]^{1.6} = 37 \text{ psi}$$

14. From the parameters monitored, we can observe that:
    - Depending on how much adjustment was needed to get a good material balance, flow meter, instrument, or analytical issues may be indicated that would bear some evaluation.
    - The reformer approach to equilibrium is fairly good. Trending the calculated value would provide an indication of deactivation rate.
    - The shift converter ATE should also be trended over time for complete analysis. An ATE of 68 °F is a little high and may indicate the shift converter catalyst has deactivated some or the temperature is not optimum. It could also indicate bad data.
    - The PSA recovery efficiency of 83 % is lower than you should expect. Recovery of at least 85 % should be achievable. This would bear further investigation.
    - The shift condensate rate is informational primarily. It may be needed for loading evaluation of the degasifier on occasion.

Table 15 Example SMR hydrogen plant material balance development

		Feed					Steam					
Component			6.87	MMscfd			66.5 Mlb/h		Ref In			
	mw	v%	mols/h	lbs/h	mols \ C/h	mols \ H/h	mols/h	mols \ H /hr	mols/h	lbs/h	C mols/h	H mols/h
H_2	2	9.3	70	140	0	140	0	0	70	140	0	140
C_1	16	80.7	609	9,741	609	2,435	0	0	609	9,741	609	2,435
C_2	30	3.4	26	769	51	154	0	0	26	769	51	154
C_3	44	1.9	14	631	43	115	0	0	14	631	43	115
C_4	58	1.6	12	700	48	121	0	0	12	700	48	121
C_5	72	1.3	10	706	49	118	0	0	10	706	49	118
C_6	86	0.2	2	130	9	21	0	0	2	130	9	21
CO	28	0.3	2	63	2	0	0	0	2	63	2	0
CO_2	44	0.6	5	199	5	0	0	0	5	199	5	0
N_2	28	0.7	5	148	0	0	0	0	5	148	0	0
H_2O	18	0.0	0	0	0	0	3,694	7,389	3,694	66,500	0	7,389
		100.0	754	13,227	816	3,104	3,694	7,389	4,449	79,727	816	10,492
				H/C Rat	3.802		Stm/Carb		4.53			
				Alpha	1.901							
		Reforming		CH_{2a}	+	XH_2O	<=>	a CO	+	b CO_2	+	(1-a-b)CH_4
			mols/h	816.2		3694.4		359.1459		369.8		87.3
			coeff.	1.000		4.526		0.440		0.453		0.107
			atm					1.26		1.30		0.31
			H	3.80		9.05		0.00		0.00		0.43
				Total In: 12.855				Total Out: 12.855				
		HTSC										
			mols/h	816.2		3694.4		114.3		614.7		87.3
			Coeff	1.000		4.526		0.140		0.753		0.107
		20.05 Atm		2.78		12.57		0.39		2.09		0.30

Reformer outlet				HTSC outlet			PSA prod			Shift condensate	
				Dry gas	31.8 MMscfd		20.6 MMscfd	PSA off-gas			
mols/h	C mols/h	H mols/h	PP, atm	v%	mols/h	lbs/h	mols/h	mols/h	v%	mols/h	lb/h
2,476	0	4,952	8.71	76.8	2,721	5,442	2,262	459	35.8	0	0
87	87	349	0.31	2.5	87	1,397	0	87	6.8	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
0	0	0	0.00	0.0	0	0	0	0	0.0	0	0
359	359	0	1.26	3.2	114	3,200	0	114	8.9	0	0
370	370	0	1.30	17.4	615	27,045	0	615	48.0	0	0
5	0	0	0.02	0.1	5	148	0	5	0.4	0	0
2,596	0	5,191	9.13		2,351	42,315	0	0	0.0	2,351	42,315
5,893	816	10,492	20.73	100.0	5,893	79,546	2,262	1,280	100.0		
5,893			20.73	Dry gas							
			Dry gas	mols C	816						
				mols H	10,492						
+	(X-a-2b) H_20	+	(3a+4b +α-2)H_2			Actual		@Act	EquivT	ATE	
	2595.7		2475.9		1,500 F	K_{WGS}	0.982	0.98	1,500	0	
	3.180		3.033		1,500 F	K_{SMR}	298.1	239.5	1,515	−15	
	9.13		8.71							Act - Equiv	
	6.36		6.07								
	2350.8		2720.8			Actual		@Act	EquivT	ATE	
	2.880		3.333		810 F	K_{WGS}	6.23	8.61	878	68	
	8.00		9.26							Equiv-Act	

  - The normalized pressure drop of 37 psi is somewhat high for most reformers and may indicate some catalyst crushing or coking from age or an incident. 37 psi is not particularly alarming. This value should be trended over time.
  - The steam carbon ratio at 4.53 is a little high for most PSA-type units, but would be common in older units using solvent CO_2 cleanup. It could probably be lowered.

15. These calculations can be built into a spreadsheet, including the trial-and-error, iterative solution to the reformer outlet composition and material balance closure. This would save a significant amount of time and enable more detailed operations evaluation to be completed more often.

References

Steam-Methane Reforming

American Petroleum Institute, Recommended Practice 571 (RP-571), Common Refinery Damage Mechanisms

Katalco Corporation (Imperial Chemical Industries Ltd.), *Catalyst Handbook*, with Special Reference to Unit Processes in Ammonia and Hydrogen Manufacture, 1st edn. (Springer, New York, 1970)

H.W. Rasmussen, Haldor Topsoe, Inc., Hydrogen Plant Catalysts and Operation, Unpublished (2001)

J.R. Rostrup-Nielsen, Haldor Topsoe, Inc, *Catalytic Steam Reforming* (Springer, Berlin/Heidelberg, 1984)

Partial Oxidation

Haldor Topsoe Inc., Brochure: Sulphur resistant/sour water-gas shift catalyst, www.topsoe.com. Accessed Dec 2013

H. Heurich, C. Higman, Partial oxidation in the refinery hydrogen management scheme. Paper presented to AIChE Spring Meeting, Houston, 30 Mar 1993 (1993)

Linde Engineering, Partial Oxidation information pages (2013), www.linde-engineering.com. Accessed 17 Dec 2013

J.D. Marano, *Gasification and Supporting Technologies*, U. S. Department of Energy, National Energy Technology Laboratory, Energy Information Administration (2003)

University of Malaysia Chemistry Department, Techniques for Hydrogen (Synthesis) Production, http://kimia.um.edu.my/staff_new/sharifa_bee/2324/SCES2340_P3_Hydrogen_Synthesis_041218.pdf. Accessed 13 Dec 2013

K. Wawrzinek, C. Keller, (Linde Engineering, 2007), Industrial hydrogen production and technology. Paper presented at Karlsruhe FuncHy-Workshop, 21 Nov 2007

Electrolytic Hydrogen

Hydrogen production article in Wikipedia (2013), http://en.wikipedia.org/wiki/Hydrogen_production. Accessed 17 Dec 2013

J. Ivy, Summary of Electrolytic Hydrogen Production, Milestone Completion Report, National Renewable Energy Laboratory, Golden (2004), www.nrel.gov. Accessed Dec 2013
NEL Hydrogen, Process Description, NEL A Atmospheric Electroliser (2012), www.nel-hydrogen.com. Accessed 17 Dec 2013

Olefin Cracking Byproduct Recovery

CB&I/Lummus, Ethylene (2012), www.CBI.com/lummus-technology. Accessed Dec 2013
Orica Ltd., *Ethylene Chemical Fact Sheet* (1999). Accessed Dec 2013

Refinery Gas Recovery

J. Alves, (UOP, 2005), Meeting the growing hydrogen demand in oil refining. Presentation to World Petroleum Congress, https://www.onepetro.org/conference-paper/WPC-18-0914. Accessed Dec 2013
S. Faraji, et al., (University of Tehran, 2005), Hydrogen recovery from refinery off-gases. J. Appl. Sci. **5**(3),459–464
G. Fleming, (Air Liquide-MEDAL, 2006), Membrane technology for hydrogen recovery. Presentation 24 Aug 2006 at Topsoe Catalysis Forum, www.topsoe.com/sitecore/shell/Applications/~/media/PDF%20files/Topsoe_Catalysis_Forum/2006/Fleming.ashx. Accessed Dec 2013
Linde Engineering Inc., Brochure: Hydrogen Recovery by Pressure Swing Adsorption (2012), http://www.linde-engineering.com/internet.global.lindeengineering.global/en/images/HA_H_1_1_e_12_150dpi19_6130.pdf. Accessed Dec 2013
UOP article, Hydrogen Purification, www.UOP.com/processing-solutions/gas-processing/hydrogen/. Accessed 18 Dec 2013

Pressure Swing Adsorption

Linde Engineering Inc., Brochure, Hydrogen Recovery by Pressure Swing Adsorption (2012), http://www.linde-engineering.com/internet.global.lindeengineering.global/en/images/HA_H_1_1_e_12_150dpi19_6130.pdf. Accessed Dec 2013
UOP article, Hydrogen Purification, www.UOP.com/processing-solutions/gas-processing/hydrogen/. Accessed 18 Dec 2013

Membranes

G. Fleming, (Air Liquide-MEDAL, 2006), Membrane technology for hydrogen recovery. Presentation 24 Aug 2006 at Topsoe Catalysis Forum, www.topsoe.com/sitecore/shell/Applications/~/media/PDF%20files/Topsoe_Catalysis_Forum/2006/Fleming.ashx. Accessed Dec 2013
UOP article, Hydrogen Purification, www.UOP.com/processing-solutions/gas-processing/hydrogen/. Accessed 18 Dec 2013
UOP website summary item, Polybed™ PSA and Polysep™ Membrane Integration for Debottlenecking: Case Study (2007), http://www.uop.com/?document=uop-psa-polysep-membrane-integration-case-study%26download=1

Cryogenic Recovery

R. Dragomir, et al., (Praxair, 2010), Paper from AIChE 2010 Spring Meeting Proceedings: Technologies for Enhancing Refinery Gas Value, http://www.praxair.com/~/media/North%20America/US/Documents/Specification%20Sheets%20and%20Brochures/Industries/Refining/AIChE_Paper_2_16_10.ashx. Accessed Dec 2013

S. Faraji, et al., (University of Tehran, 2005), Hydrogen recovery from refinery off-gases. J. Appl Sci **5**(3), 459–464 (2005). Wilson Energy Partners LLC, www.wilsonenergypartners.com/cryogenic.html

W.H. Isalski, Article on Cryogenic Plant, http://www.thermopedia.com/content/677/?tid=110%26sn=7. Accessed Dec 2013

Quality Control of Products in Petroleum Refining

David S. J. Jones

Contents

David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_27

Keywords

LPG • Gasolines • Kerosenes • Aviation turbine fuels • Jet fuels • Gas oils • Fuel oils • Lube oils • Heavy fractions • Test methods • ASTM tests and specifications

Introduction

This chapter is concerned mostly with the laboratory testing for the control of petroleum products. It will be concerned with those tests that establish the quality of refinery streams and in some finished and salable products. What are not covered are those specialized tests such as mass spectrometry, motor road tests, and the like. Where possible, sketches of test apparatus are included. Most of these tests are performed in the refinery laboratory and generally follow the methods provided by the respective ASTM numbered tests.

The most common tests to check the quality of finished products cover the following:

- Specific gravity
- ASTM distillations
- Pensky–Martens closed-cup flash point
- Kinematic viscosities
- Octane numbers
- Sulfur content tests
- LPG weathering tests
- Reid vapor pressure
- Bromine number

The chapter begins with some details of typical product specifications. More discussions and descriptions of modern-day trends in product quality (such as the effect of reformulated gasoline) are given elsewhere in this book.

Specifications for Some Common Finished Products

This chapter is concerned only with those energy products that are common to everyday living. They include LPGs, gasolines, burning oil (including kerosene), diesel fuel, jet fuels, and the black oils including fuel oil and marine diesel.

LPG

This category includes the normal specifications for propane and butane LPG. The detailed requirements for LPG are specified in ASTM D1835. Regular issues are currently available, from 1997 to 2013. Table 1 provides a typical specification.

Gasolines

Two grades of gasoline are given here. They represent the present-day and near-future quality requirements meeting the environmental parameters already discussed earlier in this volume. The two grades are:

- Regular grade
- Premium grade (100 octane)

The specifications given in Table 2 cover the present-day quality requirements. Note that only the major quality items and tests are listed here (also refer to Appendix 1 for updates).

Table 1 Specifications covering salable LPG

Propane LPG (Note 1.0)		Method of test
Vapor pressure at 113 °F, psig	255 max	IP 161
C_1 hydrocarbons, mol%	0.1 max	ASTM D2163
C_2 hydrocarbons, mol%	5.0 max	ASTM D2163
C_3 hydrocarbons, mol%	95.0 min	ASTM D2163
C_4 and heavier hydrocarbons, mol%	4.0 max	ASTM D2163
Total unsaturated hydrocarbons, mol%	1.0 max	ASTM D2163
Total sulfur content, wt%	0.1 max	ASTM D1266
Mercaptan sulfur grains per 100 cubic feet at STP (standard temperature and pressure)	3.0 max	IP 104
H_2S content	Absent	IP 103
Butane LPG (Note 1.0)		
Vapor pressure at 113 °F, psig	70–85	IP 161
C_1 hydrocarbons, mol%	Nil	ASTM D2163
C_2 hydrocarbons, mol%	0.5 max	ASTM D2163
C_5 hydrocarbons (as nC_5), mol%	2.0 max	ASTM D2163
Total sulfur content, wt%	0.01 max	ASTM D1266
Mercaptan sulfur grains per 100 cuft at STP	2.0 max	IP 104
H_2S content	Absent	IP 103

The above products shall not contain harmful quantities of toxic or nauseating substances and shall be free from entrained water. The odor of the gases shall be distinctive, unpleasant, and nonpersistent and shall indicate the presence of the gas at concentrations in air down to one-fifth of the lower limit of inflammability

Table 2 Gasoline quality requirements

	Regular gasoline	Premium gasoline	
Effective date: September 2002			
Research octane number (RON)	91.0 minimum	100 minimum	ASTM D2699
Motor octane number (MON)	82.0 minimum	91.0 minimum	ASTM D2700
Color	Off white	Orange	Visual
Distillation:			
vol% distilled @ 70 °C Minimum	20	22	ASTM D86
vol% distilled @ 100 °C		Not applicable	ASTM D86
Maximum	50	50	
Minimum	60	60	
vol% distilled @ 180 °C Minimum	90	90	
End point °C	220 °C maximum	210 maximum	ASTM D86
Residue vol%	2 maximum	2 maximum	ASTM D86
Vapor pressures			
Psig @ 100 °F	← Summer 10 max 7.0 min →		ASTM D323
	← Winter 13.5 max 8.5 min →		
Copper strip corrosion (3hr at 50 °C)	← Class 1 maximum →		ASTM D130
Sulfur wt%	← 0.035 max →		IP 336 or ASTM D5453
Existent gum (solvent washed) (mg/100 ml)	← 4 maximum →		ASTM D381
Oxidation stability induction period (minutes)	← 360 minimum →		ASTM D525
Other specifications for regular and premium grade gasoline are:			
Lead, mg/litre	5 maximum		IP 224
Benzene, vol%	4 maximum		ASTM D5580
Total aromatics	42 maximum (regular) 48 maximum (premium)		ASTM D 5580
Oxygenates, vol%	1 maximum (except ethanol)		ASTM D 4815
Ethanol, vol%	10 % maximum		
Olefins, vol%	18 maximum		ASTM D 1319

In the United States (Federal Register, vol. 79, no. 81, April 28, 2014) required reductions in the gasoline sulfur content under the Tier 2 program began in 2004 with refinery and importer caps of 300 wt-ppm and a corporate average cap of 120 ppm. For most refiners and importers, compliance with the final sulfur standards (30 annual average and 80 per-gallon cap) was required beginning in 2006. The Tier 2 program was fully implemented on January 1, 2011. Under the Tier 3 program, gasoline and any ethanol-gasoline blend is required to have a sulfur level of 10 ppm or less on an annual average basis beginning January 1, 2017. In addition, refiners and importers continue to be subject to a refinery gate per-gallon sulfur cap of 80 ppm, and gasoline downstream of the refinery gate subject to a 95 ppm per-gallon sulfur cap (possibly subject to further reductions). Many other specifications may apply; for example, the vapor lock index, the driveability index, the volatility specifications (ASTM D4814), etc. which should be consulted as appropriate.

Kerosenes

There are three grades of kerosenes which are common in most refineries. These are:

- Odorless kerosene
- Regular-grade kerosene
- Premium kerosene

Specifications for each of these are given in Table 3.

Aviation Turbine Gasoline (ATG) and Jet Fuels

This product is among the most important item produced in a refinery. Its quality must conform with stringent requirements particularly for use in commercial

Table 3 Specifications for kerosene products

	Odorless kerosene	Regular grade	Premium grade	Test methods
Specific gravity @ 15	0.820 max	0.820 max	0.820 max	ASTM D 4052
Appearance @ 15°C	←	Clear & Bright	→	Visual
Color Saybolt	←	+ 20	→	ASTM D156
Odor	Merchantable	N/A	N/A	
Distillation IBP °C	←	175	→	ASTM D86
50%	240 max	235 max	N/A	
90%	210 min	N/A	N/A	
FBP	280 max	N/A	280 max	
Residue vol%	N/A	2.0 max	N/A	
Flash point °C	75 min (PMCC)	20 min (Abel)	43 min (Abel)	
Smoke point mm	N/A	20 min	35 min	IP 57
Sulfur content Wt%	0.01 max	0.2 max	0.04 max	IP 336
Copper 3 hrs 100°C	1 max	1 max	1 max	ASTM D 130
Aromatics vol%	1 max	N/A	N/A	
Doctor test	←	Negative	→	IP 30
Burning test mg/kg	N/A	N/A	10 max	

aircraft. In this chapter the description and discussion on ATG will be confined mainly to that for civil purposes, although reference will be made to the military grades of ATG. The specification that sets the standard for commercial jet fuel quality is ASTM D1655. A summary of the specification is given in Table 4.

IATA (International Air Transport Association) publishes a document for the guidance of international users of ATG. This document is titled *Guidance Material for Aviation Turbine Fuels Specifications*. This guidance contains specifications for four aviation turbine fuel types. Three of these are kerosene-type fuels (Jet A, Jet A1, and TS1) and the other is a wide-cut fuel Jet B. Jet A meets the ASTM requirements, Jet A1 meets the Joint Checklist requirements, TS1 meets the Russian GOST requirements, and Jet B meets the CGSB requirements.

Table 5 summarizes some of the requirements of ASTM D 1655 and DEF STAN (Defence Standard) 91-91. Both specifications include many footnotes to the requirements listed in Table 5 and also address other fuel issues. Readers in need of details should refer directly to the current version of the specification of interest. Also, readers should remember that a product specification is a living document that undergoes periodic updates. ASTM standards include a suffix indicating the year of last revision, e.g., D 1655-04 was last revised in the year 2004. Table 5 accurately reflects the specifications as of this writing, but it will become out-of-date in time. Jet A1 is listed as the Defense Standard 91-91 which is close to the UK Jet A1 standard.

The properties controlled by the specification are not all independent of one another. For example, as total aromatics content increases, density, final boiling point temperature, and freezing point increase, and smoke point decreases.

Military jet fuel. The governments of the United States and many other countries maintain separate specifications for jet fuel for military use. The reasons for separate specifications include the operational and logistical differences between the military and civilian systems and the additional demands high-performance jet fighter engines place on the fuel.

There are currently two fuels in widespread use by the US military. They are JP-5 used by the Navy and JP-8 used by the Air Force. Both are kerosene-type fuels and the major difference between them is their flash point temperature. The minimum flash point for JP-8 is 38 °C while that for JP-5 is 60 °C. The higher flash point for JP-5 is for the safer handling of the fuel on aircraft carriers. Appropriate updates should be consulted as they become available. Also, separate specifications apply to biojet fuel and to synthetic fuels (e.g., Fischer-Tropsch). Detailed descriptions are available from various oil companies (e.g., Chevron, Shell, etc.)

Gas Oils

Three grades of gas oils are considered here. They are:

- Heating oil (regular-grade gas oil)
- Automotive grade (diesel fuel)
- Marine diesel

Table 4 Commercial jet fuel specification

Composition			
Acidity, total, mg KOH/g, max	0.10	–	D3242
Aromatics, vol%, max	25	25	D1319
Sulfur, mercaptan, % mass, max	0.003	0.003	D3227
Sulfur, total, % mass, max	0.30	0.3	D1266, D1552, D2622, D4294, or D5453
Volatility			
Distillation, °C			D86
Volume percent recovered			
10, max	205	–	
20, max	–	145	
50, max	Report	190	
90, max	Report	245	
Final boiling point, max	300	–	
Distillation yields, vol%			
Residue, max	1.5	1.5	
Loss, max	1.5	1.5	
Flash point, °C, min	38	–	D56 or D3828
Density, 15 °C, kg/m3	775–840	751–802	D1298 or D4052
Vapor pressure at 38 °C, kPa, max	–	21	D323 or D5191
Fluidity			
Freezing point, °C, max	−40 (Jet A)	−50	D2386, D4305, D501, or D5972
	−47 (JetA-1)		
Viscosity at −20 °C, mm^2/s, max	8.0	–	D445
Combustion			
Net heat of combustion, MJ/kg, min	42.8	42.8	D4529, D3338, or D4809
Luminometer number, min	45	45	D1740
Smoke point, mm, min	18	18	D1322
Naphthalenes, vol%, max	3.0	3.0	D1840
Corrosion			
Copper strip, 2 h at 100 °C, max	No. 1	No. 1	D130
Stability			
Thermal stability, 2.5 h at 260 °C			
Filter pressure drop, mm Hg, max	25	25	D3241
Tube deposit, less than contaminants	Code 3	Code 3	
Existent gum, mg/100 ml, max	7	7	D381
Water reaction, interface rating, max	1b	1b	D1094
	Jet A or A1	Jet B	

Table 5 Compares several of the specification properties of the major civilian jet fuels

Fuel	Jet A	Jet A-1	TS-1	Jet B
Specification	ASTM D 1655	DEF STAN 91-91	GOST 10227	CGSB-3.22
Acidity, mg KOH/g	0.10	0.015	0.7 (mg KOH/ 100 ml)	0.10
Aromatics, % vol, max	25	25.0	22 (% mass)	25.0
Sulfur, mass%	0.30	0.30	0.25	0.40
Sulfur, mercaptan, mass%	0.003	0.003	0.005	0.003
Distillation, °C				
Initial boiling point	–	Report	150	Report
10 % recovered, max	205	205	165	Report
50 % recovered, max	Report	Report	195	Min 125; max 190
90 % recovered, max	Report	Report	230	Report
End point	300	300	250	270
Vapor pressure, kPa, max	–	–	–	21
Flash point, °C, min	38	38	28	–
Density, 15 °C, kg/m3	775–840	775–840	Min 774 at 20 °C	750–801
Freezing Point, °C, max	−40	−47.0	−50 (Chilling point)	−51
Viscosity, –20 °C, mm^2/s, max	8	8.0	8.0 at −40 °C	–
Net Heat of combustion, MJ/kg, min	42.8	42.8	42.9	42.8
Smoke point, mm, min	18	19.0	25	20
Naphthalenes, vol%, max	3.0	3.00	–	3.0
Copper corrosion, 2 h at 100 °C, max rating	No. 1	No. 1	Pass (3 h at 100 °C)	No. 1
Thermal stability				
Filter pressure drop, mmHg, max	25	25	–	25
Visual tube rating, max	<3	<3	–	<3
Static test 4 h at 150 °C, mg/100 ml, max	–	–	18	–
Existent gum, mg/100 ml, max	7	7	5	–

Heating oil is used predominately as domestic heating oil in many countries. Its most important properties are the pour point and sulfur content. A full specification of the gas oil is given in Table 6.

The specification for automotive-grade gas oil (diesel fuel) is given in Table 7. Certain properties of this product are more stringent than those for heating oil to meet the present environmental requirements and the present design features of the diesel engines. The one item that stands out as being very stringent is the sulfur content of the diesel. This specification became effective in 2002.

Table 6 General specification for regular-grade gas oil

Properties		Method of test
Specific gravity at 60 °F	0.820–0.845	ASTM D1298
Color NPA	$1^1/_2$	ASTM D155
Pour point		ASTM D97
Summer, °F	14	
Winter, °F	5	
Cloud point		ASTM D97
Summer, °F	25	
Winter, °F	20	
Sulfur, wt%	0.5	ASTM D129
Diesel index	57 min	IP 21
Cetane number	50 min	ASTM D613
Distillation		ASTM D158
Recovered at 230 °C, vol%	10 min	
Recovered at 240 °C, vol%	50 max	
Recovered at 300 °C, vol%	70 min	
Recovered at 357 °C, vol%	90 max	
FBP, °C	385 max	
Flash point (PM), °F	150 min	ASTM D93
Copper strip (3 h at 100 °C)	1 A	ASTM D130
Viscosity at 100 °F SUS (Saybolt universal seconds)	37.5 max	ASTM D88
Carbon residue (Conradson) on 10 % Btms, wt%	0.1 max	ASTM D189
Ash, wt%	0.01 max	ASTM D482
Water by distillation, wt%	0.05 max	ASTM D95
Sediment by extraction, wt%	0.01 max	ASTM D473
Calorific value (gross), Btu/lb	19,300 min	ASTM D240

More stringent specifications have applied since 2006. In the past, diesel engine manufacturers have produced engines to meet the increasingly stringent emissions standards through improvements to the combustion process itself. In order to meet additional regulatory standards (U.S. 2007+, Europe 2009+), most new diesel engines will need to employ some type of advanced exhaust after-treatment technology. Because most exhaust after-treatment devices are very sensitive to sulfur (some devices can be permanently damaged by prolonged exposure to fuel sulfur levels as low as 50 ppm), vehicles so equipped must use ultra-low sulfur diesel (ULSD) fuel, officially designated as S15 in the ASTM diesel fuel standard. The term “ultra-low sulfur diesel” may refer to different levels of sulfur in different parts of the world. However, for the purposes of this review (Chevron, Diesel Fuels Technical Review, 2007), ULSD refers to diesel fuel containing less than 15 ppm sulfur in the U.S. and less than 10 ppm sulfur in Europe and the Asia-Pacific region.

In California, the Air Resources Board (ARB) has regulated an additional requirement. All diesel fuel sold in this state must have an aromatics content of 10 mass percent or less. Alternatively, a fuel supplier can test and certify a fuel with

Table 7 Specification for diesel fuels (also refer to Appendix 1 for updates)

Properties		Method of test
Specific gravity at 60 °F	0.820–0.860	ASTM D1298
Color NPA	3 max	ASTM D155
Pour point		ASTM D97
Summer, °F	15	
Winter, °F	7	
Cloud point		ASTM D97
Summer, °F	N/A	
Winter, °F	N/A	
Sulfur, wt%	0.1[a]	ASTM D129
Diesel index	54 min	IP 21
Cetane number	47 min	ASTM D613
Distillation		
Recovered at 230 °C, vol%	10 min	ASTM D158
Recovered at 240 °C, vol%	50 max	
Recovered at 347 °C, vol%	50 min	
Recovered at 370 °C, vol%	95 max	
FBP, °C	385 max	
Flash point (PM), °F	140 min	ASTM D93
Copper strip (3 h at 100 °C)	1 max	ASTM D130
Viscosity at 100 °F, SUS	35.9 max	ASTM D88
Carbon residue (Conradson) on 10 % Btms, wt%	0.25 max	ASTM D189
Ash, wt%	0.1 max	ASTM D482
Water by distillation, wt%	0.02 max	ASTM D95
Sediment by extraction, wt%	0.005 max	ASTM D473
Calorific value (gross), Btu/lb	Not specified	ASTM D240

[a] Down to 50 wt-ppm (0.005 wt%) for ultra-low-sulfur diesel

higher aromatics level, if emissions are equivalent to those of a specific reference fuel with a 10 mass percent aromatics level. In that case, other fuel properties (cetane number, sulfur, nitrogen, aromatics, and polynuclear aromatics) are recorded. Fuel marketed under this certification must be within the recorded limits of these five properties.

ULSD became widely available in Western Europe and Japan (10 ppm sulfur maximum) starting in 2005; the U.S. (15 ppm sulfur maximum) followed in 2006. Full transition to ULSD has occurred over a period of several years, with 100 % of on-highway and off-road diesel meeting ULSD specifications by 2009 in Europe and by 2010–2014 in the U.S. While ULSD enables use of advanced exhaust after-treatment technology on new diesel engines, it is also fully compatible with, and will help reduce sulfate emissions from, existing older technology diesel engines.

The third gas oil product is really a blend of the gas oil distillate and atmospheric residuum. Its color is black and has the following much reduced specification. This is given in Table 8.

Table 8 Specification for marine diesel fuel (subject to revisions, especially sulfur content)

Properties		Method of test
Specific gravity at 60 °F	0.840 min	ASTM D1298
Pour point – winter, °F	15 max	ASTM D97
Sulfur, wt%	N/A	ASTM D129
Diesel index	50 min	IP 21
Flash point (PM), °F	150 min	ASTM D93
Viscosity at 100 °F, SUS	32.0–43.9	ASTM D88
Carbon residue (Conradson) on 10 % Btms, wt%	0.2 max	ASTM D189

A variety of fuels are available for marine diesel engines (Chevron, Diesel Fuels Technical Review, 2007). There is a set of four marine distillate fuels, some of which contain small amounts of resid, and a set of 15 marine residual fuels in which resid is the majority constituent.

Marine fuels range in viscosity from less than one centistoke (cSt) to about 700 cSt at 50 °C (122 °F) (1 cSt = 1 mm^2/s). The higher viscosity grades are preheated during use to bring their viscosity into the range suitable for injection (8–27 cSt). Marine fuels also contain more sulfur than on-road diesel fuel, although, in some areas and ports, only low sulfur fuels are permitted. The maximum sulfur limit varies from 1 % to 4.5 % by mass for different grades and Sulfur Emission Control Areas (SECAs).

Several organizations issue marine fuel specifications. ISO 8217 of the International Standards Organization (ISO) is the primary standard. The International Maritime Organization (IMO) also develops regulations for shipping. Among the measures adopted within IMO is MARPOL (the International Convention for the Prevention of Pollution from Ships); this is the main international convention covering the prevention of operational or accidental pollution of the marine environment by ships. MARPOL Annex VI also limits the usage of fuels to prevent air pollution.

The shipping industry prefers higher viscosity residual fuels because they are less expensive. Although residual fuels do not burn as readily as distillate fuels, the slow speeds (60–200 rpm) of the large marine engines allow more time for combustion to occur.

Fuel Oil Products

The single most common fuel oil marketed today is the No. 6 grade. Of the lighter grades, Nos. 1, 2, and 3 were distillate fuels (mostly regular-grade kerosene and gas oil types). These pretty much disappeared from the markets during the 1980s. No. 5 fuel was a light residual fuel used mostly in the steel industry. It is no longer widely used. No. 6 fuel is a heavy residual fuel, normally a mixture of atmospheric and vacuum distillation residues cut back to adjust for viscosity with kerosene or gas oil cutter stock. This fuel oil product is almost entirely used as ship bunker oil, with some market outlet to stationary power plants in producing steam for their turbines. For the last 20 years or so, these markets have been in decline. Power plants are converting to the use of coal or natural gas, and ships are leaning more to the use of marine diesel or just diesel fuel. Environmental restrictions are calling for a continual decrease in the sulfur content of this particular product. As a result, No. 6 fuel is the least valued refinery product and is worth less than the crude feed itself. Refiners are now installing processes (such as "deep oil cracking" and residue hydrocracking) to upgrade this product to the more valued distillates such as gasoline and the middle distillates. The specification for a No. 6 fuel oil is given in Table 9.

Lube Oils

Most marketable lube oils produced in a refinery are graded by their viscosity. Proprietary brands of these lube oil grades will contain additives as provided by their particular marketing outlets. These basic grades and their specification are given in Table 10. Other specifications apply for multigrade lube oils.

These grades and their processing are described in some detail in the discussion of "non-energy refineries."

Table 9 Specification for No. 6 fuel oil product

Properties		Method of test
Specific gravity at 60 °F	0.990 max	ASTM D1298
Pour point, °F	65 max	ASTM D97
Sulfur, wt%	2.0 max[a]	ASTM D129
Kinematic viscosity at 122 °F, cSt	370 max	ASTM D445
Flash point (PM), °F	160 min	ASTM D93
Ash, wt%	0.1 max	ASTM D482
Water (by distillation), vol%	1.0 max	ASTM D95
Sediment (by extraction), wt%	0.1 max	ASTM D473

[a] Sulfur content is probably closer to 1.5 % wt for most areas now

Table 10 Specification for basic (single grade) lube oil grades

Grade	Max viscosity at 0 °F, SUS	Max viscosity at 210 °F, SUS	Min viscosity at 210 °F, SUS
5 W	6,000	–	–
10 W	12,000	–	–
20 W	48,000	–	–
SAE 20	–	58	45
SAE 30	–	70	58
SAE 40	–	86	70
SAE 50	–	110	85

Asphalts

The production of the asphalt grades and their specification have been described and discussed under “non-energy refineries.” A good source of information is the Asphalt Paving Design Guide available from the Asphalt Paving Association of Iowa (undated).

Petroleum Coke

Petroleum coke is not found in crude oil, but is the carbon compound formed from the thermal conversion of petroleum containing resins and asphaltenes. Coke is formed in the processes to convert the residuum fuels to the more desirable distillate products of naphtha and lighter, through to the middle distillates. There are two routes by which this coking process proceeds. The first and the most common is the delayed coking route. The second is the fluid coking method, and this has been made more attractive to many refiners with the development of ExxonMobil’s proprietary process of *FLEXICOKING*. This proprietary process eliminates the coke completely by converting it to low-Btu fuel gas. By far the largest production of coke is the sponge coke from the delayed coking process. Uncalcined sponge coke has a heating value of about 14,000 Btu/lb and is used primarily as a fuel. High-sulfur sponge coke however is popular for use in cement plants since the sulfur reacts to form sulfates. Sponge coke is calcined to produce a coke grade suitable for anodes in the aluminum industry. Details of the specifications for green (uncalcined) coke and calcined coke are given in Table 11.

Sulfur

Sulfur is a by-product of modern-day refineries. By the processes that make up the modern hydrogen skimming refinery, a significant portion of the sulfur contained in the crude is removed as elemental sulfur for marketing as a product. It is true to say that as the environmental requirements for the reduced sulfur levels in products and

Table 11 Specification for sponge coke

Parameter	Green coke	Calcined coke
Fixed carbon %	86–92	99.5
Moisture %	6–14	0.1
Volatile matter %	8–14	0.5
Sulfur %	>2.5	>2.5
Ash %	0.25	0.4
Silicon %	0.02	0.02
Nickel %	0.02	0.03
Vanadium %	0.02	0.03
Iron %	0.01	0.02

Table 12 Typical specifications for sulfur

Purity	99.8 wt% sulfur, on a dry basis
Ash	500 ppm by weight maximum
Carbon	1,000 ppm by weight maximum
Color	Bright yellow
Hydrogen sulfide	10 ppm by weight maximum. This is particularly important for international transport and sales
State	Shipped either liquid or solid

emissions from the refinery decrease, the sulfur produced as a product increases. In most countries today, over half of the required sulfur is produced from the petroleum and gas industries. Sulfur is stored and transported from the refinery as a molten product or as solid sulfur. Almost half the world's sulfur production is used in making sulfuric acid and phosphate fertilizers using the sulfuric acid produced from the sulfur. A typical specification for sulfur is given in Table 12.

Description of Some of the More Common Tests

The tests described here are usually carried out in the refinery laboratory. The results from these tests are used in plant control and for the quality control of finished products. There are many more laboratory and other tests that are carried out in the refinery company's research and development establishment. These later tests are carried out to improve product quality parameters or to establish design data for processes and development work. These later tests would include mass spectrometry for crude oil data and assay development, pilot plant tests to establish optimum operating data, and items such as motor vehicle road tests. Those tests described briefly in the following sections are those listed earlier.

Specific Gravity (D1298)

Density ASTM D1298 – Density, relative density (specific gravity), or API gravity of crude petroleum and liquid petroleum products by the hydrometer method. Fuel is transferred to a cylindrical container and a hydrometer is carefully lowered into the cylinder and allowed to settle. After the temperature of the sample has equilibrated, the value on the hydrometer scale positioned at the surface of the sample and the sample temperature are recorded. The hydrometer value is converted to density at 15.6 °C or API gravity at 60 °F using standard tables. The API gravity which is always quoted in degrees API can be calculated from the hydrometer test at 60 °F using the equation as follows:

$$\text{Specific Gravity} = \frac{141.5}{131.5 + {}^{\circ}\text{API}}$$

The calculation of the weight per unit volume from the specific gravity is based on the US measure of volume (i.e., US gallons). A summary table of the relationship between specific gravity at 60 °F, °API, and lbs per gallon is shown in Table 13.

ASTM Distillations

There are two types of ASTM distillations that are used in the refinery for plant control and finished product quality. These are the ASTM D86 for naphtha and its equivalent products and for kerosenesand ASTM D1160. ASTM D1160 is an equivalent method run at reduced pressures.

ASTM D86

The diagram in Fig. 1 is the apparatus used for ASTM distillations. Only the apparatus item sizes will change and the temperature levels in the condenser bath. The measured sample is introduced into a glass Engler flask (A) at 100 ml for the D86 test. The liquid fills about two-thirds of the flask, leaving the space above the liquid to the cork in the vessel neck as vapor space. About halfway along the neck of the flask, there is a vapor offtake tube. The open end of this tube is connected to the condenser tube which is routed through the condenser bath (B). This condenser tube

Table 13 Relationship of specific gravity at 60 °F, °API, and lbs/US gal

°API	10	20	30	40	50	60
Spec gravity	1.000	0.934	0.878	0.825	0.780	0.739
Lbs/gal	8.328	7.778	7.296	6.870	6.490	6.151

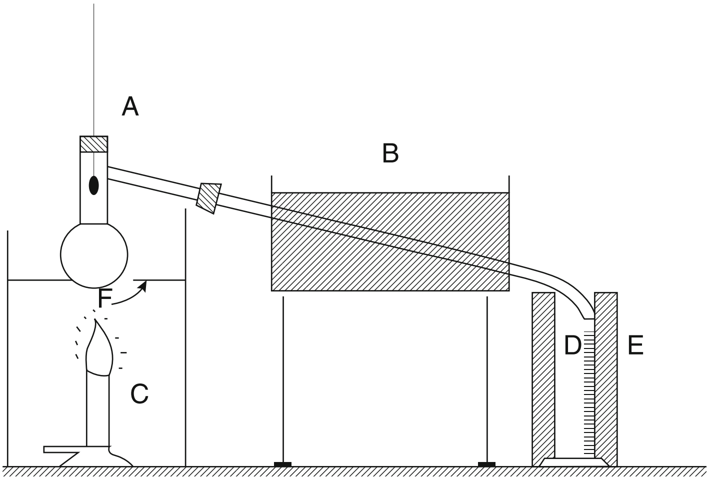


Fig. 1 Diagram of a typical ASTM distillation apparatus

emerges from the "bath" and the open end is directed into a measuring cylinder. For the lower-boiling-range samples (i.e., naphthas), this cylinder is placed in a cold water (slightly below room temperature) bath. The Engler flask rests on an asbestos or similar plate (F) which has a hole 1″ in diameter exposing the bottom of the flask to the heat source. In this case the heat source is shown as a Bunsen burner (C). A thermometer is introduced into the top of the flask and is positioned so that the bulb is directly in line with the vapor offtake. The condenser bath is filled with water and ice and allowed to reach 32 °F before heat is applied to the sample flask and the test begun. The temperature of the sample is increased slowly until the liquid begins to boil. The initial boiling point is read as the temperature measured by the thermometer located in the flask when the first condensate drop enters the receiving cylinder (D) at the end of the condensate bath (B). For low-boiling-point samples (i.e., naphthas), this receiver is cooled in a water bath (E). For kerosenes, the water bath (E) is not required. The test is allowed to proceed at a constant rate and temperature readings are taken at predetermined recovery levels of condensate (usually, these temperatures will be at 10 vol% recovered and 30, 50, and 90 vol% recovered). When the flask (A) has been boiled apparently dry, the temperature shown by the thermometer will rise sharply and then begin to fall. The highest temperature observed in this rise and fall is the final boiling point of the sample.

Flash Point Test Method

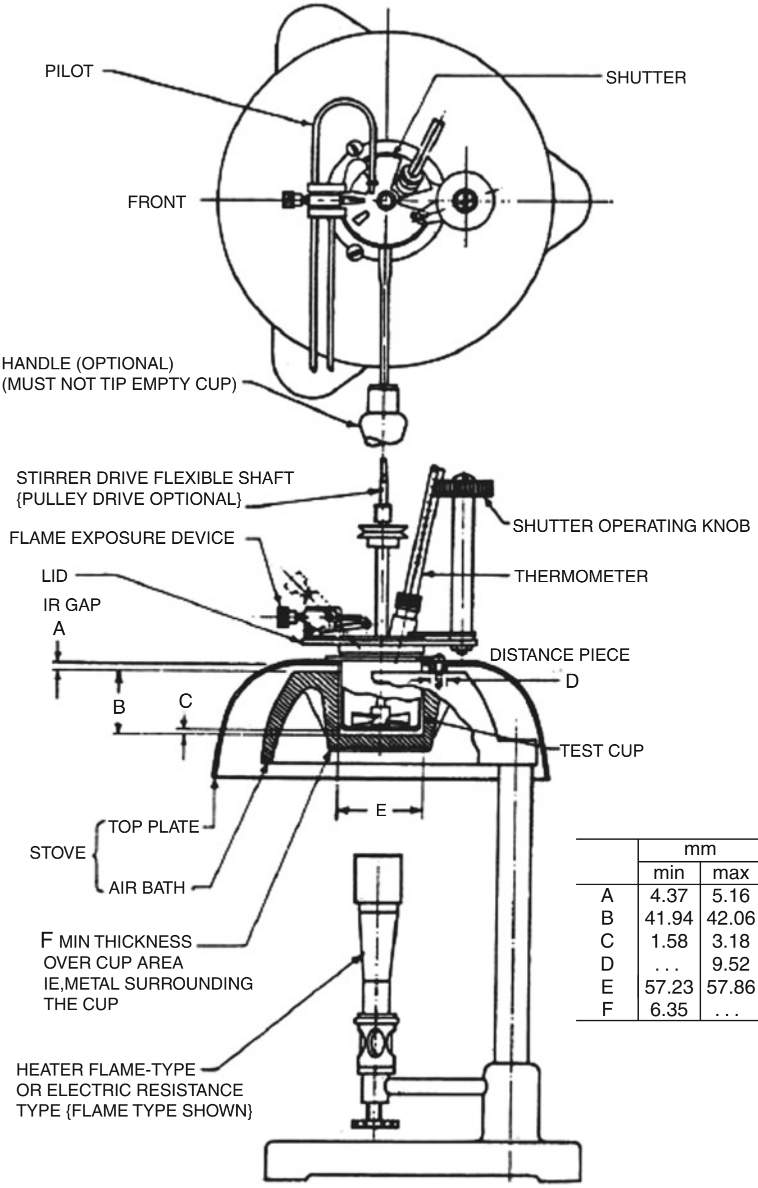
There are two methods used for determining the flash point of intermediate and finished petroleum products. These are the ASTM D56, the Tag closed-cup method (commonly known as the Abel flash point), and the ASTM D93, the Pensky–Martens closed-cup method. The D56 method is used for a material which has a flash point of between 68 °F and 148 °F, while the D93 method is used for all other distillates and residuum products with flash points above 148 °F. Based on this premise, the D56 is used almost exclusively for the kerosene-cut-range materials. Only the Pensky–Martens D93 will be described here.

ASTM D93

A brass test cup is filled to an inside mark with the test specimen. A cover is fitted of specified dimensions; see Fig. 2. The specimen is heated and stirred at specified rates. An ignition source in the form of a small flame is directed into the cup at regular intervals. When the specimen is seen to flash, the temperature of the specimen is noted as the flash point of the sample.

Significance and Use

The flash point is a measure of the tendency of the material to form a flammable mixture with air under controlled laboratory conditions. It is however only one of several properties that must be considered in assessing the overall flammable hazard of the material. The flash point is used to establish the flammable criteria in transporting the material. Generally, shipping and safety regulations will be



	mm		in.	
	min	max	min	max
A	4.37	5.16	0.172	0.203
B	41.94	42.06	1.651	1.656
C	1.58	3.18	0.062	0.125
D	. . .	9.52	. . .	0.375
E	57.23	57.86	2.253	2.278
F	6.35	. . .	0.25	. . .

Fig. 2 The Pensky–Martens closed-cup flash point apparatus

based on the flash point criteria. The flash point should NOT however be used to describe or appraise the fire hazard or risk under actual fire conditions. This test method (D93) provides the only closed-cup flash point test procedures for temperatures up to 698 °F.

Pour Point and Cloud Point

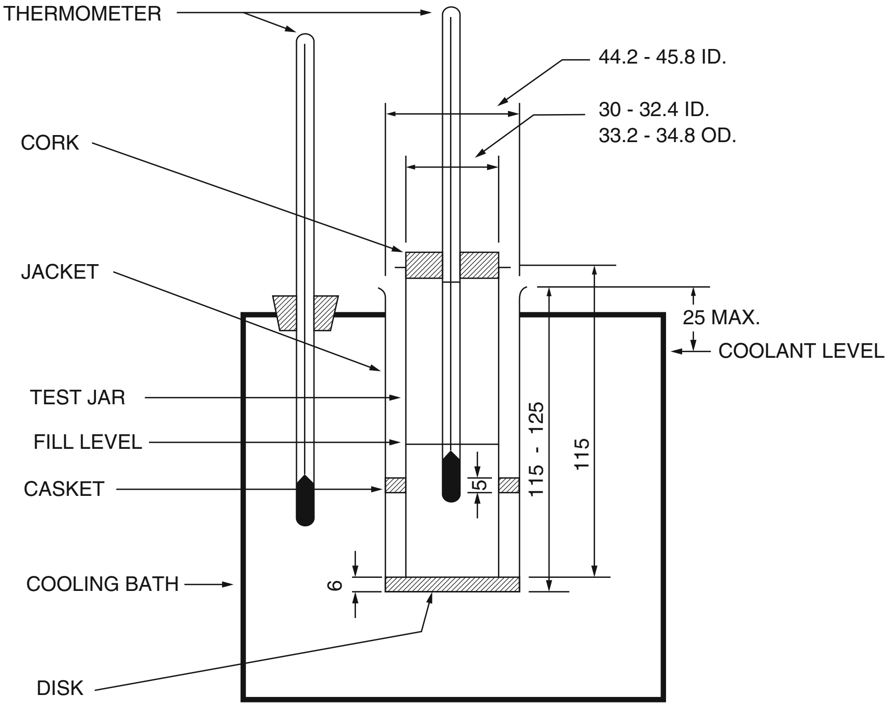
Pour points are determined initially by heat-treating the petroleum specimen above its expected pour point and then by cooling the specimen in controlled stages until the pour point is observed. The pour point is the temperature of the material at which it ceases to flow.

ASTM D97

The apparatus used to determine pour point (and cloud point) consists of a cylindrical glass jar with a flat bottom and a cork stopper at its top. A thermometer is inserted through the cork stopper so that the bulb is immersed up to 3 mm of the capillary in the specimen. The sample is inserted into the jar up to a prescribed level. The apparatus is shown in the following Fig. 3 and is self-explanatory.

The sample is first heated as follows:

Material with an estimated pour point above 33 °C – heat to a temperature of expected pour point plus 9 °C but at least 45 °C in a bath controlled to at least 48 °C. Material with an expected pour point of below 33 °C – heat to at least 45 °C and cool to 15 °C in a bath controlled at 6 °C.



NOTE 1- Dimensions are in millimetres (not to scale).

Fig. 3 Apparatus for pour point tests

Commence the test then by sequential cooling and observing the flow of the specimen using cooling baths as follows:

For temperatures down to	
Bath 1 – ice and water	9 °C
Bath 2 – crushed ice and sodium chloride	−12 °C
Bath 3 – crushed ice and calcium chloride	−27 °C
Bath 4 – acetone and solid carbon dioxide	−57 °C

The specimen is checked at regular intervals of cooling (every 3–5 °C) for flow. This checking must be done with great care by just slowly tilting the jar to the horizontal position for not more than 5 s and observing if there is flow. The moving of the sample from bath to bath should be at the following schedule:

Specimen at 27 °C	Move to bath 1
Specimen at 9 °C	Move to bath 2
Specimen at −6 °C	Move to bath 3
Specimen at −24 °C and below	Move to bath 4

The pour point is reported as the temperature where no flow is observed plus 3 °C.

Kinematic Viscosity

The kinematic viscosity of oil is obtained by measuring the time required for a sample of the oil to flow, under gravity, through a capillary. The capillary is a part of the calibrated viscometer and the flow of the oil through it is at a known temperature. These viscometers come in several sizes and differing designs. The configuration and size of the capillary are calibrated and tested to provide a constant value for that particular viscometer.

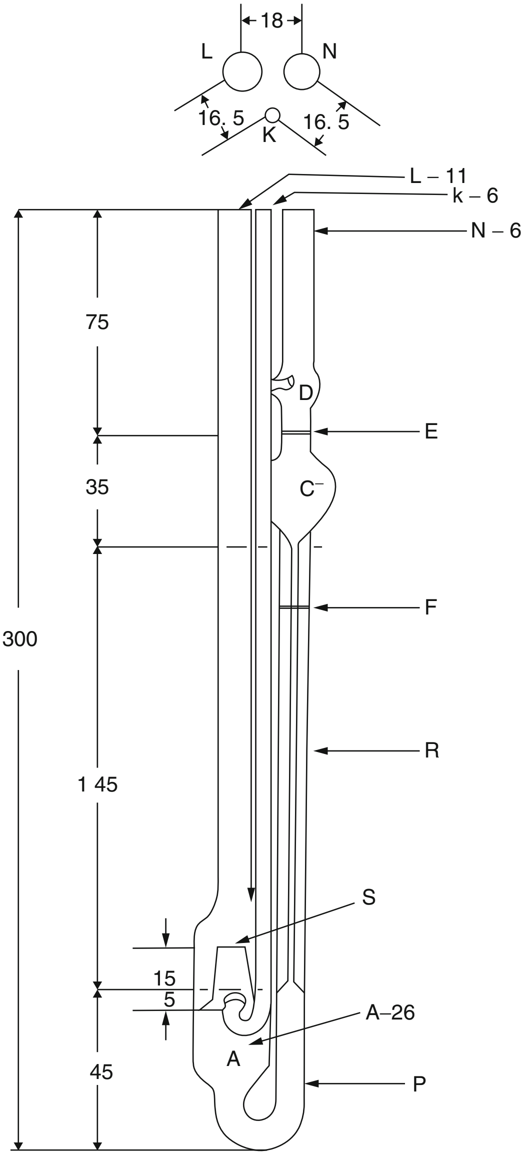
ASTM D446

The viscometer shown in Fig. 4 is one of many types. It is used for obtaining the viscosity of transparent liquids. The viscometer shown in Fig. 4 is designated as SIL. Its important features and its calibration constants are given in Table 14.

The viscometer(s) shown may be one of many. These are suspended using a specially designed holder in a bath containing water with some glycol added to reduce vaporization or prevent boiling. The bath is maintained at a constant temperature at which the viscosity is to be reported. The test temperature may be as high as 100 °C, thus the use of glycol in the bath water to prevent actual boiling.

The oil sample is introduced into the viscometer through tube L by tilting the viscometer to about 30° from the vertical with bulb A below capillary R. After introducing the sample, attach the viscometer into the holder and insert the viscometer into the bath so that it is vertical. Allow the sample to reach the bath temperature, usually about 30 min before starting the test. Using suction (all laboratories should have a vacuum system), draw up the sample through bulb C

Fig. 4 Viscometer for transparent liquids



NOTE 1–All dimensions are in millimetres.

to about 5 mm above the upper timing mark E. Release the vacuum and allow the sample to flow by gravity. Measure the time for the sample to flow from the timing mark E to the lower timing mark F. This is the time t in the equation

$$V = C \times t$$

where

V = the kinematic viscosity in centistokes
C = the approximate constant in $(\text{mm}^2/t)/t$ (from Table 14)
t = the flow time from the test

Reid Vapor Pressure

This test is the standard test for low-boiling-point distillates. It is used for naphthas, gasolines, light cracked distillates, and aviation gasolines. For the heavier distillates with vapor pressures expected to be below 26 psig at 100 °F, the apparatus and procedures will be different. Only the Reid vapor pressure for those distillates with vapor pressures above 26 psig at 100 °F is described here. The apparatus used for this test is shown in Fig. 5.

Table 14 Viscometer SIL details

Size number	Approximate constant[a]	Kinematic viscosity range, ctt	Inside diameter of tube R, mm	Inside diameter of tubes E and P, mm	Volume of bulb C, ml
0C	0.003	0.6–3	0.41	4.5–5.5	3.0
1	0.01	2.0–10	0.61	4.5–5.5	4.0
1C	0.03	6–30	0.73	4.5–5.5	4.0
2	0.1	20–100	1.14	4.5–5.5	5.0
2C	0.3	60–300	1.5	4.5–5.5	5.0
3	1.0	200–1,000	2.03	4.5–5.5	5.0
3C	3.0	600–3,000	2.68	4.5–5.5	5.0
4	10.0	2,000–10,000	3.61	4.5–5.5	5.0

[a] Constant is in $(\text{mm}^2/t)/t$

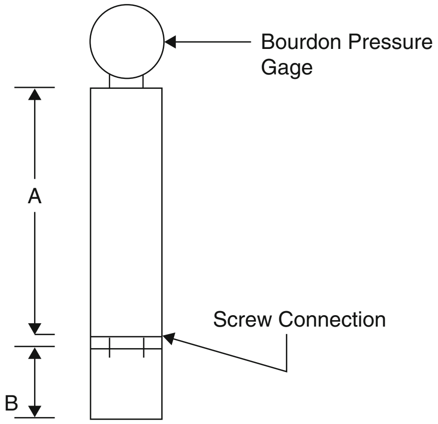


Fig. 5 A Reid vapor pressure apparatus

ASTM D323

In the above diagram, A represents the vapor chamber which has a length of 254 mm and a diameter of 51 mm. The ratio of the volume of the vapor chamber A to the liquid chamber B shall be between 3.8 and 4.2. The diameters of both the vapor chamber and the liquid chamber shall be the same. The liquid test sample is placed in the liquid chamber to fill the vessel. The liquid chamber is then connected to the vapor chamber and the pressure gauge inserted as shown in the diagram. The assembled apparatus is then immersed vertically in a water bath up to a level of 190 mm of the vapor chamber. The water bath is kept at a temperature of 100 °F for 30 min and then removed, tilted once or twice, and replaced for 15 min further. At the end of this time, the vapor pressure of the test sample is read from the pressure gauge to the nearest 0.2 psi.

Weathering Test for the Volatility of LPG

This test is a measure of the relative purity of liquefied petroleum gases (LPGs). The test results give the indication of the pentane content of butane LPG or the amount of butane in a sample of propane LPG. Volatility expressed in terms of 95 % evaporated temperature of the test sample indicates the measure of the least volatile fuel components present. The apparatus used for this test is shown in Fig. 6.

The weathering tube is a centrifuge cone-shaped tube conforming to the dimensions given in Fig. 6. The shape of the lower tip is especially important – the taper shall be uniform and the bottom rounded as shown in Fig. 6. The tube is calibrated as shown and the calibration tolerances are given in the following Table 15.

ASTM D1837

Testing a Butane or a Butane–Propane Mixture

If the sample is at a temperature of 10 °F or below, allow it to weather in the atmosphere to 10 °F then introduce the thermometer and assemble the apparatus as shown in Fig. 6. Place the weathering tube vertically in a water bath (temperature between 60 °F and 70 °F), submerging it to the 1.5 ml mark on the tube. Record the temperature when 95 % of the sample has evaporated.

Weathering Propane-Type LPG

Allow the test sample to weather in the atmosphere. Clean off the frost that will accumulate on the vessel outer surface with a swab containing acetone or alcohol. Read off the temperature at 95 % as in the case for butane.

Smoke Point of Kerosenes and Aviation Turbine Fuels

The sample is burned in an enclosed wick-fed lamp that is calibrated daily against pure aromatic blends of known smoke point. The smoke point of the test sample is

Fig. 6 Weathering tube

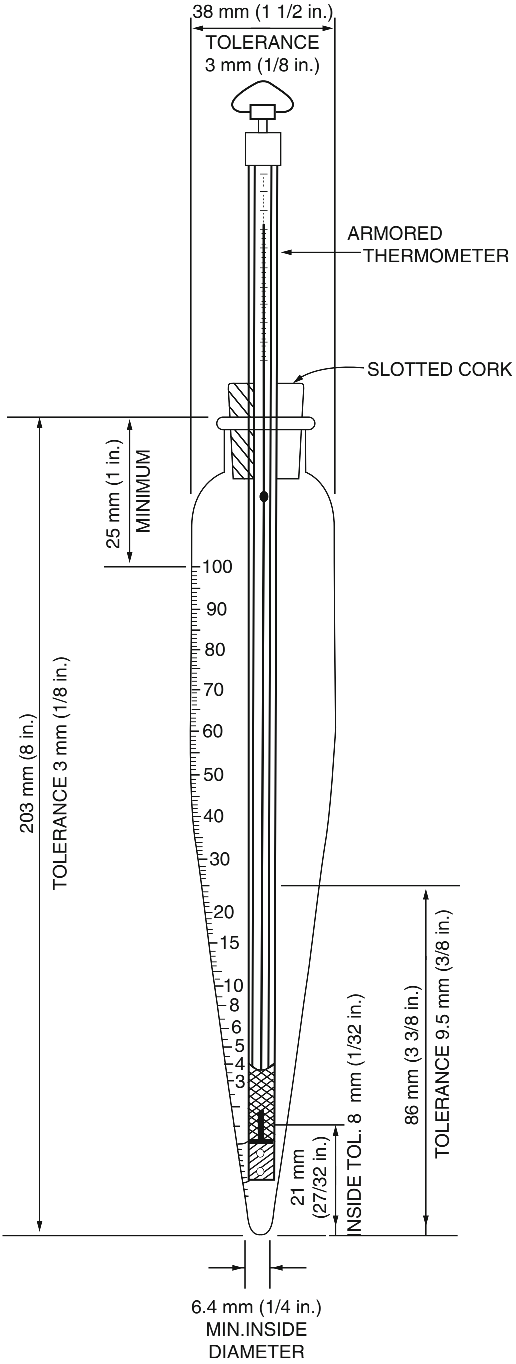


Table 15 Weathering tube graduation tolerances

Range, ml	Scale division, in ml	Limit of error, ml
0.0–0.1	0.05	0.02
0.1–0.3	0.05	0.03
0.3–0.5	0.05	0.05
0.5–1.0	0.1	0.05
1.0–3.0	0.1	0.1
3.0–5.0	0.5	0.2
5.0–25.0	1.0	0.5
25.0–100.0	1.0	1.0

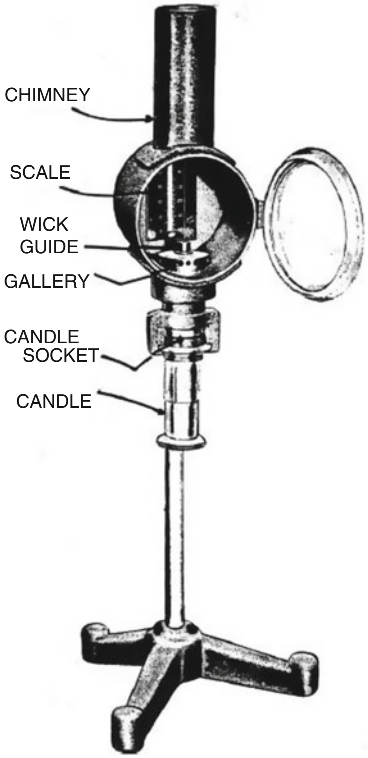


Fig. 7 A smoke point lamp

quoted as the maximum height of flame that can be achieved without smoking. The apparatus that is used for this test is shown in Fig. 7.

ASTM D1322

Calibrating the Apparatus

The apparatus is calibrated daily against known aromatic compound smoke points to establish a correction factor. The two reference fuel blends are toluene and 2,2,4-trimethyl pentane, and details of these fuels are given in Table 16.

Table 16 Reference fuel blends

Standard smoke point at 101.3 kPa, mm	Toluene % (v/v)	2,2,4-Trimethyl pentane % (v/v)
14.7	40	60
20.2	25	75
22.7	20	80
25.8	15	85
30.2	10	90
35.4	5	95
42.8	0	100

The smoke points of the blends are determined in the same way as the test procedure given below. From the calibrating readings, the correction factor f is determined from the equation

$$f = \frac{(A_s/A_d) + (B_s/B_d)}{2}$$

where

A_s = the standard smoke point of the first reference fuel blend
A_d = the actual smoke point determined for the first fuel blend
B_s = the standard smoke point of the second reference fuel blend
B_d = the actual smoke point determined for the second fuel blend

The test procedure is as follows:

Figures 8 and 9 are shown below for detailed reference.

1.0 Soak a piece of extracted and dried wick about 125 mm in length in the test sample, and place it in the wick tube of the candle. Carefully ease out any twists arising from this operation.

2.0 Introduce about 20 ml of the test sample into the clean dry candle; place the wick tube into the candle and screw and secure. Then, insert the candle into the lamp.

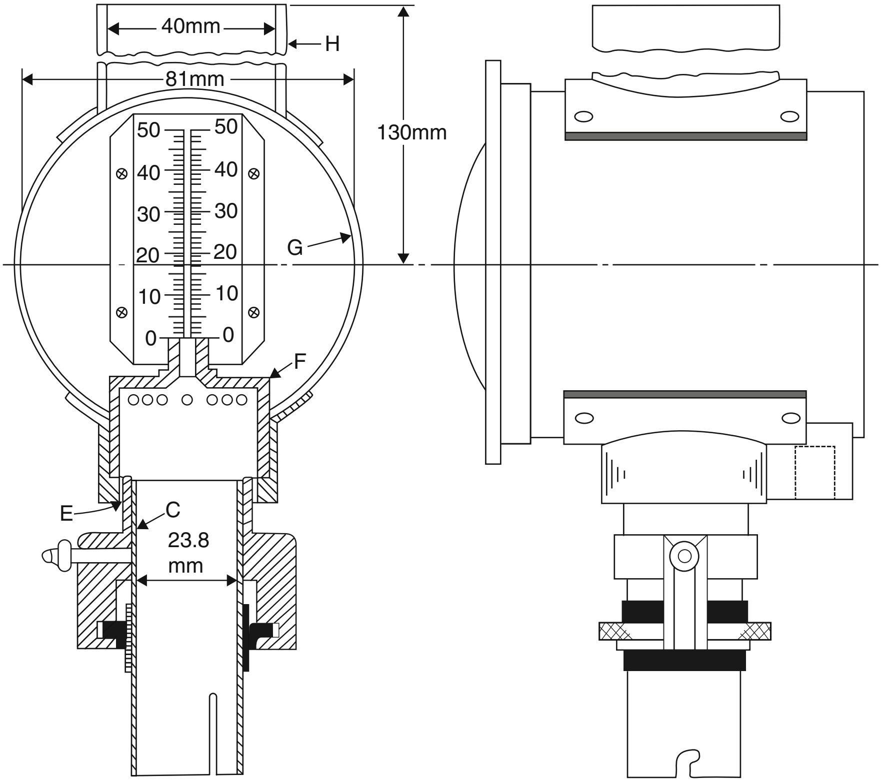
3.0 Light the candle and adjust the wick so that the flame is approximately 10 mm high. Allow the lamp to burn for 5 min. Raise the candle until a smoky tail appears, and then lower the candle slowly until the following stages occur:

- First stage: An elongated pointed tip as shown in Flame A in Fig. 10.
- Second stage: The pointed tip just disappears, leaving a slightly blunted flame shown as Flame B in Fig. 10.
- Third stage: A well-rounded flame tip as shown in Flame C in Fig. 10.

  The correct flame profile is Flame B. Determine the height of this flame and record to the nearest 5 mm.

4.0 Make three separate observations using the same flame sequence as given in item 3.0 above. If these values vary by more than 1.0 mm, repeat the test with a fresh sample.

5.0 The smoke point is calculated to the nearest 1.0 mm using the following equation

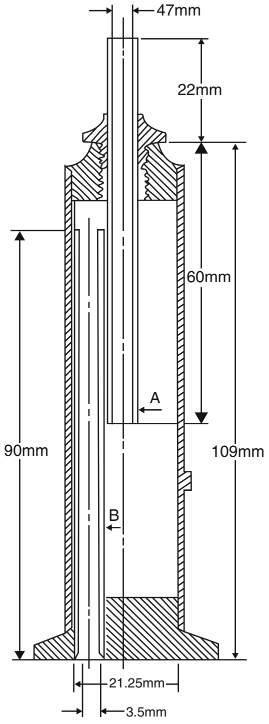


Critical Dimensions of the Lamp Body.

	Dimensions in mm
Candle Socket C internal diameter	23.8
Wick Guide C internal diameter	6.0
Air inlets 20 in number E diameter	2.9
Galary F internal diameter	35.0
Air inlets 20 in number	3.5
Lamp Body G internal diameter	81.0
Internal depth	81.0
Chimney H internal diameter	40
Top of chimney to center of lamp body	130

Fig. 8 The lamp body

Fig. 9 The candle



Critical Dimensions of the Candle.

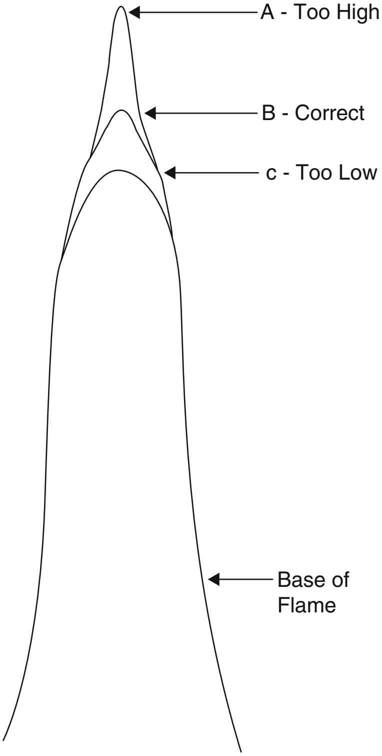
	Dimensions in mm
Candle Body: Internal diameter	21.25
External diameter	Sliding fit in holder
Length without cap	109
Thread on cap	9.5 mm dia 1.0 mm screw pitch
Wick Tube A : internal diameter	4.7
External diameter	Close fit in flame guide
Length	82.0
Air Vent B ; Internal diameter	3.5
Length	90.0

$$\text{Smoke point} = L \times f$$

where

$L =$ the average value of Flame B over the three individual test readings (item 0.4)
$f =$ the correction factor rounded to the nearest 0.01

Fig. 10 Typical flame appearance



Conradson Carbon Residue of Petroleum Products

This test is used to determine the amount of carbon residue left after complete evaporation and pyrolysis of an oil. The degree of this carbon content is indicative of the coke-forming properties of the oil. The value of the Conradson carbon content is important in most heavy oil hydrotreating and most cracking processes. A number of modern catalysts used in heavy oil cracking have been developed to withstand the adverse effect of carbon laydown. Still, excessive coke formation remains a problem in most cracking processes. The apparatus used for this test is shown in Fig. 11.

ASTM D189

The apparatus consists of a porcelain crucible containing a weighed sample of the oil. This crucible is placed in the center of an iron crucible which is itself placed in a larger iron crucible. Both iron crucibles are fitted with covers and are vented through a metallic hood. This assembly is placed on a stand with a supporting

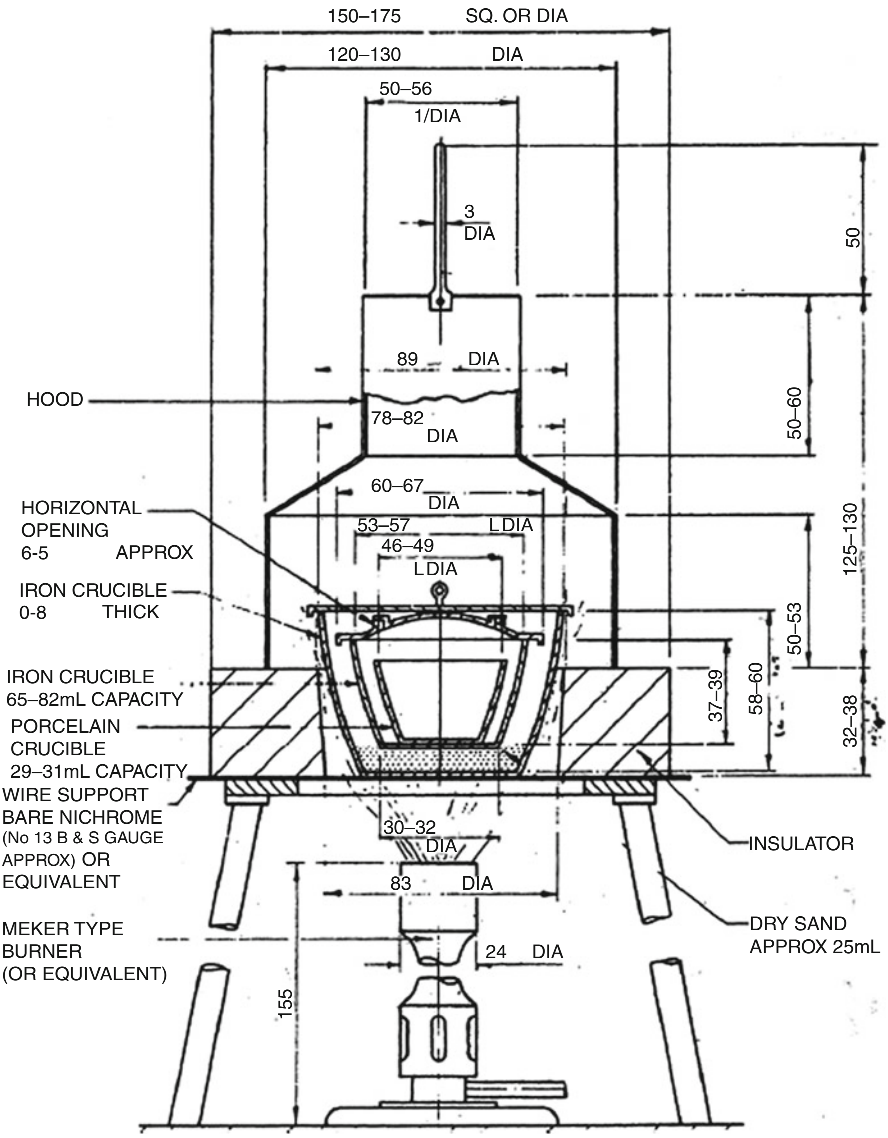


Fig. 11 Apparatus for determining Conradson carbon residue

wire mesh. The crucibles are partially surrounded by insulating brickwork on which the metallic hood rests. Heat is supplied to the crucibles by a burner located below the wire mesh support. The sample is heated for a specified period of time until all the volatile content of the oil has evaporated, leaving the carbon as residue. The carbon content of the oil is calculated as the weight of the carbon left as a percentage of the weight of the original sample.

Bromine Number of Petroleum Distillates

The bromine number is a measure of olefins in a petroleum distillate boiling up to 600 °F. The number is a supporting evidence of the purity of the product with respect to its olefin content.

ASTM D1159

The apparatus used in this test is any apparatus that can perform titration to a preset end point. Such an apparatus may include an electrical meter with two polarized electrodes of sufficient voltage to indicate the end point. The titration vessel is a jacketed glass vessel about 120 mm high and with 45 mm internal diameter. The sample contained in the vessel will be kept at 32–45 °F. The burette will be a normal titration burette capable of measuring the titration reagent in graduations of 0.05 ml or smaller. Place 10 ml of 1,1,1-trichloroethane or dichloromethane in the titration vessel, and introduce the test specimen as indicated in Table 17.

Fill the titration vessel to the mark with the selected solvent. Mix the contents well. Titrate the sample with the standard bromine–bromate solution – stir the specimen well during the titration. The end point is noted by a sudden change in potential on an electrometric end point indicator due to the presence of bromine. The bromine number is calculated by the following equation

$$\text{Bromine number} = \frac{(A - B)(M_1)(15.98)}{W}$$

where

A = milliliters of bromide–bromate solution required for titration of the test sample
B = milliliters of bromide–bromate solution required for titration of the blank
M_1 = molarity of the bromide–bromate solution, as Br_2
W = grams of the test specimen

The olefin content of the test sample can be calculated from the bromine number by the equation

$$\text{Olefin mass } \% = f(BM/160)$$

where

Table 17 Weight of test specimen vs. predicted bromine number

Predicted bromine number	Specimen weight, grams
0–10	20–16
Over 10–20	10–8
Over 20–50	5–4
Over 50–100	2–1.5
Over 100–150	1–0.8
Over 150–200	0.8–0.6

Table 18 Boiling range correction for olefins

Boiling range correction, *f*	Boiling range IBP to FBP, °C
1.0	0
0.975	7
0.950	14
0.925	21
0.900	28
0.875	38
0.850	43
0.825	53
0.800	62
0.775	72
0.750	95
0.725	99
0.700	125 or greater

Table 19 Relation of average molecular weight to 50 % boiling point

50 % boiling point, °C	Average molecular weight
30	72
66	83
93	96
121	110
149	127
177	145
204	164
232	186

f = boiling range correction from Table 18
B = bromine number expressed as grams of bromine per 100 g of sample
M = molecular weight (relative molecular mass of olefin as given in Table 19

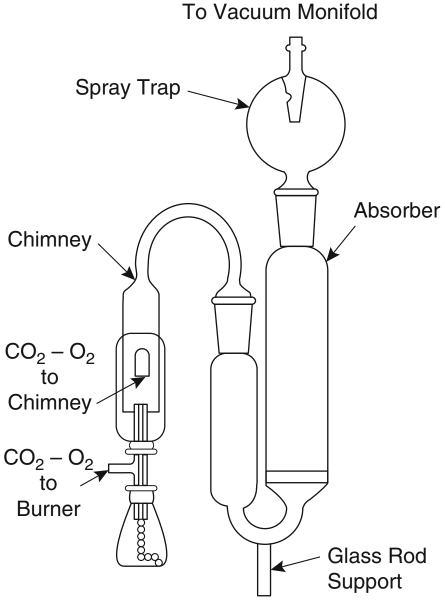
Determining the Sulfur Content by Lamp Method

This test method determines the total sulfur in liquid petroleum products in concentrations of 0.01–0.4 wt%. This method is applicable to all petroleum liquids that can be burned in a wick lamp. It therefore covers gasoline, kerosene, and naphtha. A blending procedure can be applied to determine the sulfur content in oils and heavier fractions which cannot be burned directly in the wick burner. Figure 12 shows the details of the assembled lamp unit. Figure 13 is a schematic diagram of the CO_2–O_2 supply manifold and lamp system.

ASTM D1266

The sample is burned in a closed system using a suitable lamp (Fig. 12) and an artificial atmosphere of 70 % carbon dioxide and 30 % oxygen to prevent the

Fig. 12 Details of assembled lamp unit



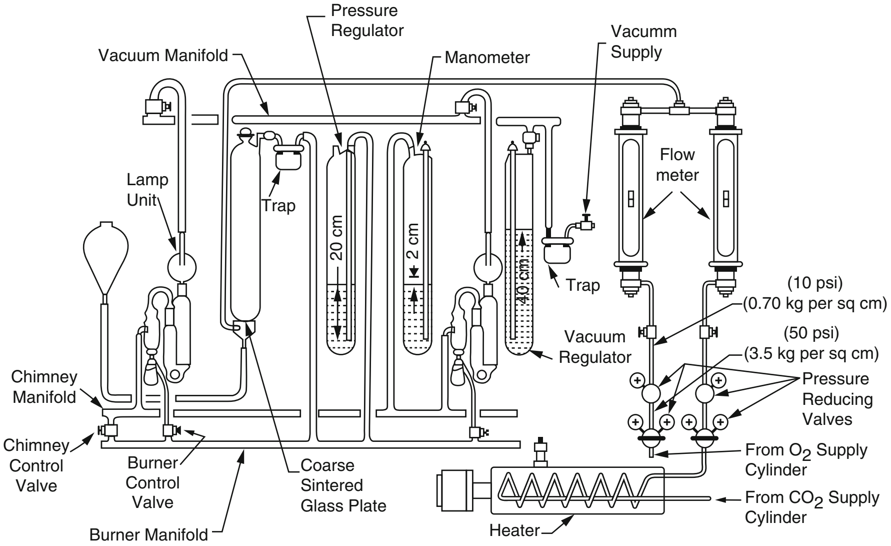


Fig. 13 Schematic diagram of the CO_2–O_2 supply manifold

formation of nitrogen oxides (Fig. 13). The oxides of sulfur are absorbed and oxidized to sulfuric acid by means of a hydrogen peroxide solution. This solution is flushed with air to remove carbon dioxide. The sulfur as sulfate in the absorbent is determined by titration of the sulfuric acid with standard sodium hydroxide. The sample size for direct combustion is 10–15 g; if the predicted sulfur content is below 0.05 % for a predicted sulfur content of 0.05–0.4 %, the sample size should be 5–10 g.

The calculation of the sulfur content from the titration is given by the following equation

$$\text{Sulfur content wt\%} = 16.03M \times (A/10W)$$

where

A = milliliters of NaOH, titrated
M = molarity of the NaOH solution (Note 1 below)
W = grams of sample burned

Note 1: The calculation can be simplified by adjusting the molarity of the NaOH solution to 0.624. Then, 1 ml of the solution will be equivalent to 0.001 g of sulfur. In this case the factor 16.03 M in the calculation becomes 1.0.

Octane Number: Research and Motor (Details of this Test Are Given in ASTM Standards, Part 7)

By definition, an octane number is that percentage of isooctane in a blend of isooctane and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90-octane gasoline matches the knock characteristic of a blend containing 90 % isooctane and 10 % *n*-heptane.

The knock characteristics are determined in the laboratory using a standard single-cylinder test engine equipped with a super sensitive knock meter. The reference fuel (isooctane and C_7 blend) is run and compared with a second run using the gasoline sample. Two octane numbers are usually given: the first is the research octane number (RON) and the second is the motor octane number (MON). The same basic equipment is used for both octane numbers, but the engine speed is increased for the motor octane number. The actual octane number obtained in a commercial engine would be somewhere between the two numbers. The significance of the two octane numbers is to evaluate the sensitivity of the gasoline to the severity of the operating conditions in the engine. Invariably, the research octane number is higher than the motor octane number; the difference between them is quoted as the “sensitivity” of the gasoline.

Conclusion

The specifications and the selected tests given here represent the control measures used to establish product quality control. Much of the testing described here is used for plant control, while all the tests are necessary to ensure that the product quality of finished products is met. In modern refinery practice, much of the plant control is achieved using "in-line" analyzers tied to control system computers. These computers automatically adjust plant conditions to meet the set product quality criteria. A similar "in-line" analysis is used for blending run-down streams for finished products. Invariably, though, laboratory testing is still used to "spot-check" plant intermediate product quality, and laboratory testing is always used as a final check on finished product quality.

Appendix 1: Typical Gasoline and Diesel Fuel Specifications in Europe and the United States

Some gasoline and diesel fuel specifications are moving targets in that they get updated on a more or less regular basis. The following attempts to summarize some of its most salient characteristics as of early 2014.

Typical gasoline (petrol) specifications in the European Union (November 2012)

RON	91/95
MON	81/85
Sulfur, ppm, max	10
Lead, g/l, max	0.005
Manganese, g/l, max	0.002 (as of January 2014)
Benzene, vol%, max	1
Aromatics, vol%, max	35
Olefins, vol%, max	18

Typical gasoline specifications in the United States (July 2012)

Antiknock index (R+M)/2	
Regular	87
Midgrade	89
Premium	91+
Sulfur, ppm, max	80 (cap), 30 (average)
Lead, g/l, max	0.013
Manganese, g/l, max	0.0083 (0)
Benzene, vol%, max	0.62 (average), 1.3 (max)
Aromatics, vol%, max	
Olefins, vol%, max	

Typical diesel fuel specifications in the European Union (February 2012)

	Temperate climate	Arctic and winter climates
Cetane number, min	51	47–49
Cetane index, min	46	43–46
Sulfur, ppm, max	10	10

(*continued*)

	Temperate climate	Arctic and winter climates
Total aromatics, vol%, max		
Polyaromatics, wt%, max	8	8
Density at 15 °C, kg/m^3, min–max	820–845	800–845
Viscosity at 40 °C, cSt, min–max	2–4.5	1.2–4

Typical 2-D diesel fuel specifications in the United States (December 2012)

Cetane number, min	40
Cetane index, min	40[a]
Sulfur, ppm, max	15
Total aromatics, vol%, max	35[a]
Polyaromatics, wt%, max	
Density at 15 °C, kg/m^3, min–max	
Viscosity at 40 °C, cSt, min–max	1.9–4.1

[a] Either specification must be met

Petroleum Refinery Planning and Economics

David S. J. Jones and Peter R. Pujadó

Contents

David S. J. Jones: deceased.
Peter R. Pujadó has retired.

D.S.J. Jones
Calgary, AB, Canada

P.R. Pujadó (✉)
UOP LLC, A Honeywell Company, Kildeer, IL, USA
e-mail: prpujado@gmail.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_28

Keywords
Refinery operation • Planning factors • Process evaluation • Cost estimates • Cash flow analysis • Linear programming • Common terms and expressions

Introduction

This chapter is divided more or less into three parts. The first part (section "Refinery Operation Planning") deals with the planning of a refinery's operation, which includes its optimized crude runs, product slate, and any process expansion or debottlenecking that may be required to meet this optimized operation. The second part (sections "Process Evaluation and Economic Analysis," "Discounted Cash Flow and Economic analysis," and "Using Linear Programming to Optimize Configurations") deals with the process economic evaluation of a proposed new refinery or new facilities within an existing refinery. (The execution of the capital project is discussed in the chapter "▶ Petroleum Processing Projects" elsewhere in this Handbook.) The third part (section "Common and Expressions Used in Standard Economic Analyses") is a summary of common terms and expressions used in a standard economic analysis.

The second part of this chapter is closely related to the first part in so far as process studies and the ultimate selection of any process or processing route are based on the approved marketing strategies for the petroleum processing company. This in turn is based on the conclusions following the work undertaken in the first part. The separate project execution chapter, as noted above, describes the final project activities to put equipment in place to implement an economic plan.

Refinery Operation Planning

The basic organization of an oil company consists essentially of three main departments:

- The transportation department
- The refining department
- The marketing department

The functions of these three main departments are coordinated by a supply department. This department undertakes this role in accordance with the following sequence:

1. The marketing department informs the supply department with the quantities of products they can sell.
2. The supply department, after making adjustments for stock levels, advises the refinery of the quantity of each product required.

3. The refining department advises the supply department of the actual quantities they can produce and how much crude they will require to do so.
4. The supply department arranges with the transportation department for the necessary shipping to:
   - Provide the crude.
   - Lift the products.
   - Import the quantities that cannot be produced.

In the above sequence of events, Item 3 is carried out by the planning section of the refinery department. Their objective is to translate the production requirements given by the supply department into a workable system, which specifies the actual operation of each plant to ensure that the final result is the most economical one practicable. This is termed the “running plan” for the operation.

Running Plans

Running plans are developed and issued on a monthly basis. They usually cover periods varying from 11 to 18 months ahead. Long-term periods are broken down into quarters, while short term (up to 6 months ahead) are broken down into months. The main uses of the running plan are to provide data for:

- Keeping the supply department and the company executives informed
- Providing information for long-term chartering of ships
- Arranging import programs
- Pinpointing future product quality and equipment difficulties

The running plan is used in a refinery as the basis for an operating program. Such a program is developed in the refinery by converting the plan into a day-to-day operation program for each refinery plant. At the end of every month, the plant operation for that month is summarized and compiled into an operations summary which compares the actual plant operation with the program. Usually, the refinery organization will include a planning department, and the production of both the operating program and the subsequent summary is their responsibility.

The Rules of Planning

Before looking at the development of running plans in some detail, it is necessary to understand some fundamental rules. These are listed below and are the “Planning Data”:

- Equipment availability
- Plant performance
- Service factors
- Product quality
- Planning properties
- Blending properties

- Crude availability
- Crude quality
- Tankage and lines availability
- Economic rules

Most of these rules are self-explanatory, but notes on a few of those items, which are not so apparent, are as follows:

Plant Performance

This is an important requirement in planning the refinery daily and long-term operation. The exact operating capability of the various refinery plants must be known. Such data that are essential are:

- Yields under any operating condition and any feed quality
- Product quality under any operating condition and feed quality
- Maximum and minimum plant throughput
- Fuel consumption

Blending Properties

Most finished products leaving the refinery are blends of one or more basic process streams. For example, all gasoline products will be blends of straight run naphtha and some high octane streams from a cracking unit and/or streams from a catalytic reformer or other units (e.g., isomerization). Full description and discussion on blending and blended products are given in the chapter entitled "▶ Introduction to Crude Oil and Petroleum Processing" of this Handbook. In planning the refinery's day-to-day operation, these blending techniques and, when applicable, blending indices are used.

Crude Availability

With most major oil refining companies, the company's central supply department issues the availability of crude slates (quantities and crude source) when they issue the requirement data. In most cases, the respective refining company has contracts for the purchase of a few specific crudes and their quantities. Of these basic crude slates, one or two of the crude oils may be increased or decreased if necessary. These are called marginal crude oils. Most often there are two types of crude oils in the slate which are marginal. One of these marginal crude oils would be used if more crude than is shown on the slate is required. The other would be backed out of the slate if the entire projected slate was not required. Thus, marginal crude oils play an important part in the economic running plans for a refinery operation.

Economic Rules

Using the planning rules, it is possible to devise an infinite number of schemes that would meet the majority of the market requirements. Only one such scheme however would be the most profitable. It is the most profitable plan or scheme that has to be determined and implemented, and to do, this it is necessary to

Table 1 Changes to running plan to maximize profit

Change base case	Crude MB/CD 200	Fuel MB/CD 83	Mid dist MB/CD 12	Naphtha MB/CD 40	Cum profit base case over $/D
Reduce viscosity of cat feed to fuel from 46.9 RI to 40.2 RI at 100 °F	198.267	81.370	11.65	40.667	595
Reduce residue length from 24 % to 22 %	189.798	73.406	9.685	43.886	3,558
Decrease octane from 50 to 45 res	189.702	73.276	9.179	42.870	4,000
Lower cat plant conversion by 3 %	187.129	71.074	8.667	46.186	5,024

MB thousands of barrels, *CD* calendar day (or alternatively, *SD* stream day)

follow some basic economic rules. These rules may be developed with answers to the following typical questions:

1. If all requirements cannot be met, in which priority order should the various products be placed?
2. Is it profitable to run the refinery to meet just a fuel oil product requirement, that is, not to produce waxy distillates at all?
3. What is the optimum octane number severity operation for the reforming and/or cracking units to meet gasoline requirements?
4. Which are the cheapest middle distillates to import if this becomes necessary to meet a product slate?
5. Is it economical to utilize a surplus unit capacity to produce feed to another, for example, to use surplus deasphalting capacity to produce feed for the catalytic cracker?
6. Does it pay to divert straight run naphtha to refinery fuel in a situation where naphtha outlet is limiting?

Table 1 is a simplified example of the use of these economic rules to determine the changing of fuel oil “length” in a middle distillate outlet limiting situation. The only units considered here are the crude distillation unit (atmospheric and vacuum), cat reformer unit, and the cat cracker (FCCU). Being a middle distillate outlet limiting, there will be spare capacity in the units considered, and all requirements are met except for fuel oil. The economic rule in this case is that the most profitable plan will be when the crude and fuel oil are at a minimum while still meeting the requirements of the other products in the slate.

Developing the Running Plan

In most refining companies with more than one refinery installation, running plans are developed in the company’s corporate offices. In this way, access to the required data (such as crude availability, product slate, etc.) is readily available to the planner. Normally, running plans are published on a monthly basis. Again normally these plans cover a period of 18 months. The early part of the period, say the first 6 months, will be studied on a monthly basis, and the remainder on a quarterly basis.

The Use and Purpose of the Refinery Running Plans

The running plans are designed to provide corporate management with data with respect to the following:

1. The anticipated pattern of production, i.e., the surpluses and the deficits that are likely to occur.
2. The likely operations of the refineries in the company. This covers crude runs and refinery throughputs.
3. Any inadequacies in refining capacities to meet projected profit margins. This may form the basis for refinery expansion program. (This is dealt with in a separate item of this section of the chapter.)
4. Indication as to where and when extra business can be accommodated in the company's operating plan.
5. The basis for financial forecasting and estimates of profit and loss.

The Planning Schemes

The content of the running plan will conform to the rules of planning listed and discussed earlier. The development of all running plans begins with schematic diagrams giving as many options as possible of the routes by which a required product slate can be achieved from a particular crude availability slate. The mechanism to arrive at this is not unlike the process configuration study described in the topic "▶ Petroleum Products and a Refinery Configuration" of this Handbook. In the case of the plan schemes, however, the objective is to fit the process streams to a fixed refinery configuration in order to meet a product slate. In these schemes, excess products are corrected by either reducing crude throughput or using the stream as blend stock or feed to other units. Deficits in the product slate may be solved by importing the necessary product components to complete a scheme. An example of a typical planning scheme to meet middle distillates (Jet Fuel in this case) and specialties (white spirit in this case) is given as Fig. 1.

Several such schemes may be developed to meet this particular product slate criterion. Each of them will be subject to an economic analysis, and this may extend to one or more of the company's several refineries. These economic analyses are made using the same criteria of cumulative product profits (including plant operating costs) as described above in *economic rules* and the example provided by Table 1. Computer technology is used extensively in planning these days. Indeed, most refinery companies possess their proprietary programs similar to the linear program discussed later in this chapter to evaluate the economics of the schemes and to determine the optimum one. However, the development of the scheme itself still remains with the planning engineer or development engineer for most companies.

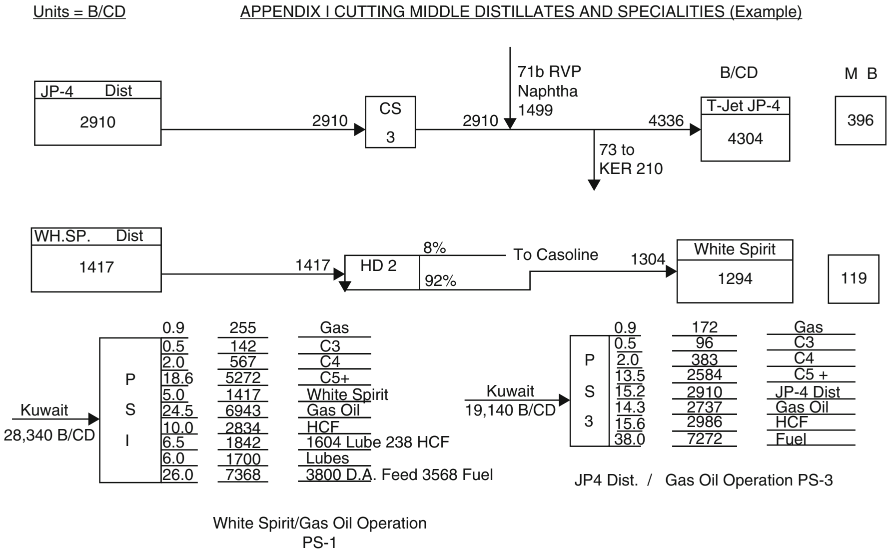


Fig. 1 An example of a planning scheme diagram

The Application of Running Plans in Identifying Refining Inadequacies

This item illustrates a function of the running plan in identifying lack of refining capacity under certain conditions. An example of a work sheet for the report is given in Appendix 1 of this chapter. The scenario surrounding this exercise is as follows:

Background

A large international oil company Concord Petroleum Company (Fictional) has requested two of its European refining affiliates to submit plans for low-cost debottlenecking of distillation capacity which can be "on stream" by next winter. The two debottleneck cases that are to be considered are the company's Kent refinery and the company's South Wales refinery. The expansion for the Kent refinery crude unit will be 34,000 BPSD and that for the South Wales Refinery crude unit will be 40,000 BPSD. The study will determine whether either or both of these debottlenecking routes represent an economic investment opportunity for Concord Petroleum Company to meet the long-range expansion program.

Basis for Assessing Requirements

The following table is the base running plan. It highlights the two UK refinery's crude availability and their respective requirements with surplus and deficit highlights:

Table 2 represents the short-range status. Other running plans for other years are summarized below. Thus, Table 3 gives the product deficiencies/surplus versus crude requirement to satisfy product deficiencies over those years.

See the following notes for Table 3:

1. *Swing capacity* is defined as the sum of international bunkers plus volume of seasonal storage. It is assumed that crude is run for international bunkers in the summer if necessary, and an equal volume of fuel oil is imported in the winter against inland fuel oil requirements. Thus, *swing capacity* represents the volume of crude which can be run in the summer against winter requirements.
2. Net crude is the volume of crude running capacity required in summer and winter when maximum use is made of *swing capacity*.
3. Minimum crude capacity is the volume of distillation capacity which must be available just to meet deficiencies and making maximum practical use of the *swing capacity*.

Eight basic schemes were studied to meet the minimum capacities for satisfying the deficiencies. These were as follow:

Case 1. Expand Kent distillation by 82 Mbpsd – Debottleneck
Case 2. Expand Kent distillation by 34 Mbpsd on CDU 101 and 50 Mbpsd on CDU 102
Case 3. Expand Kent distillation by 50 Mbpsd on CDU 101 and 34 Mbpsd on CDU 102
Case 4. Expand S. Wales distillation by 100 Mbpsd – Grassroots
Case 5. Expand Kent distillation by 100 Mbpsd – Grassroots
Case 6. Expand Kent distillation by 34 Mbpsd and S. Wales by 40 Mbpsd – Debottleneck
Case 7. Expand Kent distillation by 40 Mbpsd and S. Wales by 34 Mbpsd – Debottleneck
Case 8. Expand S. Wales distillation by 75 Mbpsd – Grassroots

There was in addition one sub-case for each of cases 4, 6, 7, and 8. These sub-cases took into account special depreciation allowances for the S. Wales refinery.

The Results

The discounted cash flows at 10 % for the eight cases and the four sub-cases were calculated for the entire period as shown in Table 4. (This took into account the company's long-range plan and forecast.) The preferred case was case 6 with the cognizance of the S. Wales refinery depreciation allowance. The cash flows for these cases are as follows:

Table 2 The base running plan

	←	Summer S.	→	←	Winter	→
MB/CD	Kent	S. Wales	Total	Kent	S. Wales	Total
Input (crude)						
Aramco	66.0	–	66.0	66.0	–	66.0
Brega	113.5	46.5	160.0	130.0	30.0	160.0
Safaniyah	20.0	–	20.0	–	20.0	20.0
Bachequero	18.5	41.5	60.0	22.0	–	22.0
Iraq	–	–	–	–	28.0	28.0
Kuwait	–	37.0	37.0	–	47.0	47.0
Tia Juana	12.0	–	12.0	12.0	–	12.0
Total crude	230.0	125.0	355.0	230.0	125.0	355.0
T. J. Dist	1.1	–	1.1	–	–	–
Output	Prod +/( )					
Gas	3.8 –	–	3.8 –	4.4 –	–	4.4 –
LPG	9.9 (2.3)	4.9 (2.3)	14.8 –	11.0 (6.6)	4.9 (1.5)	15.9 (5.1)
Chemicals	9.7 –	–	9.7 –	9.7 –	–	–
Naphtha Lt	5.9 (2.9)	3.0 (6.7)	8.9 (9.6)	–(15.2)	5.3 (11.6)	5.3 (26.8)
Hy naphtha	53.3 (9.3)	24.7 (3.1)	78.0 (12.4)	54.8 7.6	22.8 (10.2)	77.6 (2.6)
Light dist	26.4 2.7	4.0 –	30.4 2.7	27.6 (2.7)	5.2 –	32.8 (2.7)
Gas oils	36.2 –	17.7 –	53.9 –	50.1 1.9	22.0(1.9)	72.1 –
Fuel blend stk	5.7 –	3.7 –	9.4 –	7.7 –	4.9 –	12.6 –
Heavy fuel oil	–(41.3)	43.8(19.8)	43.8(21.5)	–(43.8)	–(31.4)	– (75.2)
Special FO	54.4 (7.6)	21.6 (7.6)	76.0 –	43.7 (49.9)	53.1 (31.9)	96.8(18)

Table 3 Crude requirements to satisfy deficiencies

	Year 1			Year 2			Year 3			Year 4		
Year	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave	Min	Max	Ave
Deficiencies					MB/CD							
Naphtha	–	8.8	4.4	–	17.0	8.5	9.8	13.4	11.7	9.6	26.8	18.2
Distillates	–	–	–	–	–	–	–	–	–	(2.7)	2.7	–
Fuel oil	(15.9)	32.5	8.2	3.5	48.2	25.9	8.5	70.0	39.2	21.5	93.2	57.4
Total	(15.9)	41.3	12.6	3.5	65.2	34.4	18.3	83.4	50.9	35.8	115.3	75.6
Crude equiv.	(16.3)	42.4	13.0	3.6	67.0	35.2	10.0	85.7	52.2	36.8	118.3	77.6
Swing capacity	40.8	(40.8)	–	39.4	(39.4)	–	37.0	(37.0)	–	35.0	(35.0)	–
Net cap req	24.5	1.6	13.0	43.0	27.6	35.2	55.8	48.7	52.2	71.8	83.3	77.6
Mon cap		13.0			35.2			52.2			77.6	

Table 4 Study cash flow and result

M $ out/(in)											
Year	Base	1	2	3	4	5	6	7	8	Total	Preference
Case 6A	–	5,991	1,054	2,953	380	(1,252)	(923)	(859)	(58)	7,286	1
Cash flow of some other cases are as follows											
Case 5	6,973	7,100	1,395	1,871	779	(1,760)	(1,300)	(1,196)	(81)	13,781	12
Case 7A	–	1,352	6,706	804	(401)	(1,070)	(886)	(409)	(27)	8,069	2
Case 6	–	5,991	1,054	2,953	1,841	(1,352)	(1,090)	(948)	(64)	8,385	4
Case 4	5,212	8,191	1,467	1,040	534	(1,614)	(1,233)	(1,138)	(77)	12,382	11

D.S.J. Jones Note: The names and location of the company and its refineries are, of course, fictitious. The study though is not. The author actually participated in the study itself and was later the lead engineer in the process design of one of the selected refinery (Case 6A) debottlenecking expansions.

A copy of one work sheet used in the study is given in Appendix 1 of this chapter. Most calculations at that time were done by hand, although the discounted cash flow calculations were computerized.

The Refinery Operating Program

One of the major uses of the running plan is to enable the refineries of the company to develop their own operating programs. The running plan sets the objective for the refinery production over a short term and provides a long-term forecast. The operating program translates these requirements into a day-by-day program of work. Operating programs are concerned about the short-term plans for the operation and are prepared for a monthly period. Thus, while running plans are calculated in terms of barrels per calendar day, operating programs are always in terms of barrels per stream day.

The Content of the Operating Program

The actual format of operating programs will vary from company to company; however, they will follow a similar pattern. They will consist of the following items:

- A crude oil program
- An intermediate stock report
- A table of programmed production
- A blending schedule
- An operating schedule
- Operating notes

A crude oil program is a table of the refinery's current crude oil inventory with projected imports, feed outlets, and the storage tank reference. An example of this table is given as Appendix 2 of this chapter.

An intermediate stock report is similar to the crude oil program, but it refers to the refinery's intermediate stocks, which will usually be blended to finished products. An example of this table is also given as Appendix 3.

The table of programmed production is simply the scheduled finished product make from the refinery. The blending schedule is self-explanatory and is usually in a form of simple block flow diagrams. A typical middle distillate schedule is given in Fig. 2.

Operating notes include any critical requirements or operational changes. Operating notes can be updated on a weekly or even daily basis if the company's supply department initiates a change in running plans that affect a particular refinery's operating program. An example of an operating note is as follows:

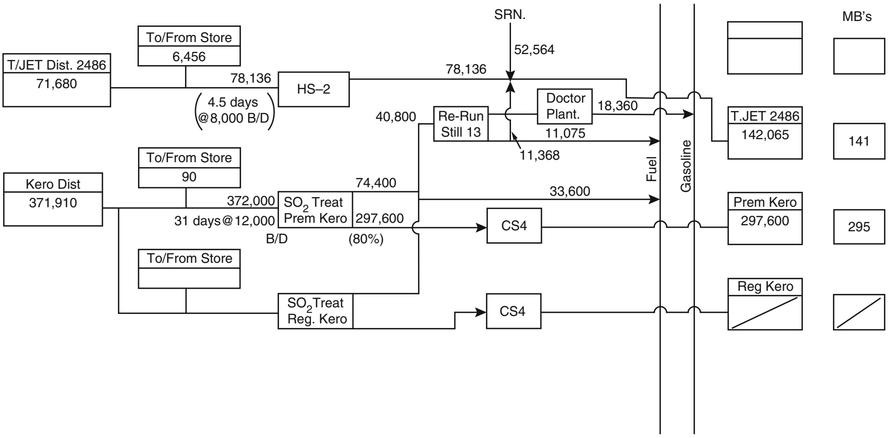


Fig. 2 A typical middle distillate schedule

Current Program

Unit F101	Light gas oil	Marine diesel	White spirit	Turbo jet JP4
Supply dept requirement	750 Mbpsd	235 Mbpsd	40 Mbpsd	181 Mbpsd
Refinery make	668	202	40	181

Supply must have absolute minimum of 725 Mbpsd of light gas oil, i.e., +57 MBs
Can stand only 152 MBs of marine diesel, i.e., −50 MBs
Action: Change kero/gas oil operation to kero/diesel operation

Preparing an Operating Program

In present day refining industry, both the running plan and the subsequent operating programs are computerized. However, their preparation requires the same input as the old manual system. In the case of the operating program, these would follow the sequence listed below:

1. In order to begin assembling the operating program, the planner will need to know the following details:
   - The running plan for the refinery for the month in question.
   - The latest crude slate data.
   - What plants are scheduled for shutdown during the life of the program?
   - Estimate of the intermediate product stocks (Appendix 3).
2. Prepare an outline operating schedule to meet intermediate product requirements and timed to maintain adequate intermediate products in tankage (Appendix 4).
3. Cut the crude(s) TBP into the required product cuts, for the crude unit operation.
4. Cut the product from the other units (such as FCCU and cat reformer) to meet intermediate products.

5. Balance the crude run against production. From the cutting scheme and schedule outline, develop the detailed and balanced refinery flow plan.
6. Develop the detailed operating program (Appendix 5).

Monitoring the Operating Program

The planning section in a refinery organization is usually delegated the duty of monitoring the program. The following activities are associated with this monitoring function:

1. A check is maintained on the actual product produced, by control room charts, tank dips, and the like. This is done daily and deviation from program noted with explanation of cause for the deviation.
2. Weekly operating schedules are issued to allow for any deviation to program. These would include such causes as:
   - Delay in tanker arrivals
   - Changes in crude slate
   - Changes in product requirements
   - Changes in crude fractionator yields
   - Plant operational problems

   Example is provided in Appendix 6.
3. Daily meeting with the department responsible for oil movements and shipping in the refinery. These meetings are to review shipping and oil movement status to and from tankage.
4. Frequent meetings with the operating and the refinery process department to review plant operations.
5. Contact the company's supply department with regard to:
   - Crude shipment and changes
   - Lifting products out of refinery schedule (see note below)
   - Changes in requirements

   Note: At times of high inventories in the refinery, prompt lifting is essential to keeping the refinery operating as programmed.

Operating Summary

An operating summary is a document giving details of the refinery's performance against plan. This is issued at the end of each month. Summaries of throughputs and yields are usually supplied by the accounts department of the refinery. Comments on production versus program are made by the refinery's planning department.

Process Evaluation and Economic Analysis

Among the principal functions of a refinery's development engineer is to generate ideas for implementing the supply department's planned requirements (both short term and long term) with the most economic process configuration. In carrying out this function, the engineer is required to study various processing routes or changes to existing process routes and configurations. When satisfied that the technical aspects of any proposed changes or additions are feasible and sound, he or she must now satisfy the company management that it is economically attractive. The proposal must also be shown to be the best of any possible alternatives that may be available to achieve the same objective.

This chapter sets out to describe some basic techniques used in carrying out this function.

Study Approach

Process studies are usually initiated after a very precise definition by the company's management of the company's immediate and long-term production objectives. Apart from this definition being a premise of the company's annual operating budget, it also aims to fulfill its marketing strategy. Often such a definition results in changes being required to be made to the process facilities either in the short term or long term to meet these objectives. The company will look to the development engineers to provide definition of these changes and to support the definition(s) with whatever technical and economic data necessary for the management to make their "GO/NO GO" decisions. Figure 3 shows the steps in a typical study.

This particular study route is to define an expansion of an existing process configuration by adding a new group of plants. The steps shown in Fig. 3 are described as follows:

Step 1. Receive and review the supply department's requirements.

This step is extremely important. The development engineer or engineers working on the study must understand completely what is required and what the end product of the study must fulfill. There is usually also a time element for the completion of the work. This too must be understood and planned for. Normally, the study premise is presented in a written document with copies to all study participants. The contents of the document must be studied by all concerned. A study "kickoff" meeting is always beneficial where participants and management review the study premises together before commencing work on the study.

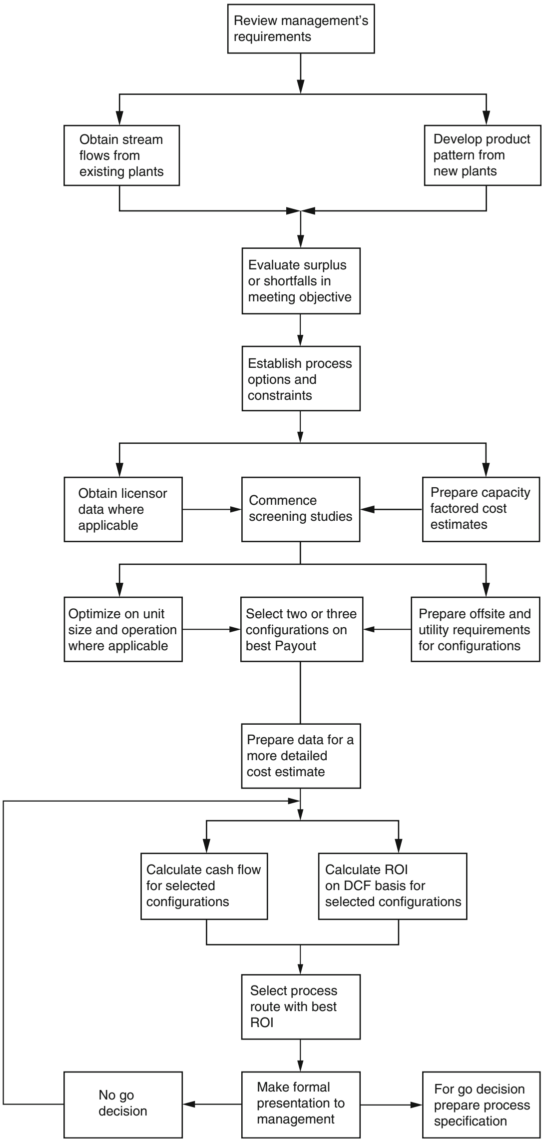
Step 2. Obtain stream flows from existing plants.

In cases where existing plants are to form part of the study premise, a detailed analysis of the performance of the plants must be made. This almost certainly will involve performance test runs under pre-calculated operating conditions. The test run results are evaluated and included in the analysis of products to meet the study's product slate.

Step 3. Develop product pattern from plant data for new processes.

This will be executed in parallel with step 2. Here new processes that may be included in the study to meet the product requirements are examined and their product pattern developed. Process licensors may be involved at this stage to

Fig. 3 Steps in a typical process study



provide data on their proprietary processes, as may the refining company's own research department.

Step 4. Evaluate surplus and shortfalls in meeting the objective.

Steps 2 and 3 are now used to determine the possible product slates achievable using plant yields and blending recipes. Any surplus or shortfalls in the product slate that may now exist must be eliminated by further work in step 2 or 3 or both.

Step 5. Establish process options and constraints.

With a firm product slate, work may now commence to map processing routes that will achieve the product objective. This will include very rough plant configurations irrespective of cost or other constraints that will fulfill a processing route. This step should end with the elimination of the more obvious undesirable routes, for example, those routes which contain very small process units or those that contain unit processes that have undesirable by-products. This step should provide five or six reasonable process options for further study.

Step 6. Commence screening studies.

The purpose of this item is to reduce the number of possible options to two or at the most three process configurations that appear most economically attractive. To arrive at the selected options, those alternates arrived at in step 5 are allocated capital and operating costs. The capital costs in this case are very rough estimates arrived at by applying factors to the installed cost for similar processes. Details of this technique in cost estimating are given later in this chapter under the discussion of section "Capital Cost Estimates." Licensors are usually requested to participate in the development of these cost items in the case of their proprietary processes. The operating costs for nonproprietary processes are also factored from similar processes. With these cost data in place, an incremental payout time is calculated for each option. The option with the lowest capital cost is used as a base case and the others compared against it. Details of this calculation are given later in this chapter. The two (or three) options with the lowest positive incremental payout time against the base case are selected for further study.

Step 7. Prepare data for a more accurate cost estimate.

The credibility of any economic study depends to a large extent on the accuracy of the data used in predicting the various cost items. The principal cost item will be the capital cost of the processes to be installed and/or revamped. The next step in the study therefore is for the development engineer to provide basic engineering for a "semi-definitive" capital cost estimate to be prepared. (Very often, the refining company may solicit third-party engineering contractors to undertake this step.) Should the project proceed from study stage to installation, this estimate may be used as the first project budget estimate for project control. Details of this type of estimate are given later in this chapter. Briefly, for this estimate, development engineers (and/or third-party engineering contractors) will:

- Prepare process flow sheets (complete with mass balances).
- Prepare preliminary mechanical flow sheets (complete with line and instrument sizes and specifications).
- Initiate all equipment data sheets sufficient for obtaining manufacturers' firm prices.
- Review and select manufacturers' offers for equipment.
- Using selected manufacturers' equipment data, prepare a preliminary utility balance and size by factoring new or expanded utility facilities.
- Factor additional offsite facilities as required.

Step 8. Calculate cash flow for selected configurations.

The selected manufacturers' equipment offer will also include a delivery time for the equipment item. Using these and other experience factors, prepare a preliminary schedule for the installation of the facilities. This is executed by the experienced schedule engineers of the company or by accepted consultants.

Using this schedule, the development engineer participates with others (usually members of the company's project management department or finance departments) to split the budget down to annual payments over the construction period as scheduled. The exercise continues to allocate payout of the capital costs on an annual basis over a prescribed period after plant start-up. This is also discussed later in this chapter.

Step 9. Calculate the return on investment based on a discounted cash flow basis.

The development engineer proceeds to develop the return on investment using the cash flow developed in step 8 for the selected configurations. A technique using the discounted cash flow principle is used for this purpose. This provides a more accurate and more credible result than an ROI arrived at by the simple method where no account is taken of the construction time and cash flow. Details of ROI calculations are given later in this chapter.

Step 10. Prepare the study report and presentation to management.

Much of the report should be written as the study project proceeds. In this way, facts which are still fresh in one's mind are recorded accurately. The final report must be concise but complete with all salient points. Techniques in report writing are not included as a subject here. Sufficient to say that communicating the study and its results effectively is as important as any technique and good engineering "know how" used in the work. The same applies to the final oral presentation to management. The study, the methodology, and, finally, the results must be presented in a manner that maintains interest and stimulates the decision-making mechanism.

This completes a typical study approach. Should the screening study reveal an option which far surpasses any of the others studied in terms of payout, this could be the only option that then needs further study as described in steps 7–10. Such a situation saves a considerable time and effort.

Building Process Configurations and the Screening Study

(See also the chapter entitled "▶ Petroleum Products and a Refinery Configuration" of this Handbook).

From item 1 above, it can be seen that the first major event that involves in-depth examination in a process study is the screening of options. Here a very simple and preliminary economic comparison of the options is carried out. This comparison is viable because the basis for the economic criteria is the same for each of the options. It must be borne in mind that a prerequisite for carrying out any of these process studies is a good working knowledge of the processes involved.

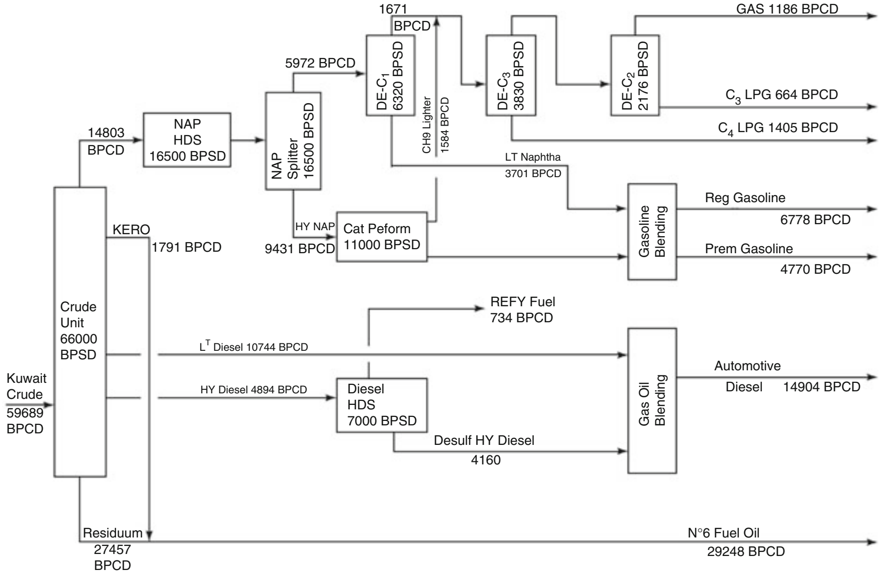


Fig. 4 The existing refinery

This example has been chosen because the ultimate product slate is achieved through the addition of new processes, changing operating conditions of existing units, and of course blending base stocks.

The example then is a requirement by a petroleum refinery to upgrade its fuel oil product to more financially lucrative lighter products. This is a fairly common program in this particular industry because of the fluctuating needs of the fuel market. The example calculation given here to illustrate the study is the base configuration published in an earlier book *Elements of Petroleum Processing by D.S.J. Jones*. This may be found at the end of the first chapter of that book, and the block flow sheet is given here as Fig. 4. The objective of this refinery configuration is to maximize gasoline and middle distillate while still retaining sufficient atmospheric residue from the crude distillation as fuel oil.

In the example given here, it is intended to reduce the amount of fuel oil and to produce as much gasoline and diesel as possible to give the best return on investment. For this purpose, six well-proven processing routes have been selected for preliminary study. These are as follows:

- Thermally crack all of the atmospheric residue. This will be a single-stage unit.
- Vacuum distill all of the atmospheric residue. The waxy distillate will be cracked in a fluid catalytic cracker producing gas, gasoline, naphtha, and light cycle oil as a diesel blend component. The vacuum residue from the vacuum unit will be thermally cracked to give additional gas, LPG, naphtha (for gasoline production), and gas oil for diesel blending.

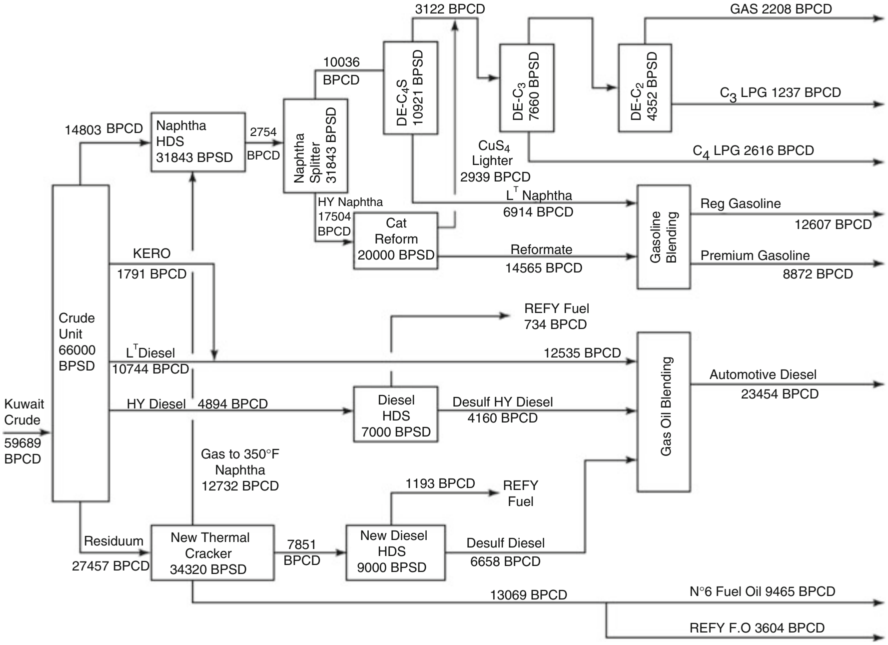


Fig. 5 Scheme 1: thermal cracker

- The same as option 2, except there will be no thermal cracker for the vacuum residue.
- Vacuum distill all the atmospheric residue and hydrocrack the waxy distillate.
- Process the atmospheric residue through a delayed coking unit.
- Finally, use a proprietary fluid coking unit for the atmospheric residue that eliminates the coke by converting it into low Btu gas.

The last two options are eliminated after a preliminary study because there is no economically attractive outlet for the coke and no effective use for the low Btu gas in this refinery.

The example calculation that follows provides the detailed calculation for scheme 1 and provides the results of the same calculations for schemes 2, 3, and 4. The configuration for scheme 1 is given in the block flow sheet (Fig. 5). Similar block flow sheets would be prepared for the other study schemes, but these are not shown here; however, a flow description is given for these three schemes.

Example Calculation

It is required to develop a processing scheme in which the gasoline and diesel products are increased at the expense of the fuel oil product. The capacity of the present units, the flow configuration, and flow rates are given in Fig. 4. The refinery fence pricing of the products are historical and do not reflect current values.

$/bbl	
LPG (C3 and C4)	20.2
Premium gasoline	35.2
Regular gasoline	27.6
Automotive diesel	28.6
No 6 fuel oil	17.2

The cost of Kuwait crude oil is posted at 17.0 $/bbl delivered to refinery tankage. Cost of utilities and labor is as follows:

Power (purchased)	$0.042/Kwh
Water	$0.5/1,000 US gals
Steam	$0.83/1,000 lbs
Fuel	$0.01/lb
Labor	$15/h salary + 40 burdens

Three 8 h shifts plus one shift off. There will be eight staff on each shift. Total man hours per month is 185.

The Calculation

Scheme 1. Thermal Cracking

The first step is to determine the yields and the quality of the products that can be obtained by the thermal cracking of the atmospheric residuum. These are obtained by methods given in the publication "Elements of Petroleum Processing," Chapter 17, by D.S.J. Jones and also in the chapter "▶ Introduction to Crude Oil and Petroleum Processing" of this Handbook. These are:

Stream	wt%	lbs/h	lbs/gal	Gph	BPCD
Gas to C5	9.02	35,079	4.67	7,506	4,289
Naphtha to 390 °F	20.29	78,899	5.34	14,775	8,443
Gas oil 390–622 °F	24.66	95,878	6.89	13,916	7,952
Residue +622 °F	46.03	179,013	7.73	22,870	13,069
Total	100.00	388,869	6.58	59,067	33,753

Note: There is a volumetric increase in the total products over the feed. This is due to the changes in gravity of the products of cracking. The total weight and moles will still be the same between feed and products.

Handling the Products

Figure 5 shows the routing of the product streams from unit to unit. The gas from the thermal cracker (Gas to C_5) and the naphtha is routed to the existing naphtha hydrotreater which will be expanded in size to accommodate this. The hydrotreated material will subsequently go to the splitter and debutanizer, respectively. The existing reformer and light end unit will also be expanded to cater for the thermal cracker light products. The gas oil from the thermal cracker will be hydrotreated in a new or expanded hydrotreater to meet diesel pool requirements. Thus, new unit sizes will be

$$\begin{aligned} \textit{Naphtha hydrotreater}: \text{Total new flow} &= 14,809 \text{ BPCD} + 12,732 \text{ BPCD} \\ &= 27,541 \text{ BPCD} \end{aligned}$$

$$\text{New size at } 86\,\% \text{ service factor} = \frac{27,541}{0.86} = 32,024\,\text{BPSD}$$

which is an increase of 72 % above the existing unit. This is too large to consider a revamp: therefore, build a new 13,500 BPSD unit in parallel. The same applies to the splitter.

Catalytic Reformer

New feed to the reformer is 16,191 BPCD. At a 86 % service factor, the new size will be

$$\frac{17,504}{0.86} = 20,353\,\text{BPSD}.$$

Revamp the catalytic reformer by 9,000 BPSD.

Light Ends

New total feed to the debutanizer is 9,283 BPCD. With a service factor of 90 %, this gives a new capacity of 10,000 BPSD, an increase of 58 %. This unit will be revamped at a cost of 10 % of a new unit.

The depropanizer and deethanizer will be expanded with parallel units the same size as the existing ones.

The Diesel Hydrotreater

A new hydrotreater of 9,000 BPSD will be designed to cater for the additional gas oil from the thermal cracker. The new total amount of gas oil to be treated is $4,894$ BPCD $+ 7,851$ BPCD $= 12,745$ BPCD. There is 706 BPCD spare capacity in the existing hydrotreater through improved catalyst and service factor. Taking this into consideration with a service factor of 80 %, the additional capacity required will be 9,000 BPSD.

Operating Costs

The following tables (Tables 5 and 6) give approximate factors for utilities and labor for some refinery plants. Note: the use of these is acceptable for the screening analysis given here. For detailed economic analysis of the selected configuration, more accurate operating costs using certified vendor and licensor data must be used.

Table 5 Utility requirements per bbl of feed

	Steam l	Water	Power	Fuel	Labor
	lbs	gals	kWh	MM Btu	Pers/shift
Light end dist	25	12	0.4	–	1
Splitter	0	9	0.4	0.1	"
Cat reformer	50	15	12	0.35	3
Nap HDS	–	4	6	0.12	1
Diesel HDS	30	8	1.5	0.12	1
Thermal cracker	70	20	3	0.5	2
FCCU	20	20	7	–	4
Wash plants	1	2.5	0.4	–	1
VDU	15	20	0.2	0.07	3

Table 6 $/Calendar day for utilities (Exc labor)

Unit	Steam	Water	Power	Fuel	Labor persons/shift
Nap HDS (13,500 BPSD)	–	27	3,400	900	1
Nap splitter (1,350 BPSD)	–	60	227	750	1
Lt Ends (3,000 BPSD)	60	18	50	–	
Ther cracker (34,320 BPSD)	1,922	343	4,324	9,500	2
Diesel HDS (9,000 BPSD)	216	36	567	600	1
Cat reformer (9,000 BPSD)	360	68	4,536	263	3
Total	2,558	552	13,104	12,013	8

Looking at the configuration under study here, the operating cost for the extension of the refinery is as follows:

$$\begin{aligned}&\text{Total cost of utilities per stream year using }\ 0.86\ \text{ average service factor}\\ &\quad = \ 28,227/\text{day} \times .86 \times 365 \ = 8.840\ \text{ MM }/\text{year}\end{aligned}$$

Labor salaries at $15/\text{h} = 15 \times 8 \times 4 \times 185\ \text{ h/month} \times 1.4$.

Notes on labor:

1. The salaries are increased by 40 % to take up government benefits, paid days off, vacation, etc.
2. There are four shifts, three on duty and one off every 24 h.
3. Hours worked per person per month is 185 h.

Then total labor cost per year $= 124,320/\text{month} \times 12 = \ 1.491\ \text{ MM }/\text{year}$.

Total operating cost per year = 10.331 MM $.

Investment Costs for the New Facilities

There are two costs which make up the overall investment outlay. These are:

- Capital cost of the plant
- Associated costs

The Capital Cost

For the screening study, a capital cost of plant estimated on experience and factors is used. This and other types of estimates are described later in this chapter. A set of capacity cost data for plants of this size are listed below: (Note that these numbers are pure fiction and bear no relationship to any company's cost data.)

Type of unit	Capital cost factor
Light end units	412 $/BPD
Catalytic reformer	3,120 $/BPD
Hydrotreater (naphtha)	780 $/BPD
Hydrotreater (diesel)	1,200 $/BPD
Wash plants	170 $/BPD
Naphtha splitters	360 $/BPD
Thermal crackers	2,000 $/BPD
Fluid catalytic crackers	3,960 $/BPD
Vacuum distillation units	700 $/BPD

Associated Costs

To complete the full investment picture, the following costs must be included as part of the investment. These are:

- Cost of first catalyst and chemical inventory.
- Cost of licensing fees for proprietary processes.
- Cost of additional utility and offsite facilities. This cost is included because additional processing plants will either require additions to utilities and offsite facilities or take up available spare capacity. This will entail at some future date an expansion to these facilities which would not be necessary if this process expansion had not occurred.

For the purpose of a screening study, a figure of 15 % of the capital cost is used for these associated costs. In more definitive studies, this item would be developed with more detail.

The capital cost of the process expansion considered here is as follows:

New naphtha hydrotreater

Capacity 13,500 BPSD at 780 $/bpsd = 10,530,000$

New naphtha splitter

Capacity 13,500 BPSD at 360 $/bpsd = 4,860,000$

Revamp debut and new light ends

$$\begin{aligned}\text{Debutanizer revamp} &= 10\% \text{ of new plant} = \frac{2,963 \times 412}{10}\\ &= 122,000\$\end{aligned}$$

$$\begin{aligned}\text{New light ends unit} &= (3,830\,\text{bpsd} \times 412) + (2,176 \times 412)\\ &= 2,474,472\$\\ \text{Total} &= 2,596,500\$\end{aligned}$$

New thermal cracker

At a service factor of 80 %, the capacity of the unit is

$$\begin{aligned}\frac{27,457\,\text{BPCD}}{0.8} &= 34,320\,\text{bpsd}\\ \text{Capital cost} &= 34,320 \times 2,000\$\\ &= 68,600,000\$.\end{aligned}$$

New diesel hydrotreater

$$9,000 \text{ bpsd} \times 1,200 \text{ \$} = 10,800,000 \text{ \$}.$$

Revamped catalytic reformer

$$9,000 \text{ bpsd} \times 3,120 \text{ \$} = 28,100,000 \text{ \$}.$$

Total capital cost = 125.490 MM $.

Associated costs

This is taken as 15 % of capital cost = 18.823 MM $.

Total cost = 144.313 MM $.

The Product Slate

The new refinery product slate is summarized below (all in BPCD):

Product	Existing	Expanded	Difference
C3 LPG	664	1,237	+573
C4 LPG	1,405	2,616	+1,211
Reg gasoline	6,778	12,607	+5,829
Prem gasoline	4,770	8,872	+4,102
Auto diesel	15,638	23,454	+7,816
Fuel oil	26,323	9,465	−16,858
Refy fuel gas	1,186	4,135	+2,949
Refy fuel oil	2,925	3,604	+679
	[a]	[a]	
Total	59,689	65,990	+6,301

[a] Note difference in BPCD between input and output is due to changes in SG's due to cracking. Mass (lbs/h) input still equals mass output

Gross Income from Increase in Product Slate

Product	Increase BPCD	$/bbl	$/day
LPGs	1,784	20.2	36,037
Reg gasoline	5,829	27.6	160,880
Prem gasoline	4,102	35.2	144,390
Auto diesel	7,816	28.6	223,538
Fuel oil	−16,858	17.2	−289,906
Refy fuel	−3,628	17.1	−62,039
Gross income			212,900 $/CD

Depreciation

In the economic analysis of the various processes, the depreciation of the plant value must be taken into account. Details of depreciation will be described and discussed later in this chapter. For the purpose of the screening study, the following depreciation factors may be used:

Crude distillation units	6.6 % of capital cost per year
Cracking units	6.6 % of capital cost per year
Light end units and gas plants	5.0 % of capital cost per year
Hydrotreaters	6.0 % of capital cost per year

The screening analysis based on a payout time and a return on investment (ROI) is given in the following table (Table 7). Note the ROI is given by

$$\frac{\text{Net income after taxes}}{\text{Net investment cost}} \times 100 = \%\text{ROI} \tag{1}$$

And payout time is given by

$$\frac{\text{Net investment cost}}{\text{Net income after taxes} + \text{depreciation}} = \text{Years.} \tag{2}$$

Details of the Other Schemes

Scheme 2. This calls for the vacuum distillation of the atmospheric residue to produce a waxy distillate and a heavy vacuum residue. The waxy distillate is cracked in a FCCU (Fluid Catalytic Cracker) to give gas, LPG, naphtha for gasoline, and gas oil for diesel. The heavy vacuum residue is also cracked in a thermal cracker to give gas, LPG, naphtha feed to the cat reformer, and gas oil for diesel.

- The total capital cost for these additional facilities = 218.580 MM $.
- Total additional product income = 108.202 MM $/year and
- Total operating cost is an additional 13.856 MM $/year.

Table 7 *Scheme 1.* Addition of thermal cracker simple economic analysis

Item	$ MM
Capital cost of plant	125.490
Associated costs	18.823
Total investment	144.313 MM $/year
Gross income	77.709
Less	
Operating cost	10.331
Depreciation	8.030
Net income before tax	59.348
Tax at 42.5 %	25.223
Net income after tax	34.125
Payout time	3.4 years
Return on investment	23.7 %

Scheme 3. This is the same as scheme 2 except the vacuum residue is not cracked. Details of this scheme are:

Total capital costs for additional facilities = 194.780 MM $.

Total additional product income = 96.509 MM $/year.

Total operating cost is an additional 8.122 MM $/year.

Scheme 4. This also includes the vacuum distillation of the atmospheric residue as in schemes 2 and 3. The wax distillate in this case however is routed to a hydrocracker where LPG, naphtha for reforming to gasoline, and diesel are produced. An additional hydrogen plant is required for this scheme. Details of the scheme are summarized below:

- Total capital cost for additional facilities = 306.012 MM $
- Total additional income 119.502 MM $/year
- Total operating cost is an additional 12.6 MM $/year.

The obvious selection in this case is scheme 1 with the lowest payout time and the highest ROI (Table 8).

Preparing More Accurate Cost Data

Once a selected configuration or study case or cases have been selected from the screening study, it is now necessary to firm up as much as possible the cost data used in those studies. Three items of data fall into this category. These are:

- The capital cost estimate
- The associated costs
- The operating cost

Development engineers supply the basic data from which an update can be arrived at. This level of data is arrived at from a process design of the facilities

Table 8 Comparison of the economic analysis of the schemes studied

Scheme	1	2	3	4
	MM $			
Capital cost	125.490	218.580	194.780	306.012
Associated costs	18.823	32.828	29.217	46.080
Total investment	144.313	251.408	223.997	352.092
	MM $/year			
Gross income	77.709	108.202	96.509	119.502
Less				
Operating cost	10.331	13.856	8.121	12.600
Depreciation	8.030	15.007	13.237	18.361
Net income before tax	59.348	79.339	75.150	88.541
Tax at 42.5 %	25.223	33.719	31.939	37.630
Net income after tax	34.125	45.620	43.211	50.911
Payout time years	3.4	4.15	3.97	5.1
Return on investment%	23.7	18.1	19.2	14.4

making up the case studies. The process design will include a material balance and a firm process flow sheet. Sufficient data will be generated for all equipment to allow manufacturers to give a good and realistic equipment budget cost. Where applicable too, the manufacturers will be requested to provide equipment efficiencies from which utility usage for the various items can be calculated. Where options exist within the process design itself, these will be optimized for equipment sizing and layout. An example of such an optimization is the case of the process heat exchange system. Full and complete equipment data sheets need not necessarily be developed for this part of the study. Usually, manufacturers are able to provide good budget costs from equipment summary sheets similar to those given in the example calculation below.

Where licensed processes are included in the case study, the development engineer will need to develop a specification to a suitable licensor soliciting:

- A budget estimate for the plant (installed)
- The utility requirements and the operating cost.
  (*Note*: In the case of a catalytic process, part of the operating cost will be the catalyst usage or loss in operation.)
- First inventory of catalyst or chemicals where applicable
- The licensing fee

The specification must include the capacity of the plant and the required product quality. It must also of course give the licensor(s) details of the feedstock, utilities conditions, and in most cases local climatic conditions. The additional information concerning feed and product pricing together with utility costs will enable the licensor to respond with a firmer and optimized cost data.

The following example follows the study screening given in Item 2.0 above.

Example Calculation

From the screening study, the new plants included in the selected case (which was case 1) were as follows:

- Naphtha hydrotreater (13,500 BPSD) licensed
- Naphtha splitter (13,500 BPSD)
- Catalytic reformer (9,000 BPSD) licensed
- Depropanizer (3,830 BPSD) and deethanizer (2,176 BPSD)
- Diesel hydrotreater (9,000 BPSD) licensed
- Thermal cracker (34,320 BPSD)

The existing debutanizer is to be revamped and a new sized equipment list will be prepared for this unit.

The units of normally licensed processes are indicated as such in the above list. The thermal cracker may be licensed or can be designed by some major engineering companies as a nonproprietary process. It is a major item of cost, and for this example, the degree of process engineering required at this stage of the study is demonstrated for this unit.

The Process Design of the Thermal Cracker

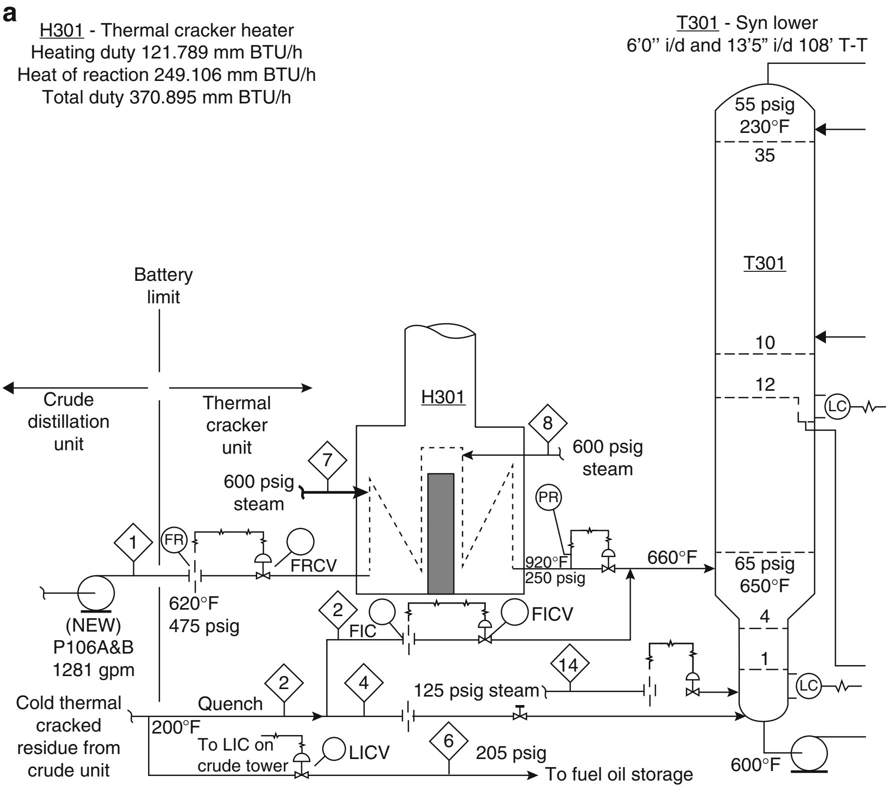
The process flow sheet for this unit is given in Fig. 6. This process flow sheet contains the overall material balance for the unit together with the calculated reflux and quench flows. Major process stream routes are shown with stream temperatures where appropriate. The material balance table also gives the flow conditions (temperature and pressure) for those major streams. The pump capacities are shown on the flow sheet next to the respective pump. These quantities are flows in gallons per minute at the pump temperature.

The major item in a thermal cracker is the furnace or heater. This has two duties, the first being to heat the feed to its reaction temperature and the second to maintain the feed at its reaction temperature for the prescribed period of time. Note therefore that the duty of this heater is shown on the flow sheet as the duty to heating the oil (which also includes the steam in this case) and the duty to supply the heat of reaction.

Data for the remainder of the equipment are given in Tables 9, 10, and 11. Sufficient data for obtaining a cost and efficiency for the heater is provided in a "process specification" shown in Table 12. A special specification sheet is required for this item because, besides being an oil heater, it is also a cracking reactor. In this function, the design of the unit must be such as to allow the oil to be retained for a specific period of time at the reaction temperature.

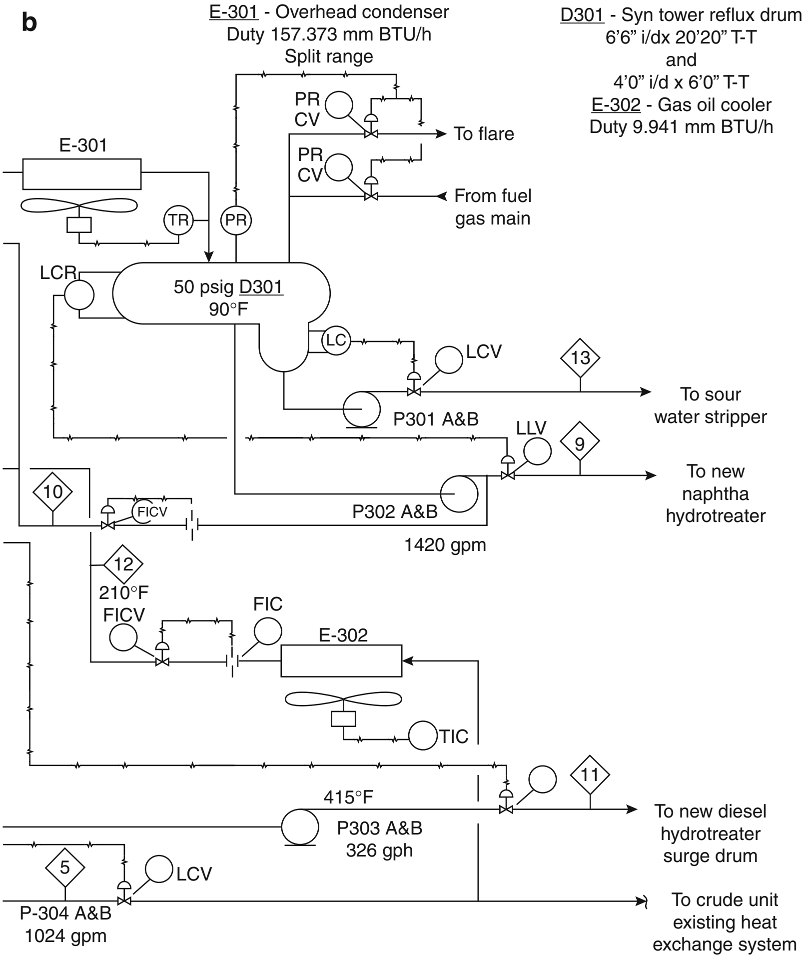
Summary Data Sheets

Coil tubes should be standard 4″ 11/13 Cr with wide radius bends. The firebox should be constructed to heat the incoming feed to a temperature of about 870 °F in the first 150 cu. ft. of coil. This should constitute the Heater Section. The Soaker



	Material balance						
Stream No.	1	2	3	4	5	6	7
Fluid	Atmos res	Res	Res	Res	Crack res	Res	Steam
Temp. of	620	200	200	200	200	200	720
lb/h	479879	153600	125600	28000	374488	220888	20000
SG at 60°F	0.960	0.929	0.929	0.929	0.929	0.929	—
mol wt (jas)	—	—	—	—	—	—	18
Gal / h	60060	19870	16248	3622	48458	28588	—
bpsd	34320	11354	9285	2070	27690	16336	—
scf / day	—	—	—	—	—	—	—
Moles/h (gas)	—	—	—	—	—	—	—
Pressure (psig)	475	220	220	220	480	205	600

Fig. 6 (continued)



Material balance						
8	9	10	11	12	13	14
Steam	Naphtha	Naphtha	Gas oil	Pump around	Soap water	Steam
6720	90	90	415	210	90	380
5000	140653	281300	118338	88755	58200	33200
–	0.6070	0.6070	0.828	0.828	–	–
18	–	–	–	–	–	18
–	27852	55703	17175	12881	7217	–
–	15915	31830	9814	7361	–	–
–	–	–	–	–	–	–
–	–	–	–	–	–	–
600	120	75	135	89	152	125

Fig. 6 (**a**) The process flow sheet for a thermal cracker. (**b**) The process flow sheet for a thermal cracker (Continued)

Table 9 Centrifugal pumps

Item no	P106 A&B	P301 A&B	P302 A&B	P303 A&B	P304 A&B
Service	Feed	S water	REF +PR	PA/prod	Bot prod
No of units	1 + 1 spare	1 + 1 spare	1 + 1 spare	1 + 1 spare	1
Fluid	Resid	Water	Naphtha	Gas oil	Cr res
lbs/h	479,879	58,200	421,953	207,093	374,488
Pump temp °F	620	90	90	415	600
Sg at PT	0.758	0.995	0.592	0.692	0.732
Visc at PT Cs	1.8	0.76	0.33	0.25	1.2
Rate (norm) at PT GPM	1,281	117	1,420	599	1,024
Rate (Max) at PT GPM	1,470	130	1,700	690	1,178
Norm suct press PSIG	39	63	63	75	72
Max suct press PSIG	89	132	132	135	122
Discharge press PSIG	475	152	85	135	480
Diff press PSI	436	89	22	60	408
Diff head ft	1,332	207	86	200	1,290
NPSH avail ft	>15 ft	>15 ft	>15 ft	>15 ft	>15 ft
Hyd horse power	323	6.1	18.3	20.9	244
Corr/erros	Sulph	H2S	H2S	Sulph	Sulph
Driver R[a] S	Motor	Motor	Motor	Motor	Turb
	Turb	Motor	Turb	Motor	[b]

[a]Driver R = Normally running, S = Normally spare
[b]Maybe common spared with P106 A&B

Table 10 Vessels

Item no	T 301	D301
Service	Syn tower	Ref drum
Type	Vert	Horiz
Dimensions:	*Feet*	*Feet*
Top Sect I/D		
Top Sect T-T	13.5	6.5
Bot Sect I/D	74.0	20.0
Bot Sect T-	7.5	4.0
Overall T-T	31.0	6.0
Skirt	108.0[a]	20.0
	15.0	In struc
Internals:		
Trays	Top sect	
	30 sieve	None
	Bot sect	
	4Disc son	
Operating conditions:		
Press PSIG		
Temp °F	55/67	50
	230/650	90
Design conditions:		
Press PSIG		
Temp °F	125	125

(*continued*)

Table 10 (continued)

Vacuum PSIA	920	810
Min temp °F	7.0	7.0
Max liquid level ft	90	90
	8.0	N/A
Materials:		
Shell	C.S[b]	C.S
(Corr allow)	0.125″	0.125″
Internals	11/13 Cr	
(Corr allow)	0.125″	
Trays	Monel/Cr	None
(Corr allow)	0.125″	
Packing.	N/A	
Insulation:		
Yes/no	Yes	No
Stress relieved:		
Yes/no	No	Yes

[a] Swage Sect 3.0 ft

[b] Clad with 11/13 Cr

Table 11 Air condensers/coolers

Item no	E 301		E302	
Service	O/head cond		Gas oil cooler	
Type	Forced		Forced	
Duty MM Btu/h	157.373		9.941	
Fluid	Nap + H_2O		Gas oil	
Temp °F	In	Out	In	Out
	230	90	415	210
Liquid				
M lbs/h HC		422	88.8	88.8
H_2O		58.2	Nil	Nil
Sg at 60 °F HC		0.607		0.828
Visc at 60 Cs HC		0.12		0.52
Therm cond HC		0.07		0.06
Specific heat		0.73		0.80
Btu/lb °F HC				
Vapor				
M lbs/hr HC	422			
H_2O	58.2			
Mol wt HC	96			
Therm cond	0.009			
Specific heat	0.41			
Btu/lb °F				
Fouling HC factor	–			
Ambient air temp °F	60			
Allowable Δpsi	5.0		10.0	

Table 12 Process specification for a thermal cracking heater/reactor

Item number: H 301 thermal cracker heater
Overall heat duty: 370.895 MM Btu/h
Feed rate lbs/hr: 479,879 lbs/h
Temperature of feed in: 620 °F temperature of effluent: 920 °F
Specific gravity of feed at 60 °F: 0.960 (+650 °F TBP Kuwait residue)
Effluent TBP and EFV curves are attached Fig. 1. [Ed: this refers to a figure in the example spec]
Effluent Sg curves versus mid Bpt curve is attached Fig. 2. [Ed: this refers to a figure in the example spec]
Feed conversion to gasoline of 390 °F cut point =30 vol%
Coil temperature profile (oil + steam) versus coil volume given as Fig. 3 attached
Steam (600 psig) injected at coil volume of 50 cu. ft. and 150 cu. ft., respectively. Total steam to be injected is 74,000 lbs/h
Outlet pressure of effluent to be 250 psig. This pressure to be maintained by downstream pressure control valve (supplied by others)
Coil pressure drop to be 225 psi max

Section and crossover should be designed to heat the oil to 920 °F and retain it at this temperature. The sections should be divided by a firebrick wall so that temperatures on both sides of the wall can be controlled independently by burner adjustments.

Vendor may recommend that the convection side of the heater be used for additional heater capacity or for steam generation or to remain unused if better temperature control may result (Table 13).

Vessels

- **T 301 Syn tower**

	$
Shell and heads	1,766,810
Trays	1,590,129
Internals	176,681
Total	3,533,620

- **D 301 Reflux drum**

	$
Shell and heads	561,222
Lining	37,415
Internals	24,943
Total	623,580

Total vessel account = 4,157,200$

Table 13 Summary of accepted prices

			Price $/unit		
Pumps	HHP	BHP	Pump	Motor	Turbine
P 106 A	323	430	606,826	489,082	–
106 B			606,826	–	503,903
P 301 A	6.1	10.1	14,253	19,563	–
301 B			14,253	19,563	–
P 302 A	18.3	28.1	39,655	39,126	–
302 B			39,655	–	40,312
P 303 A	20.9	32.2	45,441	48,908	–
303 B			45,441	48,908	–
P 304 A	244	325	458,648	–	453,513
Total			1,870,998	665,150	997,728

The above are accepted vendor prices for equipment delivered to site, subject to updates
Total pumps and drivers = 3,533,884$

Coolers and Condensers

- **E 301 overhead condenser**
  Unit including fans and structure = 1,627,540$.
- **E 302 gas oil cooler**
  Unit including fans = 243,196$ (unit located in pipeway, no stand-alone structure).

Total cooler and condenser account = 1,870,740$.

Heater/Reactor

- **H 301 thermal cracker heater**
  This unit will be field erected. Included in this account is the cost of fabricated material delivered to site.

Unit material cost = 8,314,400$.

Total Equipment Material Account Summary

	$
Pumps and drivers	3,533,884
Vessels	4,157,200
Cond and coolers	1,870,740
Heater/reactor	8,314,400
Total	17,876,224

Capital Cost Estimates

Capital cost estimates are usually prepared by specialist engineers who are fully conversant with their company's estimating procedures and their company's material and labor cost records. Refinery development engineers are involved in cost estimating only so far as they develop and provide the basic technical data that is used to prepare the capital cost of a plant or process. To execute this part of their duty properly, development engineers should know a little about cost estimates and the significance of the various items included in them. This section therefore sets out to define in broad terms the various levels of estimating, their degree of accuracy, and the scope of the engineering development that is required for each of them.

The accuracy of cost estimates will vary between that based on comparing similar plants or processes on a capacity basis to the actual cost of a plant when all the bills have been paid and the plant is operational. Obviously the accuracy based on similarity of the process or plant is very low while that based on project end cost must be 100 %. That is, it is no longer an estimate but is now a fact. In between these two levels, however, estimates may be prepared giving increasing degrees of accuracy as engineering and construction of the process advances. The accuracy of estimates increases as more and more money is committed to the project. The progress of a project uses milestone cost estimates coupled with completion schedules for its measurement and control. In the life of a construction project, therefore, about four “control estimates” may be developed. For want of better terms, these may be referred to as:

- The capacity factored estimate
- The equipment factored estimate
- The semi-definitive estimate
- The definitive estimate

Companies have their own terms for these estimates, but the important point is to develop these estimates at a time in the project when they can be most useful and when sufficient information is available for their best accuracy. Figure 7 shows typical phases of a project when these estimates may be best developed.

The following paragraphs now describe these estimates in more detail and emphasize the process engineer’s input.

The Capacity Factored Estimate

In most process studies, this is the first estimate to be prepared. It is the one that requires the minimum amount of engineering but is the least accurate. This is because the plant that is used to factor from will not exactly match the plant in question. It is good enough however when comparing different processes where the estimates are on the same basis.

Past installed costs of similar plants (definitive estimate) are used coupled with some experienced factors to arrive at this type of estimate. The cost of a higher or lower capacity plant is obtained from the equation:

$$C = K(A/B)^{b} \tag{3}$$

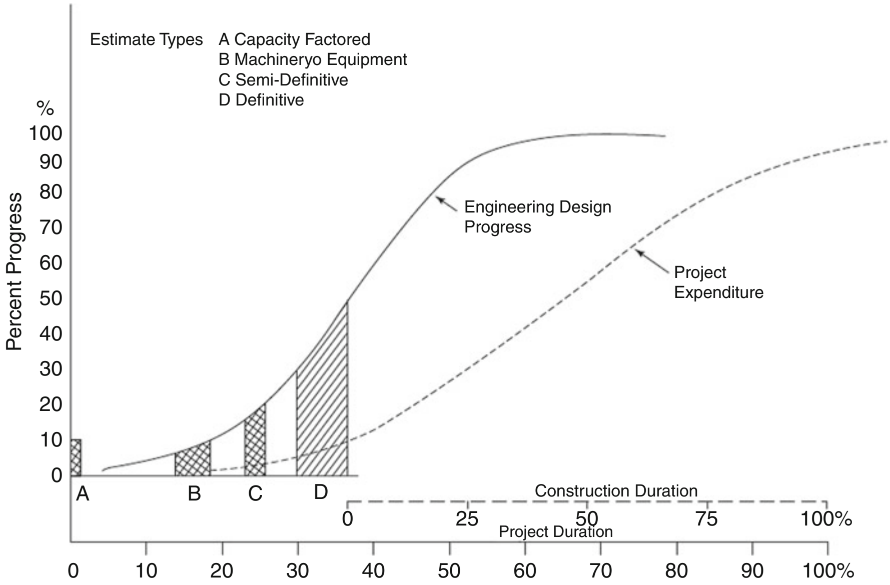


Fig. 7 Type of estimate relative to project progress

where

C = cost of the plant in question.
K = known cost of a similar plant of size B.
A = the capacity of the plant in question (usually in vol/unit time).
B = capacity of known plant.
b = an exponential factor ranging between 0.5 and 0.8.

An exponent of 1.0 is equivalent to saying that the costs are directly proportional to the unit capacity; an exponent of 0.0 corresponds to a unit where the costs remain the same regardless of capacity (this is approximately the case for labor costs). The estimator's experience and records of the type of plant determine the exponent to be used. Usually, this is 0.6; a listing of these factors is given in Appendix 7. Table 14 shows an example of a capacity factored estimate for the thermal cracking unit used in Item 3 above.

In this example, the direct field cost is used as the cost figure to be capacity factored. This allows the cost estimator to adjust between the direct field cost and the total cost using current experience for field indirects, office costs, escalation, and contingencies. In this case, a multiplier of 1.5 times the direct field cost is used to collect these items.

The Equipment Factored Estimate

This estimate requires a substantial amount of process engineering to define the specific plant or process that is to be estimated. Briefly, the following process activity is required:

Table 14 The capacity factored estimate

Plant		Description		Date		
A/C			Estimated cost, MM $			
No	Item	M/h	Labor	Subcont	Material	Total
	Excavation		0.6			
	Concrete	$C =$	$K\ (A/B)$			
	Structural steel	Where	K =28.93 m	m $		
	Buildings		A =34,320	BPSD		
	Machinery/equip		B =16,000	BPSD		
	Piping					
	Electrical	C	= 1.57×	28.93 MM $	= 45.733	
	Instruments					
	Painting/scaffold					
	Insulation					
	Direct field cost					45.733
	Temp const facil					
	Constr expense					
	Craft benefits and burdens					
	Equip rental					
	Small tools					
	Field O/heads					
	Indirect field costs					
	Total field costs					
	Engineering salaries					×1.5
	Purchasing sal					
	Gen office sal					
	Office expense					
	Payroll burdens					
	Overhead costs					
	Total office costs					
	Total field and office costs					
	Other costs					
	Total cost					68.59

- Development of a firm heat and material balance
- An acceptable process flow sheet to be developed
- An approved equipment list
- Equipment summary process data sheet for all major equipment
- Process specification for specialty items
- A detailed narrative giving a process description and discussion (this will be required for the management review and approval of the estimate)

This estimate is normally developed by the process engineer and the cost estimator only. There may be some participation from equipment vendors and licensors in the case of licensed processes. There is seldom any further input required from other engineering disciplines for this level of estimating.

The equipment summary process data sheets and any process specifications that may be required are used to solicit equipment prices from preselected vendors. In addition to the pricing data that will be used for the estimate, development vendors should also be asked for delivery time required and sufficient details to enable the operating cost of the item to be calculated. The delivery time required is important to the management to establish a project schedule and life span for the engineering and construction of the facilities. Later, process engineers will also require this schedule to develop cash flow curves and data.

On receipt of the vendor's pricing data, the cost estimator will apply factors to each of the equipment account data to arrive at a direct field cost for each group of equipment. This factored cost will be the multiplier of the equipment price which will include the materials and labor to actually install those items on site. In Table 16, this factor is shown as a composite for the *whole* equipment prices to direct field cost. In this case, the figure developed was a multiplier of 2.5. These factors are proprietary to respective companies, but most major companies do have the statistics to develop their own factors.

The total cost is again obtained by factoring the DFC (direct field cost) as in the previous "capacity factored" estimate. Note that in the case of this example of an equipment factored estimate, a factor of 1.53 has been used slightly higher than that in Table 14. This is to account for the field erection of the heater, which was not known previously. This would impact on future home office engineering and field indirects to some extent (Table 15).

The Semi-definitive and the Definitive Cost Estimates

It is not proposed to describe these two estimates in detail here. It is sufficient to say that these estimates will include input from all engineering disciplines that are involved in the engineering and construction of the plant or process. Indeed, after the equipment factored estimate, the input from process engineers consists merely of updates of the process design as it develops. However, Tables 16 and 17 show the increasing amount of actual data as opposed to factored data that is included in these two estimates.

The numbers for these estimates are not included in these tables, but the crosshatched items show where normally firm cost data would be included. The factored data are also indicated for both tables.

Although major manufacturing companies such as large oil companies and chemical companies have sufficient statistical data to develop semi-definitive and definitive estimates, these are normally left to the engineering and construction companies. These companies develop the estimates and use them during the course of the installation project as cost control tools for project management.

Table 15 The equipment factored estimate

Plant		Description		Date		
A/C			Estimated cost, MM $			
No	Item	M/h	Labor	Subcont	Material	Total
	Excavation					
	Concrete					
	Structural steel					
	Buildings					
	Machinery/equip				17.876	
	Piping					
	Electrical					
	Instruments					×2.5
	Painting/scaffold					
	Insulation					
	Direct field cost					44.690
	Temp const facil					
	Constr expense					
	Craft benefits and burdens					
	Equip rental					
	Small tools					
	Field O/heads					
	Indirect field costs					
	Total field costs					
	Engineering salaries					
	Purchasing sal					×1.53
	Gen office sal					
	Office expense					
	Payroll burdens					
	Overhead costs					
	Total office costs					
	Total field and office costs					
	Fee (contractor)					
	Escal/contingency					
	Total costs					68.377

Accuracies of Estimates and Contingencies

For an estimate to be a meaningful basis of a process study, its accuracy needs to be established and sufficient contingency be added to make the final cost figure as realistic as possible. Unfortunately, this is easier said than accomplished. Most companies have however developed analysis programs to meet this requirement, and many of these are quite sophisticated. Engineering and construction companies whose daily work depends on good cost estimates for project control are among the front runners in this exercise. Most of these programs revolve around principles of

Table 16 Semi-definitive cost estimate summary

Plant		Description		Date		
A/C			Estimated cost, MM $			
No	Item	M/h	Labor	Subcont	Material	Total
	Excavation				Xxxxxxxxx	
	Concrete				Xxxxxxxxx	
	Structural steel				Xxxxxxxxxx	
	Buildings				Xxxxxxxxxx	
	Machinery/equip				17.876	
	Piping				Xxxxxxxxx	
	Electrical				Xxxxxxxxx	
	Instruments				Xxxxxxxxx	
	Painting/scaffold					
	Insulation					
	Direct field cost	Xxxxxxxx	Xxxxxxxx		Xxxxxxxxx	Xxxxxxxx
	Temp const facil					
	Constr expense					
	Craft benefits and burdens					
	Equip rental			Factor		
	Small tools					
	Field O/heads					
	Indirect field costs					Xxxxxxx
	Total field costs					Xxxxxxxx
	Engineering salaries					
	Purchasing sal					
	Gen office sal					
	Office expense					Factor
	Payroll burdens					
	Overhead costs					
	Total office costs					Xxxxxxxx
	Total field and office costs					Xxxxxxxx
	Fee (contractor)					Xxxxxxx
	Escal/contingency					Xxxxxxx
	Total costs					Xxxxxxxx

risk analysis. Figure 8 has been developed from a collection of statistical values over a long period of time and does provide some quick guidance to judging accuracy of the estimates and then setting a contingency value. Detailed software packages are available that can provide reasonable estimates, subject to the quality of the inputs.

Figure 8 shows two sets of curves. The first is a positive to negative range of accuracy against the type of estimate. This type of estimate scale is based on Fig. 7

Table 17 The definitive cost estimate summary

Plant		Description		Date		
A/C			Estimated cost, MM $			
No	Item	M/h	Labor	Subcont	Material	Total
	Excavation		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Concrete		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Structural steel		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Buildings		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Machinery/equip		Xxxxxxxx	Xxxxxxx	17.876	Xxxxxxx
	Piping		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Electrical		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Instruments		Xxxxxxxx	Xxxxxxx	Xxxxxxxxx	Xxxxxxx
	Painting/scaffold			Factored		
	Insulation			Factored		
	Direct field cost	Xxxxxx	Xxxxxxxx	Xxxxxxxx	Xxxxxxxxx	Xxxxxxxx
	Temp const facil		Xxxxxxxx		Xxxxxxxx	Xxxxxxxx
	Constr expense					Xxxxxxx
	Craft benefits and burdens					Xxxxxxx
	Equip rental				Xxxxxxxx	Xxxxxxx
	Small tools				Xxxxxxxx	Xxxxxxx
	Field O/heads					Xxxxxxx
	Indirect field costs		Xxxxxxxx		Xxxxxxxx	Xxxxxxx
	Total field costs					Xxxxxxx
	Engineering salaries	Xxxxxxx	Xxxxxxx			
	Purchasing sal	Xxxxxxx	Xxxxxxx			
	Gen office sal	Xxxxxxx	Xxxxxxx			
	Office expense				Xxxxxxxx	
	Payroll burdens				Xxxxxxxx	
	Overhead costs				Xxxxxxxx	
	Total office costs	Xxxxxxxx	Xxxxxxxxx		Xxxxxxxx	Xxxxxxxx
	Total field and office costs					Xxxxxxxx
	Fee (contractor)					Xxxxxxxx
	Escal/contingency					Xxxxxxxx
	Total costs					Xxxxxxxx

as the progress of the project. Thus, the widest accuracy range is for a capacity factored estimate at the beginning of a project. The narrowest range therefore is at a definitive estimate stage around 30–40 % of project completion. The second set of curves gives a range of contingencies to be applied to the various estimate types. This is a plot of percent of total field and office costs against the estimate type used for the accuracy curves.

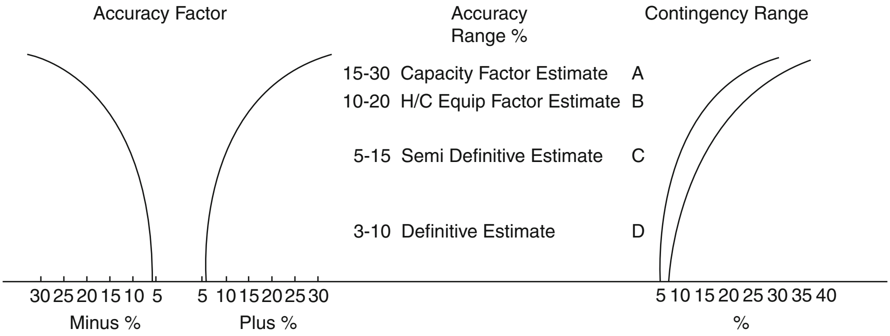


Fig. 8 Accuracy of an estimate

Discounted Cash Flow and Economic Analysis

Throughout this chapter, a major role of a process engineer in conducting economic studies has been described and discussed. The purpose of these studies is to provide the company's management with sound technical data to enable them to improve the company's profitability at minimum financial risk to the company. Up to now, the course of these studies has covered:

- Identifying the viable options that will meet the study objectives
- Short-listing and screening the options using simple return on investment techniques
- Providing process input into the preparation of a more detailed capital cost estimate of those options selected for further detailed economic evaluation

The cost estimates based on firm equipment costs are the most accurate possible without committing to more detail design and capital expenditure. Using these estimates, the detailed and more reliable prediction of the profitability of the selected options can now proceed. This prediction is based on a return on investment calculated from a projected cash flow of the process over a prescribed economic life for the facility.

There are several methods of assessing profitability based on discounted cash flow (DCF), but one such method is a return on investment method using the present worth (or net present value) concept. This concept equates the present value of a future cash flow as a product of the present interest value factor and the future cash flow. *Based on this concept, the return on investment is that interest value or discount factor which forces the cumulative present worth value to zero over the economic life of the project*. Other methods are described and discussed in section "Using Linear Programming to Optimize Process Configurations," which follows.

Whereas the development of capital cost of plants is usually a combined effort between the development engineer and cost estimator, so is the development of a

DCF return on investment a combined effort between the development engineer and the company's financial specialist. The development engineer provides the technical input to the work such as operating costs, type of plants, construction schedules and cost, yield, refinery fence product prices, and the like. While the financial specialist provides the financial data based on statutory and company policies, such as the form of depreciation, tax exemptions, tax credits (if any), items forming part of the company's financial strategy, etc., the calculation itself is in two parts, which are:

- Calculation of cash flow
- Present worth calculation

These are described in the following paragraphs.

Calculating Cash Flow

Figure 9 gives a graph of the cumulative cash flow of a typical project in relation to its project life.

Initially, there is a financial loss when the company has to purchase land and equipment, pay contractors to erect equipment, and the like. To do this, not unlike

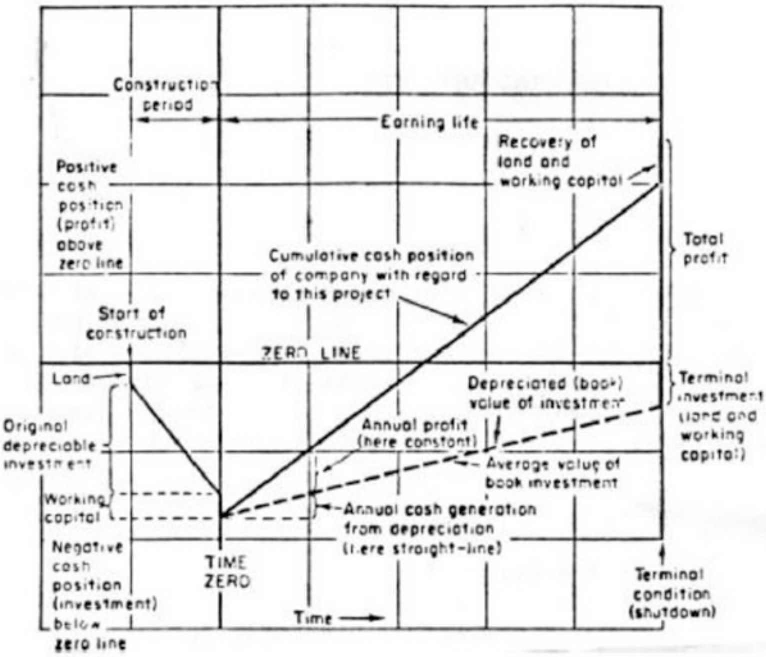


Fig. 9 A diagram of cumulative cash flow

most private individuals, companies borrow money, on which of course they have to pay interest. In addition to the cost of construction, the company must keep in hand some capital by which it can buy feedstock and chemicals and pay the salary of its staff during the commissioning of the plant. This working capital must also be considered as debt at the project initiation.

At the end of construction and commissioning, the cash flow into the system moves upward toward a positive value and, after a prescribed number of years, moves into a positive value. During this period of positive cash flow, the money recovered from the operation must be sufficient to:

- Repay the loan and its interest.
- Pay all associated taxes.
- Pay all the operating costs of the project.
- Make an acceptable profit.

When these conditions have been met over the prescribed period of time called the "earning life" or "economic life," there still remains the plant hardware, the land, and the working capital. These are considered as the project's terminal investment and are added to the final project's net cost recovery.

The cash flow calculation recognizes the financial milestones shown in Fig. 9, and the contents of a typical cash flow calculation are discussed below.

Economic Life of the Project

This is the number of years over which the project is expected to yield the projected profit and pay for its installation. These are the number of years starting at year 0 which indicates the end of construction and the commissioning of the facilities. The last year (usually year 10) is the year in which all loans and other project costs are repaid and the "terminal investment" released.

Construction Period

This is the period before year 0 during which the plant is constructed and commissioned. Assuming that this period is 3 years, then these are designated as end of year −2, −1, 0. During this period, the construction company will receive incremental payments of the total capital cost of the plant with final payment at the end of year 0. The construction cost may be paid from the company's equity alone, or from equity and an agreed loan, or entirely from a loan. In the case of a loan to satisfy this debt, the payment of the loan interest commences in this period. The interest payment over this period however is usually capitalized and paid over the economic life of the project.

Net Investment

The net investment for the project includes the capital cost of the plant, which is subject to depreciation, and the associated costs, which are not subject to depreciation. The capital cost of the plant is the contractor's selling price for the engineering, equipment, materials, and the construction of the facilities. In a process study using a DCF return on investment calculation, the capital cost should be an estimate with an accuracy at least that based on an equipment factored type.

The associated costs include the following elements:

- Any licensor's paid up royalties
- Cost of land
- First inventory of chemicals and catalyst
- Cost of any additional utilities or offsite facilities incurred by the project
- Change in feed and product inventory
- Working capital
- Capitalized construction period loan interest

Revenue

This is the single source of income into the project. In most cases, it is the income received for the sale of the product(s). This is calculated from projected process yields of products multiplied by the marketed price of the products. A market survey should already have been completed to ensure that the additional products generated by the project are in demand and the prices are in an acceptable range. Later, a sensitivity analysis of the DCF return on investment may be conducted changing the revenue recovered by price escalation or other means.

Expenses

This is the major cost of carrying out the project. It consists of the following items:

- *Plant operating cost*. This includes the cost of utilities used in the process, such as power, steam, and fuel. It also includes the cost of plant personnel in salaries, burdens, and indirects and the cost of chemicals and catalysts used.
- *Maintenance*. There are two kinds of maintenance costs included in this item. These are the preventive maintenance carried out on a routine basis and those costs associated with incidental breakdowns and repair.
- *Loan repayment*. The loan principal is paid back in equal increments over the economic life of the plant (see later for a discussion). This item includes the payback increments and the associated interest on a declining basis.

These are incurred running costs and as such are considered tax free.

Depreciation

The second cost to the project which is considered as a deductible from the gross profit for tax purposes is the depreciation of the plant value. This is calculated over the plant life as the plant capital cost divided by the plant life. The term plant life is the predicted life of the facility before it has to be dismantled and sold for scrap. Usually, this is set at 20 years and indeed all specifications relating to engineering and design of the facilities will carry this requirement. All material and design criteria such as corrosion allowances associated with the plant should meet this plant life parameter.

Ad Valorem Tax

This is the fixed tax levied in most countries payable to local municipal, provincial, or state authorities to cover property tax, municipal service costs, etc.

Taxable Income

Taxable income is revenue less operating cost, depreciation, and Ad Valorem Tax. This of course is simply put as in most countries, states, or provinces there will probably be certain local tax relief principles and tax credits that will affect the final taxable income figure. The company's financial specialist will be in the position to apply these where necessary.

Tax

This is quite simply the tax rate applied to the "taxable income" figure. This will vary from location to location but will be taken as one rate over the economic life of the project for the purpose of a process study, unless there are legislative changes already in place.

Profit After Tax

This is the gross profit less the tax calculated in the previous item.

Net Cash Flow

This item is calculated for each year of the project's economic life. It commences with year zero with the net investment shown as a negative net cash flow item. Then for each successive year until the end of the last year of the economic life, the net cash flow is calculated as the sum of profit after tax plus the depreciation.

The depreciation is added here because it is not really a cost to the project. It is a "book" cost only and is used specifically for tax calculation. The cash flow item for the last year of the economic life must now include the "terminal investment item." This item is the sum of the salvage or net scrap value of the plant (scrap value less cost of dismantling), the estimated value of the land, and the working capital initially used as part of the "associated costs."

Thus, the final cash flow item will be the sum of profit after tax, plus depreciation, plus terminal investment.

With the net cash flow in place, the second part of the calculation, which is the determination of the return on investment based on the present worth concept for the project, can be carried out.

Calculating the Cumulative Present Worth

This is an iterative calculation using three or more values as the discounting percentage. The result of the cumulative values of the present worth at the end of the economic life from these calculations is plotted against the discount percentages used for each case. The discount value when the cumulative present worth is zero is the return on investment for the project.

For each value of the discount percentages selected, first calculate the discount factor for each year of the economic life starting at year 0 where the discount factor is always 1.0. Then divide the discount factor for year 0 which is 1.0 by (1.0 + d) where d = discount percent divided by 100. Do the same for each successive year. Thus, if the discount percent selected is 10 %, then the discount factor for year 0 = 1.0, for year 1 = 1/1.1 = 0.909, for year 2 = 0.909/1.1 = 0.826, for year 3 = 0.826/1.1 = 0.751, and so on until the last year.

The present worth value for each year is then calculated as the net cash flow value for that year multiplied by the discount factor for that year. Remember that the cash flow value for year 0 is always negative. Next determine the cumulative present worth value by adding the value for each successive year to the value of the year before. Starting with that value for year 0 which is negative, add that value for year 1 which is positive to give a positive or negative cumulative value for year 1. Continue by adding the present worth value for year 2 to the cumulative value for year 1 to give the cumulative value for year 2 and so on through the last year. The cumulative value of the present worth for the last year in each of the discount percentages selected is plotted linearly against the discount percentage. This cumulative value can either be positive or negative. Indeed, to be meaningful, the discount percentages selected must be such that the calculated present worth values for the last economic years be a mixture of negative and positive values. In this way, the resulting curve plotted must pass through zero.

The following example calculation is based on scheme 1 in Item 8.2. Similar calculations may also be carried out on one or more of the other schemes that were screened to confirm their comparative profitability. In this case, it is important to remember that the economic parameters used for each case are identical to enable a proper comparison and analysis to be made.

Example Calculation

This scheme includes the addition of the following units into an existing oil refinery:

- New naphtha hydrotreater (13,500 BPSD)
- New naphtha splitter (1,350 BPSD)
- Revamped debutanizer and new light ends units (3,830 BPSD)
- New thermal cracker (34,320 BPSD)
- New diesel hydrotreater (9,000 BPSD)
- New catalytic reformer (9,000 BPSD)

The capacity factored capital cost estimate used in the screening studies for this scheme was 125.490 MM $. A subsequent estimate based on a more definitive design and equipment definition (equipment factored estimate) gave a capital cost figure of 119.216 MM $ for this configuration. This latter figure will be used as the capital cost in this example calculation.

Net Investment Cost

This will consist of:

- The capital cost
- Associated costs
- Capitalized construction loan interest

Associated Costs

1. Paid up royalties. This is a once off licensing fee paid to the licensors of the hydrotreater processes and the catalytic reformer process. There may also be a running licensing fee for these processes, but this will be included into the operating cost.
   Paid up royalties = 2.026 MM $.
2. First catalyst inventory = 4.052 MM $. Note: noble metals on the catalysts are normally recovered and thus carried out as a working capital except for recovery losses which can be treated as expenses as they occur.
3. Cost of land = 1.0 MM $.
4. Cost of incremental utility/offsite facilities = 2.501 MM $.
5. Cost of increased product/feed inventory (only product inventory is considered here as there is no change in crude oil throughput). Statutory requirements for this refinery location is a mandatory inventory of 14 days feed and product.

$$\text{Additional inventory cost} = 14 \times ((564{,}845 + 162{,}798) - (452{,}756))$$
$$= 3.848 \;\text{ MM \$.}$$

6. Working capital – taken as 5.0 % of the capital cost = 5.835 MM $.

Total associated costs = 19.262 MM $.

Construction Cost and Payment

End of year	−2	−1	0
Constr. payments MM $	11.922	47.686	59.608

The construction costs will be paid out of equity up to the limit of the equity. The remainder will be paid by a loan at 8.0 % interest. Initial equity is 60 % of capital + associated costs = 0.6 (119.216 + 19.262) = 83.087 MM $.

The loan to complete the construction schedule of payments is raised during year zero and interest on this is 2.89 MM $. This is capitalized but will be paid out of an increased equity.

Net investment:

	MM $
Capital cost of plant	119.216
Associated costs	19.262
Construction loan interest	2.89
Net investment	141.368

Operating and Maintenance Costs

Operating cost for year 1 is made up as follows:

	MM $
Operating labor	=1.49
Utilities	=8.32
Chemicals, catalyst, running royalties	=1.20
Total	=11.01

Operating costs escalate at a rate of 3.0 % per year. The yearly operating cost schedule is given in Table 18.

The maintenance cost for year 1 is taken as 4 % of capital cost which is 0.04 ×119.216 = 4.76 MM . Maintenance costs are escalated at a rate of 1.0 % per year. The annual schedule for this item is also given in Table 18.

Loan Repayments and Interest

The total loan for the project is 55.390 MM $ and is repaid over 10 years at an interest rate of 8.0 % per annum discounted annually.

Table 18 Schedule of operating and maintenance costs

End of year	Operating costs MM $	Maintenance MM $
1	11.01	4.76
2	11.34	4.81
3	11.681	4.86
4	12.031	4.904
5	12.392	4.953
6	12.764	5.003
7	13.147	5.053
8	13.541	5.103
9	13.947	5.154
10	14.366	5.206

Table 19 Schedule of debt repayments and interest (assuming uniform principal repayments)

End of year	Principal, MM $	Principal repayments, MM $	Interest, MM $	Total, repayments total, repayments MM $
0	55.390			
1	49.851	5.539	4.431	9.970
2	44.312	5.539	3.988	9.527
3	38.773	5.539	3.545	9.084
4	33.234	5.539	3.102	8.641
5	27.695	5.539	2.659	8.198
6	22.156	5.539	2.216	7.755
7	16.617	5.539	1.772	7.311
8	11.078	5.539	1.329	6.868
9	5.539	5.539	0.886	6.425
10	0	5.539	0.443	5.982

The schedule of repayments and interest is given in Table 19 assuming uniform returns in principal (as opposed to uniform total payments of principal plus interest)

Revenue

There is a single source of revenue which is from the sale of all products at the refinery price given in Item 2 of this section of the chapter. For the base case given in this example, there is no escalation of this figure which remains at 77.7 MM $ per year.

Sensitivity analysis performed later gives the change in ROI for escalated product pricing of 3 % and 4 % per year, respectively.

Schedules of increased pricing are given in Table 20.

Depreciation

Depreciation is normally the capital cost of the plant divided by the plant life. The plant life in this example is 20 years, but the capital cost in this case has been taken

Table 20 Schedule of escalated revenue (for sensitivity analysis)

End of year	Escalated at 3.0 %, MM $/year	Escalated at 4.0 %, MM $/year
1	77.709	77.709
2	80.040	80.817
3	82.441	84.050
4	84.915	87.412
5	87.462	90.901
6	90.086	94.545
7	92.789	98.327
8	95.572	102.260
9	298.439	106.351
10	101.392	110.601

as the original capacity factored estimate of 125.490 MM $. This allows for such items in the associated costs such as the precious metal content of catalysts which are subject to depreciation. For this example, therefore, depreciation is taken as 7.7 MM $ per year throughout.

Ad Valorem Tax

This item includes plant insurance and is set at 2.0 % of capital cost per year.

Tax

This is 40 % of taxable income. For the purpose of this study, it is assumed there are no tax credits.

Results

Consolidation of the net cash flow is given in Table 21.

Figure 10 gives a plot of the cumulative net present worth versus percent discount from the results of the calculations given in Table 22.

From Fig. 9, the DCF return on investment for this scheme is 20.5 % per year. Based on the plant location and the current investment environment, return on investment above 18 % DCF makes the venture economically attractive. Similar calculations for scheme 3 will also be conducted to verify its ROI on a DCF basis for comparison with scheme 1.

The sensitivity of scheme 1 to escalation of refinery fence product costs are as follows:

- At an escalation rate of 3.0 % per year, the ROI becomes 23.5 %.
- At an escalation rate of 4.0 % per year, the ROI becomes 24.8 %.

Table 21 Consolidation of net cash flow

	MM $										
End of year	0	1	2	3	4	5	6	7	8	9	10
Investment											
Cap cost	*119.2*										
Assoc cost	*22.2*										
Net investment	*141.4*										18.7
	[a]										[b]
Revenue at 0 % Esc		77.7	77.7	77.7	77.7	77.7	77.7	77.7	77.7	77.7	77.7
Expenses[a]											
Operating		*11.0*	*11.3*	*11.7*	*12.0*	*12.4*	*12.7*	*13.1*	*13.5*	*13.9*	*14.4*
Maintenance		*4.8*	*4.8*	*4.8*	*4.9*	*4.9*	*5.0*	*5.1*	*5.1*	*5.2*	*5.2*
Loan repayment											
		10.0	*9.5*	*9.1*	*8.6*	*8.2*	*7.8*	*7.3*	*6.9*	*6.4*	*6.0*
Total expense[a]		*25.8*	*25.6*	*25.6*	*25.5*	*25.5*	*25.5*	*25.5*	*25.5*	*25.5*	*25.6*
Depreciation[a]		*7.5*	*7.5*	*7.5*	*7.5*	*7.5*	*7.5*	*7.5*	*7.5*	*7.5*	*7.5*
Ad valorem tax[a]		*2.4*	*2.4*	*2.4*	*2.4*	*2.4*	*2.4*	*2.4*	*2.4*	*2.4*	*2.4*
Taxable income		42.0	42.2	42.2	42.3	42.3	42.3	42.3	42.3	42.3	42.2
Tax at 40 %		*16.8*	*16.9*	*16.9*	*16.9*	*16.9*	*16.9*	*16.9*	*16.9*	*16.9*	*16.9*
Profit after tax		25.2	25.3	25.3	25.4	25.4	25.4	25.4	25.4	25.4	25.3
Net cash flow	141.4	32.7	32.8	32.8	32.9	32.9	32.9	32.9	32.9	32.9	51.5
	[a]										

[a] These are costs and therefore negative values in cash flow (shown here in Italics)

[b] These are cash recoveries and therefore have positive values in cash flows

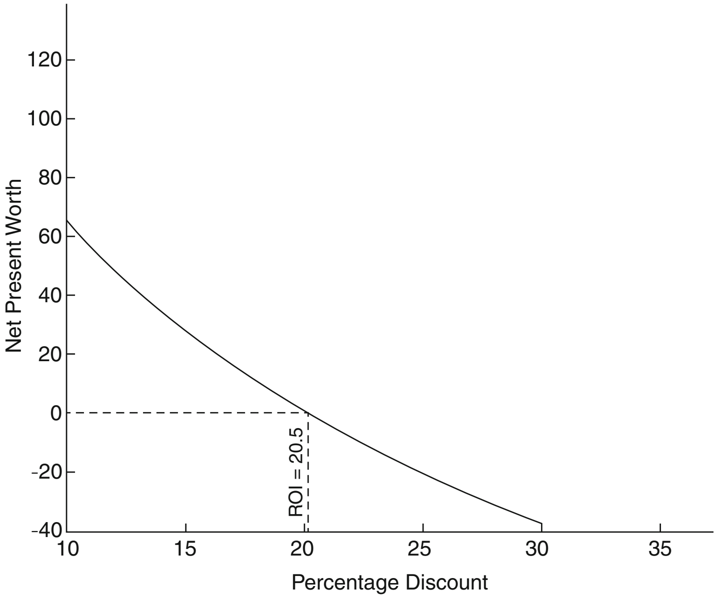


Fig. 10 A plot of net present worth versus percent discount

Using Linear Programming to Optimize Process Configurations

Linear programming is a technique to solve complex problems having multivariable conditions by the use of linear equations. The equations are developed to define the interrelationship of the variables. Computers are used to solve these equations and to select from a matrix of these equations the solution or solutions to the problem.

This is not a new technique. It has been used for many years in industry and particularly the oil industry to plan and optimize its operation. Indeed, in oil refining today, there is considerable development in process control using linear programming "online" to optimize the unit operation. In its use as a management tool, it can refine the calculations described in this chapter to a very fine degree. It is possible also by using this technique to examine many more options than could be examined in a manual operation.

The first objective using this technique is to build a mathematical model that fully defines the problem. The main model constitutes the "objective function." The purpose of linear programming is to either maximize or minimize the objective function (e.g., maximize overall profit or minimize overall costs) subject to a number of constraints. The model itself will consist of many submodels which will be interrelated by linear equations. In the case of an oil refinery configuration study, the data for the model development will include:

Table 22 Present worth calculation

Net cash flow	*141.4*	32.7	32.8	32.8	32.9	32.9	32.9	32.9	32.9	32.9	51.5
Discounted at 10 %											
Discount factor	1.0	0.909	0.826	0.751	0.683	0.621	0.564	0.513	0.467	0.424	0.385
Present worth	*141.4*	29.7	27.1	24.6	22.5	20.4	18.6	16.9	15.4	13.9	19.8
Cumulative											
PW	*141.4*	*111.7*	*84.6*	*60.0*	*37.5*	*17.1*	1.5	18.4	33.8	47.7	67.5
Discounted at 15 %											
Discount factor	1.0	0.870	0.756	0.658	0.572	0.497	0.432	0.376	0.327	0.284	0.247
Present worth	*141.4*	28.4	24.8	21.6	18.8	16.4	14.2	12.4	10.8	9.3	12.7
Cumulative											
PW	*141.4*	*113.0*	*88.2*	*66.6*	*47.8*	*31.4*	*17.2*	4.8	6.0	15.3	28.0
Discounted at 25 %											
Discount factor	1.0	0.800	0.640	0.512	0.410	0.328	0.262	0.210	0.168	0.134	0.107
Present worth	*141.4*	26.2	21.0	16.8	13.5	10.8	8.6	6.9	5.5	4.4	5.5
Cumulative											
PW	*141.4*	*115.2*	*94.2*	*77.4*	*63.9*	*53.1*	*44.5*	37.6	32.1	27.7	22.2
Discounted at 30%F											
Discount factor	1.0	0.769	0.592	0.455	0.35	0.269	0.207	0.159	0.123	0.094	0.073
Present worth	*141.4*	25.1	19.4	14.9	11.5	8.9	6.8	5.2	4	3.1	3.8
Cumulative											
PW	*141.4*	*116.3*	*96.9*	*82*	*70.5*	*61.6*	*54.8*	*49.6*	*45.6*	*42.5*	*38.7*

- All the processing plants to be considered
- The yield from each plant
- The product and feed stream properties
- All the possible routing of the streams
- All the possible final blending recipes
- Utility and operating requirements for each process on a unit throughput basis
- Investment cost for each process

These data are coded and the coded items used in equations that represent all the relationships to one another. The coded data items are shown graphically in Fig. 11. The relationship equations representing physical and financial data are inputs to the computer program. Proprietary subroutines included in the program resolve nonlinear relationships to linear. Such routines as the DCF calculation are also added into the main program. The computer solves the many hundreds of equations meeting the problem premises and any other applied constraints. The selected configurations are optimized within the program, and the final printout shows product quantities, product quality, stream flows, unit capacities, investment costs, operating cost, and the ROI. The graphical representation of the model, part of which is shown here as Fig. 11, contains 511 variables and over 400 equations. By present linear program standards, this is a fairly small model.

Appendix 12 provides a detailed discussion and example of a linear program application.

Common Terms and Expressions Used in Standard Economic Analyses

Introduction to Economic Terms and Expressions

This section provides a summary of common terms and expressions used in standard economic analyses. In this introductory economic analysis, we cover two main subjects:

Economic analysis at one point in time

This “instantaneous” analysis is the most common since it entails the least difficulty and requires the least amount of information. This is the type of analysis seen in Chem Systems’ PERP reports and in SRI’s PEP reports. If properly done and properly used, the results derived from this analysis are excellent. In this write-up, we devote most of the attention to this analysis; in particular, we try to analyze each of the terms in detail. Although this analysis requires the least information, in order to do a proper job, the amount of information required is usually still beyond what is commonly available in the initial screening stages of a project. However, the insight provided by examining

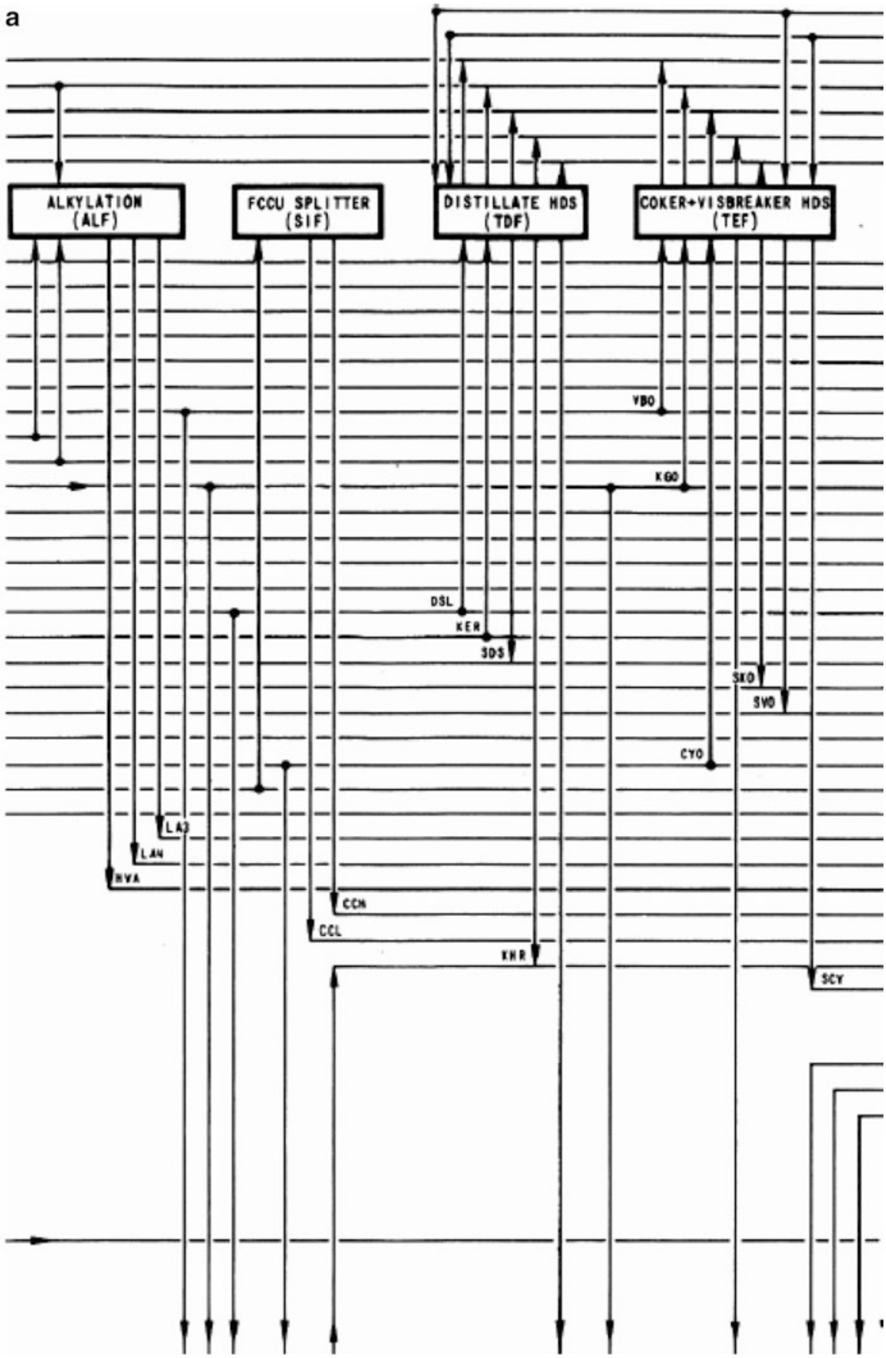


Fig. 11 (continued)

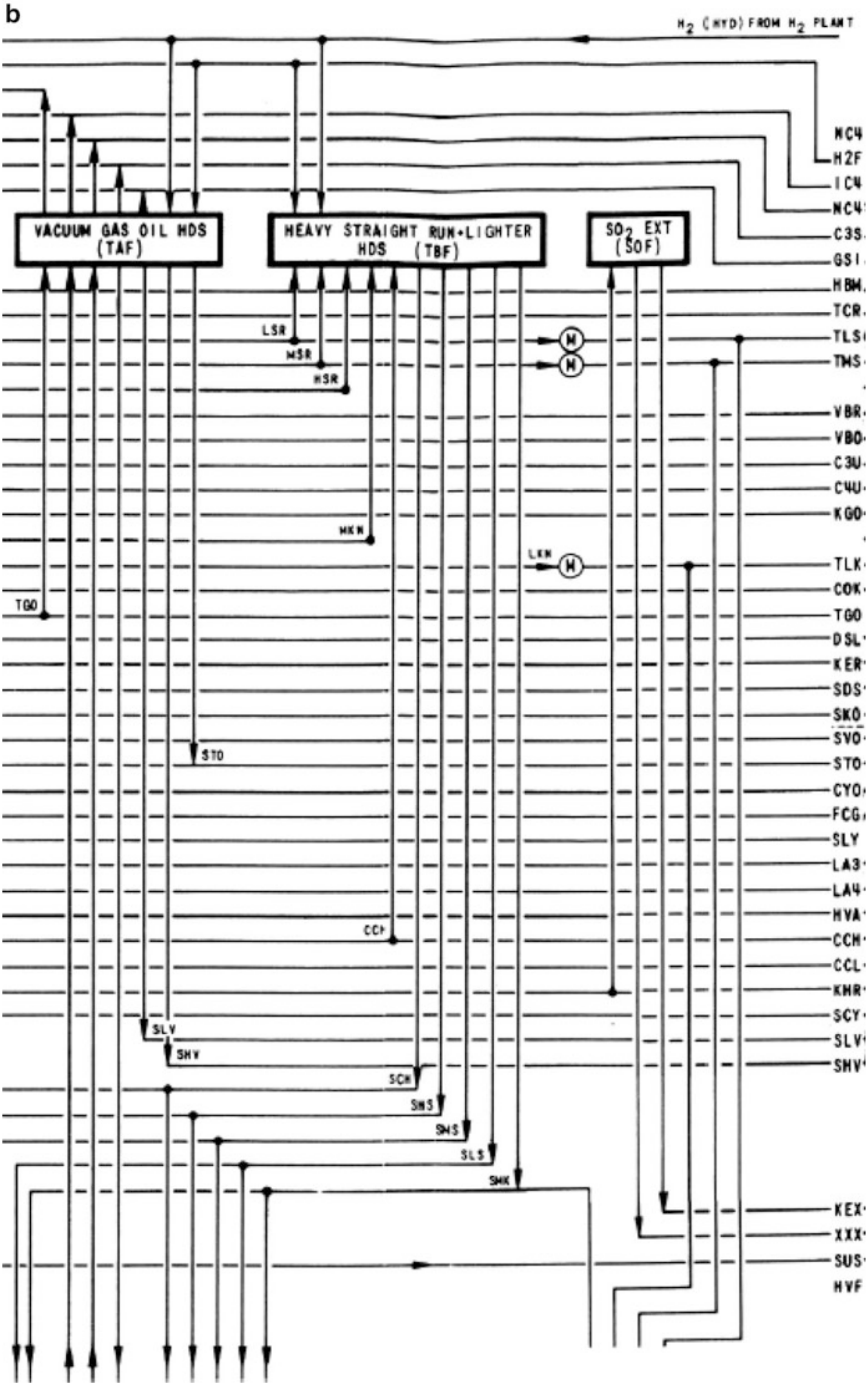


Fig. 11 (continued)

c

	BLENDING STOCKS												
	REF FUEL	C_3 LPG	C_4 LPG	PREM GASOL	INT GASOL	REG GASOL	DERV	GAS OIL	MARINE DIESEL	PREM KERO	REG KERO	FUEL OIL	$C_3/C_3^{=}$ LPG
PURCHASED NORMAL BUTANE				●	●	●							
REFORMER HYDROGEN	●												
ISOBUTANE	●		●	●	●	●							
NORMAL BUTANE	●		●	●	●	●							
PROPANE	●	●											●
FUEL GAS	●												
930⁺VAC. RESID												●	
650⁺ATM. RESID												●	
SWT.C_5-180 LT.S.R.	●		●	●	●	●							
SWT.180-210 MED.S.R.	●			●	●	●							
VISBREAKER RESID												●	
LT.VISBREAKER G.O.												●	
PROPYLENE	●	●											●
BUTYLENE	●		●		●	●							
COKER G.O.												●	
SWT.LT.COKER NAP.	●					●							
COKE													
650-930 TOTAL G.O.												●	
520-650 DIESEL							●	●	●				
380-520 KEROSENE							●	●	●				
SWT.DIESEL							●	●	●			●	
SWT.COKER G.O.												●	
SWT.VISBREAKER G.O.							●	●	●			●	
SWT.TOTAL GAS OIL												●	
FCCU CYCLE OIL												●	
FCCU GASOLINE				●	●	●							
FCCU SLURRY												●	
C3 ALKYLATE				●	●	●							
C4 ALKYLATE				●	●	●							
HVY.ALKYLATE							●	●					
250-430 FCCU GASOLINE				●	●	●							
C_5-250 FCCU GASOLINE	●			●	●	●							
SWT.REG.KEROSENE							●	●	●		●		
SWT.CYCLE OIL												●	
SWT.LT.VAC.G.O.							●	●	●			●	
SWT.HVY.VAC.G.O.												●	
SO_2 EXTRACT												●	
PREM.KEROSENE										●			
SULFUR													
FUEL OIL	●												

Fig. 11 (**a**) An example of a mathematical model used in linear programming. (**b**) An example of a mathematical model used in linear programming (Continued). (**c**) An example of a mathematical model used in linear programming (Continued)

the various entries is of great value as it helps to identify missing data. Also, even with incomplete information, this type of analysis is especially useful to determine the sensitivity of a project relative to a number of parameters.

Economic analysis over an extended period of time

This analysis, usually known as "cash flow analysis," is performed by analyzing the (expected) performance of a project over an extended period of time, usually a number of years at least equal to the capital depreciation or amortization period. The value of this type of analysis is that it recognizes the "time value of money."

A cash flow analysis does not require more information than an instantaneous analysis, but it does introduce some additional concepts in the calculation of the discounted cash flow rate or return or internal rate of return (IRR) and other discounting parameters. Calculation of the IRR used to be difficult when slide rules prevailed, since it entails a trial-and-error calculation; it is quite trivial with just about any computer or even a small programmable calculator. A cash flow analysis is an absolute necessity to account for the effects of taxation and inflation since these are usually spread out over a number of years and the effects are carried over from year to year, especially when deferred taxes accrue out of the different depreciation and/or amortization methods used for tax accounting as opposed to financial accounting. However, in order to keep it simple, this introductory economic analysis will not cover multiple depreciation schedules, tax accounting, and the like.

Indirectly, the cash flow analysis can also be used to decide what the prospective sale price of a product should be. The price can be calculated so as to yield a desired discounted cash flow rate of return.

Accounting for Inflation

The effects of inflation, though important in real life, tend to be irrelevant and misleading for economic evaluations and can best be dismissed by always performing a constant-dollar analysis.

If inflation needs to be taken into account, it is easy to incorporate inflationary factors that adjust the numerical values on an annual basis. The formulas provided in the appendices in general do not apply when variable annual cash flows have to be accounted for. The calculations are then performed by creating a series of estimated annual cash flows and conducting the calculations by trial and error. Some of the trial-and-error calculations are already programmed in the functions usually available in most PC software packages. Other calculations may require some simple program coding; half interval splitting (dichotomous search) is usually suitable for convergence.

The interpretation of the results when inflation is accounted for tends to be muddied by the additive effect of inflation. The gross returns will increase if inflation leads to increasing cash flows but may decrease if inflationary pressures raise the costs faster than the revenues.

Analysis at One Point in Time

This section examines what can be regarded as an analysis at one given point in time. This "instant" analysis is normally confined to a typical period in the life of the project, usually 1 year. This is the usual type of economic analysis and is also the type found in Chem Systems' reports, SRI's reports, etc.

An analysis of this type normally entails three parts:

- Capital summary
- Production cost summary
- Reporting parameters

In the first part, capital summary, we tabulate those items that may be candidates for depreciation, amortization, or interest charges for both long-term and short-term capital. Typical items are:

- Erected plant cost
- Erected offsite cost
- Interest during construction
- Catalyst and metals inventory
- Working capital

If the economic analysis is intended to account for tax effects, a far more detailed breakdown is required for capital items since, for tax purposes, the depreciation schedules may vary considerably from item to item, principally as concerns the treatment of machinery, equipment, and offsites.

The second part, production cost summary, provides a condensed tabulation of the various items that contribute toward the final cost of the manufactured product. There are two basic ways of conducting an "instantaneous" economic analysis as described herein: (a) to arrive at a cost of production or (b) to arrive at a given return on capital (ROI). Both formats are similar in concept and execution, the only difference being that the latter, (b), requires the assignation of cash values to the main product or products.

The following items are normally included:

Variable credits (often shown as credits against variable costs)
    Materials
        Product revenue (only shown if required to set margins)
        By-product credits
    Utilities
Utility credits
Variable costs
    Materials
        Raw materials costs
        Catalysts and chemicals

- *Utilities*

Utility requirements

Operating costs

- Labor
- Maintenance

Operating expenses

- Plant insurance
- Property taxes
- Direct overhead
- General plant overhead
- Sales and administration (often accounted for as overhead)

Capital items

- Depreciation
- Amortization
- Interest on capital
- Interest on working capital

Taxes

- (only if the analysis is to consider tax effects)

The following is an itemized summary of each section.

The final section of an economic analysis, instantaneous or over time, may be referred to as "reporting parameters." In this section, the project performance is measured by using some commonly acceptable yardsticks: return on investment (ROI), payback or payout time, internal rate of return (IRR), discounted cash flow rate of return (DCFRR), etc. They will be discussed in more detail later.

Capital Items

The first part of an economic analysis requires an exposition of the capital items. This includes those items that can be either depreciated, amortized, or that enter indirectly in the cost of production through either a long-term or a short-term interest charge. Typical entries are:

- Erected plant cost
- Erected offsites cost
- Interest during construction
- Royalties
- Catalyst and metals inventory
- Working capital

Erected Plant Cost

By erected plant cost, we mean the estimated cost of construction inclusive of materials, equipment, and labor plus design, engineering, and contractor's fees within battery limits as usually provided by cost estimating [estimated erected cost or EEC]. It is usually assumed that all the elements included within battery limits qualify for the same depreciation rate; this need not be the case in real life.

Erected Offsite Cost

An estimated erected cost of offsites usually is not available at the early stages of a project. Estimating the cost of offsites is difficult, but not impossible. Two approaches are available:

- A gross estimation approach
- An itemized estimation approach

The first approach provides only a very rough estimate and makes use of some simple but often unreliable guidelines. Essentially, these guidelines dictate that if a plant is a grassroot facility, the cost of the offsites is about the same as the cost of the plant within battery limits; if the plant is built on a developed site, the cost of the offsites is about 30–50 % of the cost of the plant within battery limits. These rules are good only to show an allowance for offsites, but are inadequate for quantification purposes. The scope of offsites to be built for a grassroot facility can vary enormously from case to case: tank age, flare, feedwater treatment, steam plant, power distribution center, cooling water facilities, effluent treatment facilities, road terminals, rail terminals, marine terminals (jetties, etc.), canteen, shops, administration buildings, etc., just to give a few examples; units in remote locations may include "offsites" such as workers' housing, sports, religious and recreational facilities, etc.

The second approach entails more work, but yields results that, at least, are more justifiable. In this approach, the various offsites and their capacities are itemized and cost estimating rules are applied. An example can be found in the guidelines provided by Chem Systems.

Interest During Construction

This concept is often ignored or overlooked. Unfortunately, it is a significant amount that greatly contributes to the final erected cost of a unit or complex.

A unit is not built overnight. Expenditures normally accrue over the procurement, fabrication, and construction period that, for a plant of average complexity, can usually take anywhere from 2 to 4 years. Not knowing further details, 2 years may be assumed for relatively simple units and 3 years or more for more complex ones; very simple units may be assumed built in 1–1.5 years.

It is common practice to assume that the cost of the capital expenditures that accrue over the construction period is covered by a short-term loan on a 100 % debt basis. This assumption is not unreasonable: even if the funds are provided on an equity basis, the expenditures represent a short-term opportunity cost that can be accounted for through the short-term loan concept. It is true that, often, funds are provided through a long-term loan, but this is of relatively little consequence over the construction period; assumption of a short-term loan at worst provides for a more conservative estimate.

How are the capital expenses allocated over the construction period? Unless actually known, there is no common school of thought as to how construction costs ought to be spread. Equal shares (i.e., one-third each over a 3-year period) can be used for simplicity; others might prefer to use a 30 % – 50 % – 20 % distribution over a 3-year period to account for the fact that expenses tend to occur up-front.

Regardless of the way used to allocate capital over the construction period, the interest charges accrued over this period are accumulated and capitalized (usually on a year-end basis) as part of the erected cost of the unit. If properly accounted for, separate allocations should be made for items within battery limits and for offsite items. In fact, because different individual items such as columns, heat exchangers, etc., may have to be retired and replaced at different times over the life of the unit, a running count of interest expenses should be maintained for each individual piece of equipment. To provide an example in a similar, but unrelated, situation in a plane, the jet engines have a different depreciation schedule and tax treatment than the main body within the fuselage. It is therefore always advisable to account for the capitalization of as many individual items as possible; it is not an impossible task with a relatively small computer to keep track of events and charges.

Royalties

Royalties are normally added to and capitalized with the plant investment even though a different depreciation schedule may be used for royalties.

Adsorbent, Catalyst, and Metal Inventories

Catalyst base and metal make-up, additions, and reprocessing costs should be handled as an operating expense, along with chemicals and other consumables, in the production cost summary.

A question arises as to how to handle a catalyst base inventory or an adsorbent inventory, principally when the life of the catalyst or adsorbent is expected to span several years.

Essentially, there are two ways:

- We can treat the catalyst as a consumable with the annual consumption calculated by prorating the inventory over the expected life span of the catalyst. The catalyst inventory itself can still be treated as a capital item for the purposes of calculating interest on capital, if the investment is leveraged.
- We can treat the catalyst inventory purely as a capital item. The catalyst inventory can then appear in the production cost summary as (a) an amortization term *and* (b) interest on capital.

Tax law considerations may favor or dictate which approach should be taken. In general, however, the latter approach is preferred; namely, the catalyst or adsorbent inventory is capitalized and amortized over its expected useful life. While, in principle, both approaches would seem to be numerically equivalent, the amortization approach has a more favorable impact on the cash flow since amortization is an add-back item. Whenever allowable, this approach also makes it possible to use accelerated amortization schedules.

Catalysts should *never* be amortized and treated as a consumable at the same time!

Those metals that are not recovered and are disposed of with the catalyst base are treated as an integral part of the catalyst and accounted for as the catalyst base.

Metals – principally noble metals – that are recovered at the end of the useful life of each catalyst batch are carried only as working capital and, therefore, appear in the production cost summary only as an interest item.

Small metal losses incurred when the spent catalyst is reprocessed and the cost of reprocessing itself can also be amortized over the useful life of the catalyst, but are most often handled as operating expenses.

Catalyst stockpiled as inventory for future use is part of the working capital.

Working Capital

Working capital items are those items that:

- Require an additional front-end investment even though they are not part of the physical plant
- Accrue additional interest charges, usually in the form of short-term loans
- Can be recovered at the end of the useful life of the project

For timing purposes, working capital is usually assumed to be available upon completion of construction. The following items comprise the working capital in most economic studies:

Additive items

- *Feedstock inventory*

  Includes the supply of raw materials valued at delivered prices. Excluded are any materials that are not normally stored (gases, e.g.). Unless specified otherwise, a 0.5-month supply or equivalent liquid and solid feedstock storage is assumed.
- *Finished product inventory*

  Comprises the inventory of all principal products and by-products, if any, valued on a gross cost of production basis. Again, a 0.5-month storage is assumed unless differently specified. Excluded too are items that are not normally stored (e.g., hydrogen or light ends).
- *Accounts receivable*

  Typically, it is assumed to consist of 1 month's worth of production. Production includes main products, by-products, and any other items that might be sold on a regular basis.
- *Cash on hand*

  Typically estimated as the equivalent of 1 week's cash flow.
- *Adsorbent, catalyst, and metals*

  Normally, only those items that are fully recoverable, and thus not amortizable, are part of the working capital. Typical is the inventory of noble metals in the plant.

- *Warehouse and spare parts inventory*

  Any spare items kept in storage on a regular basis are included as part of the working capital. Excluded are items ordered and kept in storage on a short-term temporary basis until installed. Typical working capital items would be spare loads of adsorbents or catalysts and spare parts such as compressor rotors, rotary valve gaskets, replacement pumps, etc. Since a detailed inventory of spare parts is not usually available for a preliminary economic analysis, it is common practice to assume that the total amounts to, say, 2 % or 3 % of the erected cost within battery limits.

Subtractive items

Accounts payable

Typically assumed as 1 month's worth of raw materials and other consumables at delivered prices

Cost of Production

The concepts usually included as part of the cost of production summary were itemized in the opening section. Essentially, they were grouped under five major sections:

- Variable costs
  - Materials
  - Utilities
- Operating costs
- Operating expenses
- Capital items
- Taxes

Variable Costs

Variable costs are those that can be directly associated with the production process as concerns the consumption of materials and services or utilities. A characteristic of variable costs is that they are roughly proportional to the amounts produced. Thus, if the total annual production were to increase by, say, 20 %, the annual variable costs would be expected to also increase by roughly 20 % (any differences would be due to changes in production efficiencies only) so as to maintain a uniform variable cost of production per unit item. Typical variable costs of production are:

- Raw materials costs
- Catalysts and chemicals
- Utility requirements

In general, any other consumables expended in the production process.

Although not part of the costs, it is customary practice to subtract here any variable credits such as:

- By-product credits
- Utility credits

More appropriately, these concepts should be entered under a separate heading of variable credits.

If the establishment of a cost of production is the main objective of the analysis, all the various costs are added up to the final grand total. If, on the other hand, it is desired to calculate an income or cash flow result, the various costs will be added up and the result subtracted from a base term that will comprise the revenue generated by the production of all major products or coproducts assumed sold at prevailing market prices estimated at an equivalent production level from other manufacturers.

Operating Costs and Operating Expenses

These are typically fixed operating charges unless there is a major revision of the plant's operating conditions. Typical items are:

- Labor
- Maintenance
- Plant insurance
- Property taxes
- Direct overhead
- General plant overhead
- Sales and administration expenses

and, possibly, many others depending on an individual plant's characteristics and accounting basis. In general, all these expenses are fixed in that they remain about the same on an annual basis irrespective of the plant's actual running capacity. Naturally, if business is poor and production rates are low on a consistent or extended basis, we can expect that measures will be taken to lower these charges to the extent that it may be feasible (e.g., reduction in labor through layoffs or reduction in overheads through some other belt-tightening measures), but, in general, changes in these concepts will always be limited, short of shutting down the plant.

Labor

Labor includes the personnel required at various skill levels to operate the unit on a 24-h basis. Since shifts usually run for 8 h, a minimum of three operators are required to staff each position. Actually, because of holidays, vacation, leave time, etc., the staffing requirements are considerably higher.

An average year of 365.25 days consists of 8,766 h. The basic work load per individual at 8 h/day and 5 days/week is about 2,090 h/year, corresponding to an average of 4.2 operators/shift. This value is often seen in economic estimates, but is not quite correct. If we instead estimate the time off as follows:

	Days/year
Weekends	104
Vacation (3 week average)	15
Holidays	10
Sick leave (estimate)	10
	139

The corresponding annual workload is 1,810 h. Therefore, the number of individuals required to fill each shift position is 4.84 (say 4.8) rather than 4.2.

Labor rates are those prevailing within a particular geographical area. Base labor rates are typically used. Fringe benefits, often estimated at 35–45 % of base labor rates, are more commonly accounted for as direct overhead.

Supervision, including overall supervision and shift foremen, is frequently estimated as 25 % of labor. Otherwise, one foreman per shift may be assumed together with one single overall supervisor on a day shift basis only.

Maintenance

Maintenance labor and maintenance materials are always accounted for as a percentage of the investment cost within battery limits (ISBL). This percentage may be as high as 4 % or 7 %, but it should be estimated based on past experience. Often an allowance of 3 % and in many cases as low as 2 % is often sufficient for most of refinery or petrochemical units built according to heavy-duty specifications (e.g., API). The periodic replacement of parts due to corrosion, wear, etc., should be accounted for as part of the overall annual maintenance allowance.

Property Taxes and Plant Insurance

It is customary to estimate the total of these charges at about 2 % of the plant erected cost within battery limits (EEC). (Others may use, say, 1.5 % of fixed investment, including battery limits, and offsites.)

Direct Overhead

Direct overhead in its usual interpretation consists of fringe benefits and other labor-related concepts (personnel department, etc.). It is often allowed for at 35–45 % of the total charges for labor and supervision. Some estimates include direct overhead as part of labor expenses.

General Plant Overhead

This allowance is best estimated based on past experience; it may vary considerably depending on each company's practice. A common practice is to assign to it, say, 65 % of the total of labor and maintenance. Others may use, say, 80 % of labor.

The general plant overhead concept is meant to include the costs of operating shops, labs, etc., as they are allocated to the operation of the plant. Research and analytical expenses are often allocated also as part of plant overhead unless accounted for separately.

Sales and Administration

In order to avoid further complexity, it is best to assume that these expenses are included as part of the general plant overhead. At times, however, this is not practical, principally if the plant is part of a more extensive organization. A corporate overhead entry may be included in these cases. If not part of the general plant, overhead, sales, and administration can then be assumed to be part of corporate overhead. At other times, a cost of sales, say 5 %, is allocated as a percentage of product revenue.

The actual accounting for this item is largely immaterial except for those few cases when one wishes to distinguish a cost of production from a cost of manufacturing, thus making a distinction between plant-related costs and other extraneous costs.

Capital Items

Capital items are those directly related to the plant investment and include:

- Depreciation
- Amortization
- Interest on capital
- Interest on working capital

Depreciation and amortization expenses are significant in that they are substantial, but are not real. Thus, while both depreciation and amortization charges are subtracted in order to calculate a net (pretax or posttax) income, they in no way affect the cash flow out of the unit and, therefore, are added back for the purpose of determining the cash flow.

Depreciation

Depreciation represents a capital recovery. As such, it is a certain amount of money related to the capital investment spent up-front that is set aside on a regular basis, without interest, over a certain period of time to represent the recovery of the original capital.

Depreciation is accounted for separately, apart from any return on capital (ROI). The reasoning behind this practice is that, as the plant ages, provision should be made to accumulate capital for its eventual replacement. Obviously, in actual practice, financing of an actual replacement, if any, will rarely depend on capital accumulated in such a manner. If viewed as a capital build-up for plant replacement, depreciation would be equivalent to a zero-interest sinking fund.

Apart from philosophical interpretations, the real value of depreciation is that it is almost universally tax deductible. On the basis that depreciation represents a gradual recovery of the original capital, it is regarded as not being part of the profits generated by the plant and, therefore, not subject to taxation.

An interesting – and legal – dichotomy arises at this point. From an actual operating viewpoint, one wishes to show as much profit as possible and, therefore, as little depreciation as possible. However, from a tax viewpoint, one wishes to maximize depreciation so as to minimize the immediate tax liability. This is the only place where two perfectly legal and different accounting methods can be applied that lead to different results.

For financial reporting purposes, the Financial Accounting Standards Board (FASB) in the United States dictates what minimum depreciation levels should be used. If not subject to any particular requirements, it is customary to use 10-year straight-line depreciation for plant equipment and 20-year straight-line depreciation for (most) offsites. (Sometimes, however, in order to bring depreciation schedules closer to those used for tax accounting, 5- and 10-year straight-line depreciations are used for plant and offsites, respectively.)

For tax accounting purposes, it is advisable to use whichever fastest rate of depreciation is allowable under the local current tax laws. (Whenever allowed, it may be advisable to start with the fastest rate of accelerated depreciation allowable and later, when the amount to be depreciated is relatively small, switch to, say, straight-line so as to prolong the depreciation benefits.) The golden rule in tax accounting is

pay the least and the latest . . . within the law!

Since tax effects are ignored in most of our representations, this discussion is largely irrelevant. However, when tax effects are included, it becomes apparent that the tax liability incurred under financial accounting principles is much higher than the tax actually paid. This gives rise to a deferred tax liability. The reasoning is that eventually this deferred tax will have to be paid; in actual practice, if sufficient capital items are added or replaced over the life of the plant, depreciation can be rolled over so as to largely neutralize the effects of deferred tax liabilities.

Amortization

Amortization is akin to depreciation. Amortization is the general term for the process of allocating the acquisition cost of assets to the periods of benefits as expenses. It is called depreciation for plant assets, depletion for wasting assets or natural resources, and amortization for intangibles.

We use the general term amortization to allocate expenses for the initial catalyst inventory costs. (In the sense that a catalyst life is relatively brief, we could think of this amortization as a depletion allowance.)

It is customary to amortize the catalyst inventory over its estimated useful life, irrespective of what the actual life might be.

Interest on Capital

Though very important in real life, interest on capital should not be used in a preliminary economic analysis.

Most commercial plants are heavily leveraged; namely, most plant owners choose to borrow as much capital as possible instead of investing their own money. Usually, the final investment will consist of a certain amount of debt (amount borrowed as long-term loans) and the rest equity (investors' capital). If the return on capital is calculated relative to equity, its value is distorted by the relative percentage of debt. For example, if the plant is financed through 100 % debt, a net return of $1.00 will represent an infinite rate of return for the investors who have exposed none of their own capital.

Also, the interest paid on capital ultimately is part of the plant return on investment and should be added back to the usual return on investment calculation in a traditional analysis.

Finally, if interest on capital must be used, it should be used on an average interest basis as explained in Appendix 11. The base interest rate, typically the prime rate applicable to a large long-term loan, will be averaged over the preestablished life of the loan or calculated on a year-to-year basis if a cash flow analysis is performed over time.

Interest on Working Capital

Working capital is normally assumed carried as 100 % debt. Because of its nature, working capital revolves somewhat like a line of credit and, therefore, is more representative of a short-term loan for which a higher rate of interest applies than for a long-term loan. Also, there is no interest averaging for working capital loans as they are assumed renewed on a year-to-year basis.

Reporting Parameters

Several terms are often used for reporting purposes.

Cost Basis

The summation of all costs without capital items leads to what is called the cash cost of production. The cash cost of production represents the total of raw material costs, chemicals and catalysts costs, utility costs, operating costs, and overheads.

The net cost of production is obtained by taking the cash cost of production and adding capital items: depreciation and amortization. As indicated above, interest on capital should not be used; interest on working capital may or may not be included at this point depending on individual practice. It is customary to include it, but others prefer to calculate cash flows on a total equity basis, including working capital.

Return Basis

The simplest parameter is the return on investment (ROI). This simply is the difference between product revenue (product value) and net production cost divided by the total investment. For this purpose, total investment is normally viewed as total fixed investment or total plant investment. Total fixed investment is the plant investment (EEC) within battery limits (ISBL) plus the plant investment outside battery limits (OSBL). EEC may be used instead of total fixed investment if clearly understood and agreed upon that this is the case. ROIs are normally calculated on a pretax basis; they can also be estimated on a posttax basis, if desired. Royalties and interest during construction should be included as part of the total plant investment.

A second simple return parameter often used is payout time (or payback time). This represents the ratio of total fixed or plant investment to operating cash flow. (This type of payout time will not agree with the payout times calculated on a discounted cash flow (DCF) basis.)

Typical rules of thumb are that a new smallish project is attractive if a, say, 25 % pretax ROI can be obtained. If this is coupled with overall depreciation estimated at 10 % (10-year straight-line), the corresponding simple payout time is about 3 years. Very large, expensive projects may be justified with longer payout times of about 5 or even 7 or more years.

Higher pretax ROIs and shorter payout times are usually required for revamps or retrofits. Typical 1–2 years maximum payout times are often required for revamp projects, again depending on their relative magnitude.

Other Parameters

Other common reporting parameters are:

- Discounted cash flow (DCF) rate of return (internal rate of return)
- Required sales price for a given DCF rate of return
- Cash flow payout time

These parameters are associated with the use of discounting over a time series of cash flows.

Cash Flow Analysis

The previous section examined the economic summary prepared at one particular point in time, usually a "typical" production year. In this section, we examine the economic analysis extended over an extended period of operation, usually 10 or 20 years.

The basis for the analysis is identical to what has been said before, so there is no need to repeat it here. All that needs to be discussed is the discounting effect over time.

A *cash flow analysis* is a *net present value analysis*. If we assume an initial outflow or investment at time zero, the total of the net present values of all future cash flows must exceed the initial investment for the project to be attractive.

Obviously, the result will be highly dependent on the rate of discounting used to bring future cash flows to time zero. What rate of discounting should be used? We should use a rate of discounting equivalent to the money market rate, namely, the rate of return that we would obtain if we were to grant a loan to others. On this basis, then, the appropriate rate of discounting is equivalent to the long-term interest rate that we would be charged for any debt incurred in connection with the construction of the plant. The rate of discounting should be increased above this value if we feel that the project involves risks such as market potential, future obsolescence of the project, etc.

If, when we use this rate of discounting, the net present value of all future cash flows exceeds the net present value of all investments (initial and future, if any), the project is regarded as profitable relative to a passive interest-generating activity. If the net present value of all future cash flows is less than the net present value of the investments, the project is relatively less attractive than a passive interest-generating activity.

One may ask, if a project is attractive at a certain rate of discounting, what would be the rate of discounting that renders the project unattractive? The break-even rate of return at which the summation of the net present values of all future cash flows (inflows) just equals the net present value of the outflows (investments, etc.) is the so-called internal rate of return (IRR). If, therefore, the IRR exceeds the discounting rate, the project may be regarded as profitable and economically attractive. If it does not, the project is not attractive or less attractive. The IRR has no real meaning of its own; it must always be viewed relative to the appropriate discount rate.

The IRR is also called the discounted cash flow rate of return or DCF rate of return or DCFRR. Everything else being the same, one can raise or lower the IRR by adjusting the sale price of the product and, therefore, the projected revenue. If we then fix the desired IRR, we can calculate the necessary sale price. The desired IRR should eventually be higher than the discounting rate as explained above.

There is a further complexity. Sometimes, one wishes to examine the overall return over an extended period – say, 10 or 20 years. Whether we consider an active activity (i.e., a plant investment) or a passive activity (i.e., a loan to others), the capital is always returned in discrete parcels over this period. What becomes of this capital once it is returned? Logically, one can expect that it will be reinvested, but at what rate? Treatments found in the literature often assume that the capital that is returned can be reinvested at the same rate of return as the original project. This tends to be unrealistic, principally for highly profitable projects; a more conservative approach is to assume that the capital that is returned can be reinvested at a then prevailing rate (constant or varied, depending on the desired complexity) so as to generate a fund at the end of the economic analysis timeframe. This fund can then be discounted to time zero to add to the overall cash flow. Depending on the choice of rates and discount rates, this adjustment can have a positive or negative effect on the overall analysis.

It is often customary to assume a gradual sales buildup, for example, 60 % of capacity the first year, 80 % the second year, and 100 % the third year and thereafter. A simple computer program can easily keep track of this and any other assumptions. For the sake of simplicity, however, we normally assume a uniform production capacity over the entire period of 10 or 20 years.

Tax accounting, whenever desired, should be done on an extended discounted cash flow basis. In this format, it is easier to keep track of such terms as financial depreciation, tax depreciation, tax liability, taxes paid, carryover losses, investment tax credits, etc., so as to be able to determine the actual cash flow every year. Even if done on a constant-dollar basis, the annual cash flows can be expected to vary from year to year. A discounted cash flow analysis can easily keep track of such variations. Again, for simplicity, the concept can be explained equally well if we assume a uniform stream of cash flows.

It is helpful to visualize expenses and cash flows as a series of arrows: positive arrows for positive cash flows (net inflows) and negative arrows for outflows such as capital investment and negative cash flows. We start with a fully capitalized investment figure at time zero, the start of production.

Let n be the total number of periods. For simplicity, let us assume that n are years and that we consider either 10 or 20 years.

Let I represent the initial investment at time zero and CF the annual cash flow that is assumed uniform on a constant-dollar basis (i.e., no inflation).

The internal rate of return (IRR) is that at which the cash flows over n years just pay back the invested capital or, equivalently, when the capital equals the stream of net present values:

$$I = \frac{\mathrm{CF}}{1+r} + \frac{\mathrm{CF}}{(1+r)^2} + \cdots + \frac{\mathrm{CF}}{(1+r)^n} \tag{4}$$

Then, by using the summation formula (Appendix 9), we can write

$$I = \mathrm{CF}\frac{(1+r)^n - 1}{r(1+r)^n} \quad \text{or} \quad \mathrm{CF} = I\frac{r(1+r)^n}{(1+r)^n - 1} \tag{5}$$

Internal Rate of Return

In the formulas above, given I, n, and CF, find r. The calculated rate of return, r, is the "internal rate of return" of the project over a period of n years. Note that it varies with the number of years and it increases with the number of years. Thus, the IRR calculated for 20 years will be slightly higher than the IRR calculated for 10 years.

Computers use an iterative built-in function to calculate the IRR, often in the form

$$\text{@irr}(0.15,\ -I,\ \mathrm{CF}_1,\ \mathrm{CF}_2,\ \mathrm{CF}_3,\ \ldots,\ \mathrm{CF}_\mathrm{n})$$

where "0.15" is an initial guess that should be modified if the function does not converge in some 20 iterations. –I is the initial investment expressed as a negative number and CFs are the values of the annual cash flows.

Some software packages require that the cash flow numbers be entered in a separate array of cells; others allow for direct input.

The summation formula (b) derived above only applies if the annual cash flows are uniform. The net present value summation (a) applies however even if the CFs vary from year to year. The @irr function also accepts variable annual CFs.

Discounted Payback Time

Given I, r, and CF, find n. This calculated n is a discounted payback time. The simple payback time (I/CF) is equivalent to a discounted payback time when $r = 0$ (i.e., with no discounting). Likewise, if we calculate IRR for, say, $n = 20$ and then we set $r =$ IRR, we will just back-calculate $n = 20$. Therefore, for $0 < r <$ IRR, the calculated payback time will be (I/CF) $< n <$20. Likewise, if $r >$ IRR, then $n >$20.

If the cash flows, CF, are uniform, we can solve for n as follows:

$$n = \frac{l\mathrm{n}\left[\frac{\mathrm{CF}}{\mathrm{CF} - Ir}\right]}{\ln(1 + r)}. \tag{6}$$

Sales Price Required to Obtain a Given Discounted Cash Flow Rate or Return

Given I, n, and a desired rate of return, r, we can calculate the required cash flow, CF, according to formula (b). This cash flow can be used in the economic analysis to calculate the product sales price that will be necessary to generate this cash flow. If this cash flow is obtained, then we have the desired discounted cash flow rate of return, r.

This calculated sales price is a function of both r and n.

For the calculation of the cash flow, CF, the appropriate computer function, if available, is

$$@\mathrm{pmt}(I,\ r,\ n)$$

where r must be used in the decimal form for the corresponding period.

Appendix 1: Refinery Plant Inadequacies Report: Example Work Sheet

See Fig. 12.

Appendix 2: Example of a Crude Oil Inventory Schedule

See Fig. 13.

Appendix 3: Example of a Product Inventory and Schedule

See Fig. 14.

Appendix 4: An Outline Operating Schedule

See Fig. 15.

CASE 6

40 MB/SD (39 MB/CD) ON S. WNES : 34 MB/SD (33 MB/CD) on KENT.

NORMAL DEPRECIATION Debits/(Credits)

	1967	1969	1969	1970	1971	1972	1973	1974
Crude Run MB/CD	–	35	39	72	–	–	–	–
Imports MB/CD	–	–	13	6	–	–	–	–
Investments $M								
Onsite	3,456	–	2,943	–	–	–	–	–
Offsite & Utilities	1,285	–	–	–	–	–	–	–
Expense	62	–	221	–	–	–	–	–
Inventory	907	–	188	–	–	–	–	–
Tankage	–	–	332	–	–	–	–	–
Jetty Debit	874	–	–	395	–	–	–	–
Utilities	–	–	–	128	–	–	–	–
Services, etc.	–	–	–	594	–	–	–	–
Total Net Costs (Cumulative)	6,584	6,584	10,268	11,385	–	–	–	–
Operating Cost								
Utilities Costs	–	654	729	1,504	–	–	–	–
Ship Waiting Time	–	(266)	(106)	(394)	–	–	–	–
MElfordMarine Credit	–	(132)	(52)	(291)	–	–	–	–
Maintenance, etc.	–	361	361	958	–	–	–	–
Sub-Total	–	617	932	1,777	–	–	–	–
Net Feedstock Costs	–	906	767	1,162	–	–	–	–
Gross Annual Costs	–	1,523	1,414	2,939	–	–	–	–
Tax Relief	–	(253)	(1,161)	(1,349)	(2,180)	(1,946)	(1,858)	(136)
Net Cash Outgoings	6,584	1,270	3,937	2,707	(2,180)	(1,946)	(1,858)	(136)
10% Discounted Cash Outgoings	5,991	1,054	2,953	1,841	(1,352)	(1,090)	(948)	(64)

Total Outgoings Discounted at 10% = $ M8,385

CASE 6A

SPECIAL DEPRECIATION RATES AT S.WALES.

	1967	1968	1969	1970	1971	1972	1973	1974
Net Cash Outgoings	6,584	1,270	3,937	559	(2,019)	(1,648)	(1,684)	(124)
10% Discounted Cash Outgoings	5,991	1,054	2,953	380	(1,252)	(923)	(859)	(58)

Total Outgoings Discounted at 10% = $M7, 286

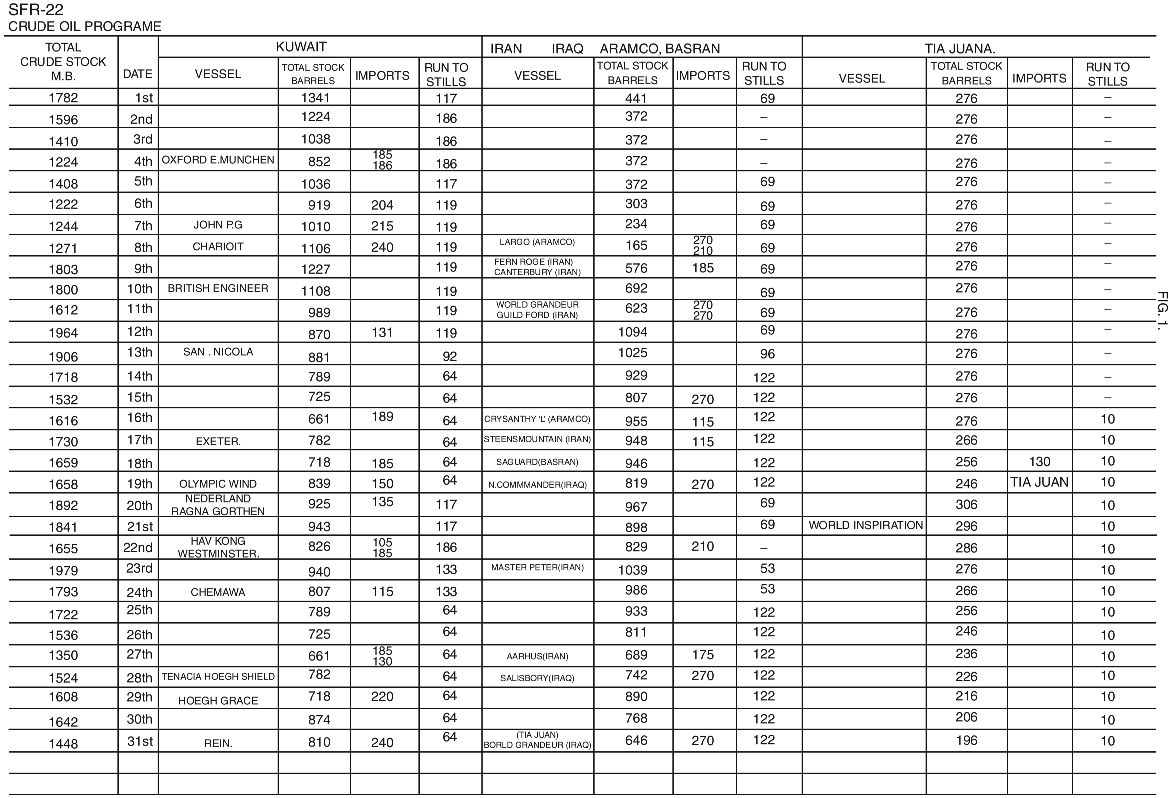
Fig. 12 Refinery Plant Inadequacies Report: Example Work Sheet

Appendix 5: A Typical Detailed Operating Program and Schedule

See Fig. 16.

Appendix 6: A Typical Weekly Program

See Fig. 17.



SFR-22
CRUDE OIL PROGRAME

TOTAL CRUDE STOCK M.B.	DATE	KUWAIT				IRAN IRAQ ARAMCO, BASRAN				TIA JUANA.			
		VESSEL	TOTAL STOCK BARRELS	IMPORTS	RUN TO STILLS	VESSEL	TOTAL STOCK BARRELS	IMPORTS	RUN TO STILLS	VESSEL	TOTAL STOCK BARRELS	IMPORTS	RUN TO STILLS
1782	1st		1341		117		441		69		276		–
1596	2nd		1224		186		372		–		276		–
1410	3rd		1038		186		372		–		276		–
1224	4th	OXFORD E.MUNCHEN	852	185 186	186		372		–		276		–
1408	5th		1036		117		372		69		276		–
1222	6th		919	204	119		303		69		276		–
1244	7th	JOHN P.G	1010	215	119		234		69		276		–
1271	8th	CHARIOIT	1106	240	119	LARGO (ARAMCO)	165	270 210	69		276		–
1803	9th		1227		119	FERN ROGE (IRAN) CANTERBURY (IRAN)	576	185	69		276		–
1800	10th	BRITISH ENGINEER	1108		119		692		69		276		–
1612	11th		989		119	WORLD GRANDEUR GUILD FORD (IRAN)	623	270 270	69		276		–
1964	12th		870	131	119		1094		69		276		–
1906	13th	SAN . NICOLA	881		92		1025		96		276		–
1718	14th		789		64		929		122		276		–
1532	15th		725		64		807	270	122		276		–
1616	16th		661	189	64	CRYSANTHY 'L' (ARAMCO)	955	115	122		276		10
1730	17th	EXETER.	782		64	STEENSMOUNTAIN (IRAN)	948	115	122		266		10
1659	18th		718	185	64	SAGUARD(BASRAN)	946		122		256	130	10
1658	19th	OLYMPIC WIND	839	150	64	N.COMMMANDER(IRAQ)	819	270	122		246	TIA JUAN	10
1892	20th	NEDERLAND RAGNA GORTHEN	925	135	117		967		69		306		10
1841	21st		943		117		898		69	WORLD INSPIRATION	296		10
1655	22nd	HAV KONG WESTMINSTER.	826	105 185	186		829	210	–		286		10
1979	23rd		940		133	MASTER PETER(IRAN)	1039		53		276		10
1793	24th	CHEMAWA	807	115	133		986		53		266		10
1722	25th		789		64		933		122		256		10
1536	26th		725		64		811		122		246		10
1350	27th		661	185 130	64	AARHUS(IRAN)	689	175	122		236		10
1524	28th	TENACIA HOEGH SHIELD	782		64	SALISBORY(IRAQ)	742	270	122		226		10
1608	29th	HOEGH GRACE	718	220	64		890		122		216		10
1642	30th		874		64		768		122		206		10
1448	31st	REIN.	810	240	64	(TIA JUAN) BORLD GRANDEUR (IRAQ)	646	270	122		196		10

FIG. 1.

Fig. 13 Example of a Crude Oil Inventory Schedule

INTERMEDIATE STOCK SHEET Distribution

Refinery Month of

	TANKS 335/336	WHITE SPIRIT.		MAX. 26.5 MR'S MIN. 1.5 •		TANKS 450/457	KEROSENE		MAX. 82 MR'S MIN. 4 •		TANK 353	T/JET 2486		MAX. 58 MR'S MIN. 5 •		TANK 332	T/JET 2482		MAX. 16 MR'S MIN. 1 •
DAY OF MONTH	PRODN.	RUN	DIFF.	EST. STOCKS	ACT. STOCKS	PRODN.	RUN	DIFF	EST. STOCKS	ACT. STOCKS	PRODN.	RUN	DIFF	EST. STOCK	ACT. STOCK	PRODN.	RUN	DIFF.	EST STOCK
1	2.9	2.0	+0.9	9.2		15.1	12	+ 3.1	46.0										
2	2.9	2.0	+0.9	10.1		15.1	12	+ 3.1	49.1										
3	2.9	2.0	+0.9	11.1		15.1	12	+ 3.1	52.2										
4	2.9	2.0	+0.9	11.9		15.1	12	+ 3.1	55.3										
5	2.9	2.0	+0.9	12.8		15.1	13	+ 2.1	57.4										
6	2.9	2.0	+0.9	13.7		15.1	13	+ 2.1	59.5							6.3	–	+6.3	6.9
7	2.9	2.0	+0.9	14.6		7.5	13	+ 2.1	61.6							6.3	–	+6.3	13.2
8	2.9	2.0	+0.9	15.5		–	13	– 6.5	55.1							6.3	–	+6.3	19.5
9	2.9	2.0	+0.9	16.4		–	13	– 13.0	42.1							6.3	8	–1.7	17.8
10	2.9	2.0	+0.9	17.3		–	13	– 13.0	19.1							6.3	8	–1.7	16.1
11	2.9	2.0	+0.9	18.2		15.1	13	– 13.0	6.1							6.3	8	–1.7	14.4
12	2.9	2.0	+0.9	19.1		15.1	13	+ 2.1	8.2							6.3	8	–1.7	12.7
13	–	2.0	+0.9	20.0		15.1	13	+ 2.1	10.3							4.0	8	–4	8.7
14	–	2.0	+2.0	18.0		15.3	13	+ 2.1	12.4								7	–7	1.7
15	–	2.0	–2.0	16.0		15.5	12	+ 2.3	14.7										
16	–	2.0	–2.0	14.0		15.5	12	+ 3.5	18.2										
17	–	2.0	–2.0	12.0		15.5	12	+ 3.5	21.7					31.0					
18	–	2.0	–2.0	10.0		15.1	12	+ 3.5	25.2		9.6	8	–8	23.0					
19						15.1	12	+ 3.1	28.5		9.6	8	+1.6	24.0					
20						15.1	13	+ 3.1	31.4		9.6	8	+1.6	26.2					
21						–	13	+ 3.1	34.5		9.6	8	+1.6	27.8					
22						–	13	– 13.0	21.5		9.6	8	+1.6	28.4					
23						15.1	13	– 13.0	8.5		9.6	8	+1.6	30.0					
24						15.1	12	+ 2.1	10.6		9.6	8	+1.6	31.6					
25						15.1	12	+ 3.1	13.7		9.6	8	+1.6	33.2					
26						15.3	12	+ 3.1	16.8		–	8	+1.6	34.8					
27						15.5	12	+ 3.3	20.1		–	8	–8	26.8					
28						15.5	12	+ 3.5	23.5										
29						15.5	12	+ 3.5	27.0										
30						15.1	12	+ 3.5	30.5										
31						15.1	12	+ 3.1	33.6										
TOTALS																			

Fig. 14 Example of a Product Inventory and Schedule

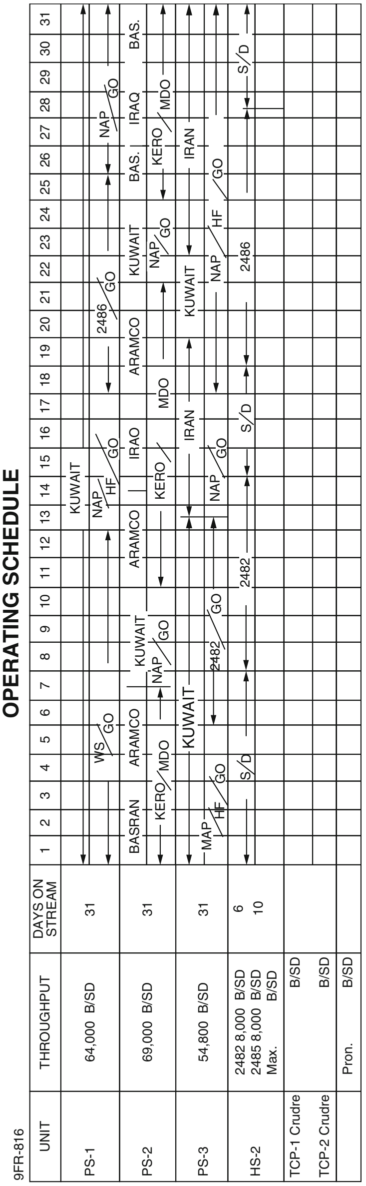
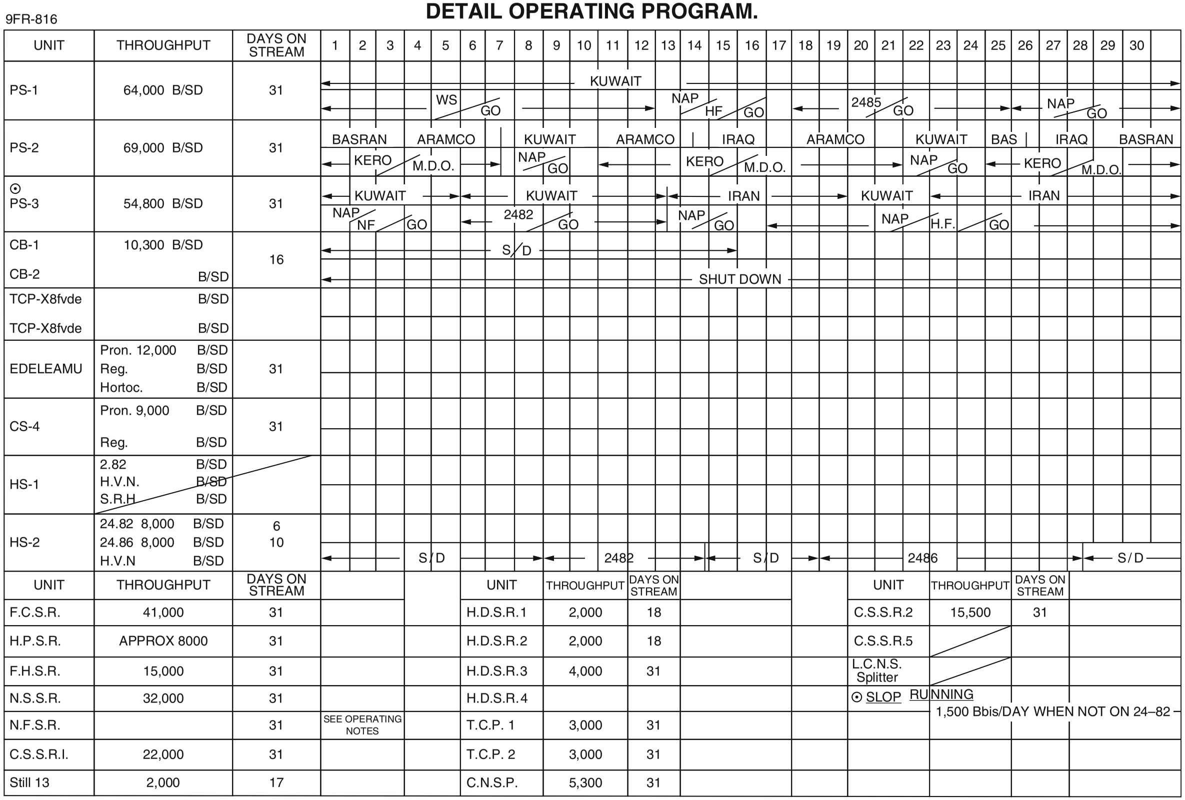


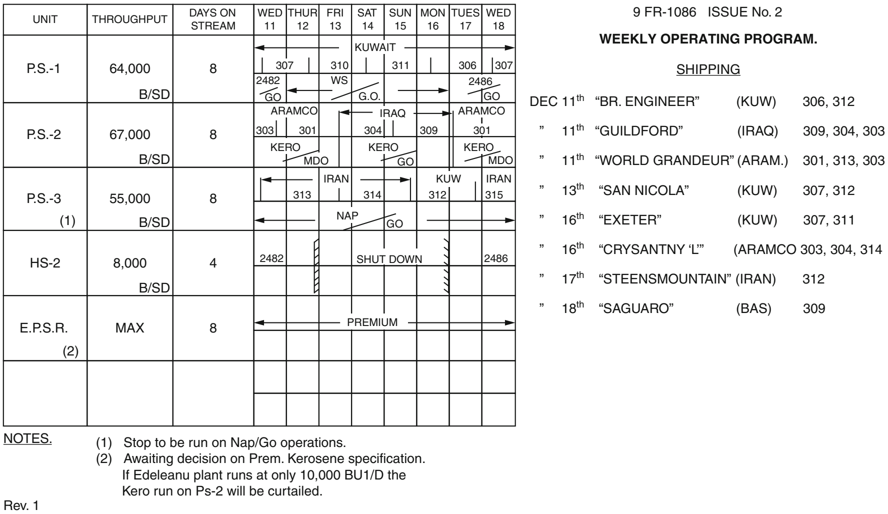
Fig. 15 An Outline Operating Schedule



UNIT	THROUGHPUT	DAYS ON STREAM
PS-1	64,000 B/SD	31
PS-2	69,000 B/SD	31
⊙ PS-3	54,800 B/SD	31
CB-1	10,300 B/SD	16
CB-2	B/SD	
TCP-X8fvde	B/SD	
TCP-X8fvde	B/SD	
EDELEAMU	Pron. 12,000 B/SD Reg. B/SD Hortoc. B/SD	31
CS-4	Pron. 9,000 B/SD Reg. B/SD	31
HS-1	2.82 B/SD H.V.N. B/SD S.R.H B/SD	
HS-2	24.82 8,000 B/SD 24.86 8,000 B/SD H.V.N B/SD	6 10

UNIT	THROUGHPUT	DAYS ON STREAM		UNIT	THROUGHPUT	DAYS ON STREAM	UNIT	THROUGHPUT	DAYS ON STREAM
F.C.S.R.	41,000	31		H.D.S.R.1	2,000	18	C.S.S.R.2	15,500	31
H.P.S.R.	APPROX 8000	31		H.D.S.R.2	2,000	18	C.S.S.R.5		
F.H.S.R.	15,000	31		H.D.S.R.3	4,000	31	L.C.N.S. Splitter		
N.S.S.R.	32,000	31		H.D.S.R.4			⊙ SLOP	RUNNING	
N.F.S.R.		31	SEE OPERATING NOTES	T.C.P. 1	3,000	31		1,500 Bbis/DAY WHEN NOT ON 24–82	
C.S.S.R.I.	22,000	31		T.C.P. 2	3,000	31			
Still 13	2,000	17		C.N.S.P.	5,300	31			

Fig. 16 A Typical Detailed Operating Program and Schedule



UNIT	THROUGHPUT	DAYS ON STREAM
P.S.-1	64,000 B/SD	8
P.S.-2	67,000 B/SD	8
P.S.-3 (1)	55,000 B/SD	8
HS-2	8,000 B/SD	4
E.P.S.R. (2)	MAX	8

NOTES.
(1) Stop to be run on Nap/Go operations.
(2) Awaiting decision on Prem. Kerosene specification. If Edeleanu plant runs at only 10,000 BU1/D the Kero run on Ps-2 will be curtailed.

Rev. 1

9 FR-1086 ISSUE No. 2

WEEKLY OPERATING PROGRAM.

SHIPPING

DEC 11th	"BR. ENGINEER"	(KUW)	306, 312
" 11th	"GUILDFORD"	(IRAQ)	309, 304, 303
" 11th	"WORLD GRANDEUR"	(ARAM.)	301, 313, 303
" 13th	"SAN NICOLA"	(KUW)	307, 312
" 16th	"EXETER"	(KUW)	307, 311
" 16th	"CRYSANTNY 'L'"	(ARAMCO	303, 304, 314
" 17th	"STEENSMOUNTAIN"	(IRAN)	312
" 18th	"SAGUARO"	(BAS)	309

Fig. 17 A Typical Weekly Program

Appendix 7: Typical Factors Used in Capacity Factored Estimates

Type of plant	Factor (b)
Atmospheric and vacuum distillation	0.6
Catalytic reforming	0.6
Fluid cat cracking	0.7
Naphtha splitter	0.7
Thermal cracker	0.7
Delayed coking	0.6
Fluid coking	0.65
Gas compression – recip	0.9
Gas compression – centrif	0.75
Hydrogen plant	0.55
Sulfur production	0.55
Steam generation	0.55
Utilities (general)	0.55

All other type of plants including tankage and offsites generally may be taken as 0.6

Appendix 8: Background for Economic Calculations

The following summary provides the background necessary for most economic calculations and should be used for reference as needed.

First of all, let us consider the following terms:

P present value of a sum of money or a series of sums
F future value of a sum of money or a series of sums
C capital (investment or loan) at one given time
A sum of money every compounding period
n number of compounding periods
i annual rate of interest
r rate of interest per compounding period
L salvage value

The rate of interest *per compounding period* (r) should be used in all cases.

The interest rate stated legally is the nominal annual rate i). If the compounding period is less than 1 year, the rate of interest per compounding period is obtained by dividing the nominal annual rate, i, by the number of compounding periods in a year. It is done this way by law.

A commercial year is understood to consist of 360 days. Likewise, a generic commercial month consists of 30 days. Thus, if the compounding is done daily, the annual rate of interest, i, will have to be divided by 360; if monthly, the annual rate will be divided by 12, irrespective of the month. Note, however, that the amount compounded over a period of time will be calculated on the basis of the actual days. Thus, 28 days for a normal February, 31 days for May, 365 days for a normal year, or 366 days for a leap year.

Future Value

$$F_n = P(1 + r)^n \tag{7}$$

F_n, or simply F, represents the value *at the end* of the nth period of a sum of money, P, at time zero (e.g., present time).

The factor, $(1 + r)^n$, is sometimes called the (F/P) factor or the "compound amount factor for a single sum," (CAFS). Thus,

$$F = P(F/P)_n^r \tag{8}$$

Or

$$F = P(\mathrm{CAFS})_n^r \tag{9}$$

Present Value

The present value, P, of a future sum of money, F_n, represents the reciprocal of the future value calculation.

$$P = F_n \frac{1}{(1+r)^n} \tag{10}$$

The reciprocal factor is also called the (P/F) factor or the “present worth factor for a single sum” (PWFS). Thus,

$$P = F(P/F)_n^r \tag{11}$$

Or

$$P = F(\mathrm{PWFS})_n^r \tag{12}$$

In all these formulas, the compounding becomes effective *at the end of the period.* This is true in all the expressions used in economic calculations; modified formulas are needed if the compounding becomes effective at the beginning of the period, but this is seldom, if ever, the case. The formula modification, if needed, involves a $(1 + r)$ factor.

Future Value of a Uniform Series of Payments (Made at the End of Each Period)

See Appendices 9 and 10 for justification.

If the amount paid at the end of each period is A, the future value, F_n, of the sum is given by

$$F_n = A\frac{(1+r)^n - 1}{r} \tag{13}$$

The multiplier is also known as the (F/A) factor or the “compound amount factor for a uniform series” (CAFUS).

$$F = A(F/A)_n^r \tag{14}$$

Or

$$F = A(\mathrm{CAFUS})_n^r \tag{15}$$

Sinking Funds

A sinking fund consists of a series of payments made for the purpose of accumulating a given amount of money, F, at some future time. As usual, we assume a uniform series of payments, A being the amount paid at the end of each period. The calculation assumes that the rate of interest does not change over time; trial and error would be required otherwise.

In order to accumulate an amount F_n at the end of n periods, the amount A to be deposited at the end of each period is

$$A = F_n \frac{r}{(1+r)^n - 1} \tag{16}$$

This is the reciprocal of the future value of a series of uniform payments.

The multiplier is at times called the (*A*/*F*) factor or the "sinking fund factor" (SFF). Thus,

$$A = F(A/F)_n^r \tag{17}$$

Or

$$A = F(\mathrm{SFF})_n^r \tag{18}$$

As used in economic estimates, depreciation and amortization are essentially sinking funds at zero rate of interest. Again, to repeat, no item should ever be treated both as a sinking fund amortization and as an expense at the same time.

Loan Repayments

The loan repayment calculation, or "mortgage formula," is one of the most useful expressions in economic calculations. It is a combination of the previous cases. It represents the series of uniform payments, A, to be made *at the end of each period* to repay a loan, P, taken out at time zero. In this situation, the present value, P, often is just denoted by "capital" C.

The derivation of the formula is given in Appendices 9 and 10.

$$A = P \frac{r(1+r)^n}{(1+r)^n - 1} \tag{19}$$

The multiplier is also variously known as the (*A*/*P*) factor or the "capital recovery factor" (CRF).

$$A = P(A/P)_n^r \tag{20}$$

Or

$$A = P(\mathrm{CRF})_n^r \tag{21}$$

It ought to be very clear what these formulas mean: A, the uniform series of payments, represents a constant amount paid to the lender at the end of each compound period. This quantity, A, is made up of two variable parts: a capital return part and an interest payment part. The capital return part represents a very small fraction at the beginning of the loan repayment period, but it increases slowly (and nonlinearly) until it becomes the dominant term toward the end. Conversely, the interest payment term is proportionately very large at the beginning of the loan repayment period and decreases progressively until it becomes small at the end.

This formula is predicated on the idea of making uniform payments, as is often done with mortgages, hence the name. Naturally, there are many other ways of repaying loans, and expressions could be derived for other situations too, if desired.

An offshoot of the mortgage formula is the concept of an "average rate of interest," sometimes used in economic calculations to reflect the average cost of long-term debt. See Appendix 11 for this concept.

Present Value of a Uniform Series

Logically, this represents the reciprocal of the loan repayment schedule.

$$P = A\frac{(1+r)^n - 1}{r(1+r)^n} \tag{22}$$

The multiplier is also called the (*P*/*A*) factor or the "present worth factor for a uniform series," (PWFUS).

$$P = A(P/A)_n^r \tag{23}$$

Or

$$P = A(\mathrm{PWFUS})_n^r \tag{24}$$

The above expressions represent most of the situations encountered in economic evaluations. There are other expressions available for other situations (e.g., when the series of payments increases or decreases progressively at a uniform rate – the "gradient" method), but these are far rarer and need not be discussed here.

Appendix 9: Progressions in Economic Analyses

Though trivial, the concept of arithmetic and geometric progressions is useful in economic calculations. These concepts are outlined as a refresher.

Arithmetic Progressions

An arithmetic progression (or an arithmetic series) is a series of terms such that each is made up of the previous term plus an additive (positive or negative) constant.

The following series is an arithmetic progression:

Term:	1	2	3	4	...	n
Value:	a	$a + q$	$a + 2q$	a $+3q$	...	$a + (n - 1)q$

where a is the first term and q is the constant addendum.

As seen, the nth term of an arithmetic progression is given by

$$b = a + (n - 1)q \tag{25}$$

The sum of the first n terms of an arithmetic progression is

$$S = \frac{(a + b)n}{2} \tag{26}$$

For example, if we wish to add, say, the first 100 numbers – 1–100 – we can observe that 1 + 100 = 101, 2 + 99 = 101, and so on to 50 + 51 = 101. Since there are 50 such pairs, the answer is immediate, 5,050.

Geometric Progressions

Geometric progressions (or geometric series) are of more interest for economic calculations.

A geometric progression is a series of terms such that each term is the previous one multiplied by a constant factor.

Term	1	2	3	4	...	n
Value	a	aq	aq^2	aq^3	...	$aq^{(n-1)}$

Therefore, the nth term of a geometric progression is given by

$$b = aq^{(n-1)} \tag{27}$$

More importantly, the sum of the first n terms is

$$S = \frac{bq - a}{q - 1} \tag{28}$$

Or

$$S = \frac{aq^n - a}{q - 1} = a\frac{q^n - 1}{q - 1} \tag{29}$$

Often $q < 1$. In this case, both the numerator and the denominator will be negative, and for comfort, we can write

$$S = a\frac{1 - q^n}{1 - q} \tag{30}$$

These expressions are the basis for the mortgage formula and many other economic calculations.

Appendix 10: Loan Repayments (Mortgage Formula)

Let us assume that we have borrowed a certain amount of money, C, that we plan to return over a total of n periods such that at the end of each period, we repay the same amount, A. We further assume that the rate of interest remains constant and is r for each period.

Time Zero

Take the loan out. We owe C.

End of the First Period

We owe $C(1 + r)$. We repay an amount A. Therefore, we now owe $C(1 + r) – \mathrm{A}$.

End of the Second Period

We owe $[C(1 + r) - A](1 + r) = C(1 + r)^2 - A(1 + r)$. Again we repay an amount A. Therefore, we now owe $C(1 + r)^2 - A(1 + \mathrm{r}) - A$.

End of the Third Period

After repaying the amount A, we owe $\left[C(1 + r)^2 - A(1 + r) - A\right](1 + r) - A$, or $C(1 + r)^3 - A\left[(1 + r)^2 + (1 + r) + 1\right]$.

Keep repeating the reasoning for all other intermediate periods.

End of the *n*th Period

After making the last payment, A, we owe $C(1 + r)^n - A\left[(1 + r)^{(n-1)} + (1 + r)^{(n-2)} + \cdots + (1 + r) + 1\right]$. But since we are repaying the loan in n periods, at this time the balance must be zero!

By applying the summation formulas in Appendix 11, we can rewrite this as

$$C(1+r)^n - A\frac{(1+r)^n - 1}{(1+r) - 1} = 0 \tag{31}$$

Or

$$C(1+r)^n = A\frac{(1+r)^n - 1}{r} \tag{32}$$

Or, solving for A

$$A = C\frac{r(1+r)^n}{(1+r)^n - 1} \tag{33}$$

which is the "mortgage" formula.

Appendix 11: Average Rate of Interest

The "average rate of interest" is a concept that arises when a loan is repaid over a number of time periods, but we wish to conduct a preliminary economic analysis over one of the time periods only. We saw in Appendix 10 that if a uniform series of payments is used, the actual amounts paid as interest vary from a high at the beginning to relatively small amounts toward the end. The question then is: what is the "average" amount of interest paid over a typical period? This value is normally calculated by adding up all the interest payments and simply prorating them by dividing the sum over the total number of periods. Calculation of this value has interest in cases when the capital may be strongly leveraged (i.e., a high percentage of debt) since, obviously, the *average* interest paid will be less than the interest paid over the first period on the basis of the total amount of debt outstanding.

How much interest is paid over the life of the loan? Since we have borrowed a capital C and we have made a total of n payments of A dollars each, the difference between the amount paid and the capital borrowed must be the amount paid as interest.

$$\text{Total interest paid} = nA - C \tag{34}$$

Therefore, the average amount paid out as interest every compounding period is

$$\text{Average interest payment} = A - \frac{C}{n} \tag{35}$$

Or, on a percentage basis relative to C, we obtain

$$\text{Average rate of interest} = \frac{A}{C} - \frac{1}{n} \tag{36}$$

This rate is per compounding period; it should be annualized by multiplying it by the number of compounding periods in 1 year.

What is the effect of using interest averaging? Just to give an example, a 10-year loan at 10 % compounded annually ($A = 0.1627454$, if $C = 1$) represents an average annual interest of only 6.27 %.

Appendix 12: An Example of an Exercise Using Linear Programming

From: Linear programming aids decisions on refinery configurations, D. S. J. Jones (Fluor (England) Ltd.) and J. N. Fisher (Bonner & Moore Associates, Inc., Houston, Texas)

Mathematical modeling using linear programming can solve many problems associated with refinery operation and planning. The technique, compared with the cost of an error of judgment, represents only an insignificant financial outlay.

It is becoming more and more evident that there is a definite economic incentive to studying problems associated with refinery planning by mathematical modeling using linear programming.

Ever-increasing investment costs associated with the tightening of product specifications, changing crude slates, alterations in the energy pattern in marketing countries, and expanding petrochemical requirements all make an error in decision judgment of refinery processing increasingly costly. Wherever this basic risk can be reduced by modern mathematical techniques, the potential saving in capital or investment could make the financial outlay on such a study insignificant.

What follows is a description of a typical refinery simulation study, but this is only one of an increasing number of problems that can be solved by mathematical modeling using linear programming.

Wider impetus. The application of linear programming techniques using computers has long been used in the oil refining industry for the development of planning and operating policies. With the introduction of modern high-speed, large-capacity computers, this technique grew considerably within the industry.

Briefly, linear programming is the developing of linear submodels which mathematically describe many of the various operations within the industry, such as refinery processing, crude and product flows, marketing demands, etc. These linear submodels are interrelated to build up a complete mathematical model of the specific operation. By the use of the computer, the equations within the model can be solved to optimize, on a selective basis, the operation under study.

The growth of mathematical models using this technique provides management with a means of making an increasing number of decisions which do have a calculable basis. Thus, in many cases, the need for decisions based only on individual experience or “feel,” with its obvious inherent dangers, is being eliminated.

One such study illustrates a relatively simple refinery problem application of mathematical modeling and linear programming techniques.

Definition of Problem

A client wished to build a new refinery. It had already executed a marketing survey in the area and could specify quantity and quality, together with prices, of the products which would meet its market requirements. Its management now had to decide the economic optimum refinery configuration that would satisfy its crude and product slate. At this stage, only one type of crude was intended for the refinery, and to some extent, this simplified the problem. However, to satisfy other considerations, management required the solutions to the following premises:

- The refinery configurations, which would satisfy a minimum investment, when producing a high volume of gasoline with and without a low sulfur content limitation of the fuel oil. All other products were to meet quality and quantity requirements.
- The refinery configurations which would give the maximum return on investment to satisfy a fixed crude throughput with no quantity restriction on the product slate and then to satisfy a limited restriction on the product slate with no limit to the crude throughput.

Such a problem lends itself readily to linear programming, and thus, a refinery simulation model was developed to solve these two premises.

Process Consideration

The first step in constructing the model was to establish as many processing units as could conceivably contribute to the solution of the problem. For instance, with such large requirements of gasoline, there would obviously be required a cracking unit of some kind. Thus, the model included a reformer, fluid cracker, hydrocracker, coker, and visbreaker. Some combination of these processes must satisfy the premises of the problem.

Similarly, the lower sulfur content of the fuel oil would probably require some form of residue treating. Thus, two severity desulfurizers for both short and long residue, respectively, were included together with a process for hydrocracking these residues.

The many process units now included were then defined in terms of feed streams, product yields and quality, and operating costs, all based as a percentage on the feed streams. This part of the study was the first important step which required the expertise of specialists. This data forms the basis for the rational solution to the problem, and therefore, it was necessary to be accurate and to augment prediction and theory with realism and technical experience.

For instance, in arriving at the yields from the crude and vacuum units, the effect of fractionation on the product yield was considered. Realistic ASTM distillation gaps were used that could be met by a commercial distillation unit.

In the fluid catalytic cracking units, a more sophisticated approach was needed to correlate the yields from the many feedstocks which would be independent of thermodynamic considerations. Here, a base case feed yield data (in this case a straight run waxy distillate) at a conversion of 75 % using zeolite catalyst was used.

Yields from all other feedstocks (including those which had been hydrotreated) were related by first principle kinetic and thermodynamic considerations to the base case. A short and simple computer program was used for this purpose, and it was also possible to simulate the effect of changing the quantity of zeolite catalyst by this means. The results of these computerized calculations were checked against existing plant data before being incorporated into the study.

In other processes such as hydrocracking, hydrotreating, visbreaking, etc., care was taken that only proven yield data or correlations were used.

Catalytic reforming yield data was obtained from a correlation which related yield to severity for a basic naphthene and aromatic content of the feedstock. A whole range of severity operations from 95 to 105 O.N. (Research) clear was encompassed in the study. Spot checks of the predicted yield by this method against actual yield from an operating unit showed that the method was viable and acceptably accurate.

Basic Economic Data

Having developed the physical yield structure of the "model," the next step was to complete the basic data by providing investment and maintenance costs.

There is, of course, a considerable wealth of plant cost data available to a contractor from the projects he has completed over the years. However, there is always the need to analyze these costs and to review them in terms of up-to-date material and labor cost changes.

For this study, a large amount of cost data was statistically analyzed for each type of plant. From this analysis, a base cost and an empirical exponential factor was developed in order to relate a total investment cost to capacity in as realistic way as possible. This relationship can be expressed mathematically in a nonlinear form.

$$\mathrm{C} = \mathrm{C_o}(\mathrm{T}/\mathrm{T_o})^{\mathrm{k}} \tag{38}$$

where

C = Investment cost
$\mathrm{C_o}$ = Base cost at a base throughput To
T = New throughput
K = An empirical constant

The inclusion of a nonlinear form for investment costs in a linear program required special consideration, and we shall see later how this was utilized.

In the models, many of the units considered were licensed processes, for which a royalty would be paid. A value in terms of a paid-up royalty in dollars per barrel of throughput was included in the investment. Where chemicals and catalysts were used, the first inventory of these was also included as part of investment.

Chemicals and loss of catalyst was considered as an operating cost based on usage as were utilities. Labor, a fixed operating cost, was included with the return on investment. Maintenance cost was fixed as a percentage of the total maintenance cost.

Model Development

At the same time as the process and cost data were being generated, the basic form that the model would finally take was also being developed. This consisted of defining the various optional routes of each stream within the simulated refinery model.

The optional routing of the streams was carefully selected. This selection had to satisfy at least one of two requirements. Firstly, would such a routing actually contribute to satisfying the product slate and the premises of the problem? Secondly, would such a routing be feasible under actual operating conditions?

Just as a refinery is described by the units of which it is comprised, so also was the refinery linear model described. Here, each processing unit was considered a submodel in itself, and these submodels were defined by their process and economic data.

These data were arranged in tabular from which were easily accessed and listed in recognizable terminology. An example of a submodel tabulation as used in this study is shown in Table 23. From this tabulation, a matrix generator, called GAMMA was used to assemble the many submodels into a complete LP matrix. The matrix was solvable by a linear programming system called OMEGA. These tabular input arrays were also used by the solution report writers as we shall see later.

This complete mathematical model of the refinery was displayed by an equation listing of the entire contents of the data. The equations showed the interrelationships of the many variables, including the refinery streams, the blending constraints, the unit to investment ties, etc. These were also in a form which was recognizable to the engineers working on the project.

Having now assembled all the data in a manner usable for linear programming, it was necessary to check it for errors. Various computer techniques had been developed for this purpose, and these, together with a secondary check by the process engineers, substantially eliminated the possibilities of obvious error and invalid data.

However, as an added safeguard, a final checkout was carried out by actually solving a test case. These results were scrutinized to ensure that the output gave a realistic refinery configuration and that all was in balance.

Optimizing and Other Techniques

A major value of linear programming is that once environment is reflected within an LP framework, this environment can be optimized. In this study, optimization could be accomplished either by maximizing profit or minimizing expense. In this specific

Table 23 An extract from a typical LP base data file (table TEF – H2 treat of cracked gas oils)

	KGO coker gas oil	VBO VIS BR gas oil	CYO CAT cycle oil	
Reformer H2 FOEB	0.0244	0.0209	0.0096	XX+H2F
Gas, FOEB	–	–	–	XX+GS1
Propane	–	–	–	XX+C3S
Isobutane	–	–	–	XX+IC4
N-butane	–	–	–	XX+NC4
C5–380 hydro GASL	−0.0916	−0.0550	−0.0527	XX+TNP
Loss or gain	−0.0169	−0.0109	−0.0034	XX+LOS
Desulf coker gas O	−0.9159	–	–	XX+SKO
LT coker gas oil	1.0000	–	–	XX +KGO
LT VIS BR gas oil	–	1.0000	–	XX +VBO
H2 treat LT VIS GO	–	−0.9550	–	XX+SVO
H2 TRTED cycle oil	–	–	−0.9603	XX+SCY
Cycle oil	–	–	1.0000	XX +CYO
Fuel MMBTU/ unit	0.1113	0.1113	0.1113	XX+FUL
Elec KWH/unit	3.0764	3.0764	3.0764	XX +KWH
Steam MLB/unit	0.0029	0.0029	0.0029	XX+STM
Chem royalty catal	0.0023	0.0023	0.0023	XX+CRC
Rept feed collecto	1.0000	1.0000	1.0000	XX+FOR
Report writer aid	1.0000	1.0000	1.0000	UNPACK
Sulfur to recover	−8.8500	−5.1400	−5.9800	XX+SUA
H2 TRT LT go cap	1.0000	1.0000	1.0000	HTXCPE
Gas plant max cap	–	–	–	GPXCAP

case, the former was selected. It should be emphasized that optimization can only be achieved for the environment reflected in the model. Great care was taken therefore to reflect all the meaningful, worthwhile options known to be available.

There are many refinery variables that are of a nonlinear nature. Among these nonlinearities are the effects of blending on motor gasoline, the capital expenditures in relation to size of the units, and many severity effects within the various processes. When these effects could be described on a cost basis by a *CONVEX* curve, they were generally included in the model as linear segments of a curve (see Fig. 18).

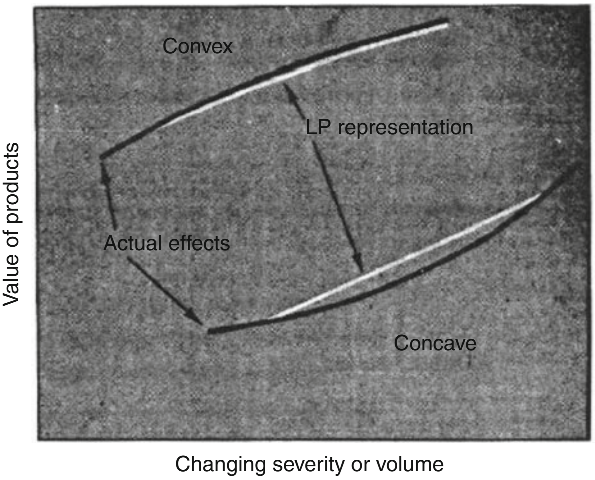


Fig. 18 LP representation of the convex and concave

If the severity to value of product relationship was a concave curve, only one variable could be used to reflect changing severity. This by nature has to be an estimate with a review of the estimate upon solution.

The blend to octane relationship is highly nonlinear and a new approach was used to reflect this in the model. This approach had considerable advantage over the older techniques in that it was relatively easy to understand and use.

It was capable of reflecting the value of octane susceptibility to the individual components available for the blends. It also had the capability to represent accurately more than one type of octane (i.e., research, motor, road, etc.) with these effects also reflected back to the various components.

This technique required the aid of a recursive routine to update various model coefficients that reflected the actual susceptibilities at the solution point. The model then re-optimized with the recalculated octane for various blendstocks and again they were checked. This was repeated until no further change was required.

The nonlinearities of the capital expenditures are concave in nature. Thus, the initial investment cost estimate was updated by means of a recursive routine which calculated the investment cost per unit of activity at the solution level. This recursive routine is described in detail next. Among the various factors that could be considered in investment costs are total investment cost to size relationships, offsites, insurances, taxes (both income and property), overhead, maintenance, labor, royalties, escalation, plant or service factors, depreciation, and the expected economic life of the various facilities.

Solution Approach

In a study of capital expenditure (commonly called facilities planning) such as this, there are many possible mathematical techniques which can be used to obtain a

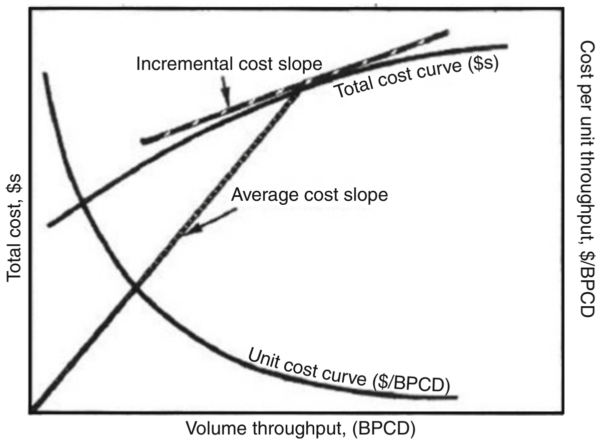


Fig. 19 Cost parameters for any typical refinery unit

solution. Experience has shown, however, that linear programming on a computer is by far the most economic approach to solving this type of problem. By this method, most of the many possible solutions can be examined quickly and effectively. Before discussing the solution approach used in this study, let us quickly review the investment environment for any typical refinery unit. This is illustrated in a simplified form in Fig. 19.

The total cost curve, on linear graph paper, shows that as a volume throughput is increased, the total cost of a unit will increase. However, the plot of unit volume cost ($/BPCD) against throughput shows the reverse; that is, the cost per unit of throughput will decrease as the volume of throughput increases. It is this type of cost that is reflected in an LP model.

Figure 19 also shows a plot of the average cost slope and the incremental cost slope at a given throughput level. This *average cost* slope includes all the costs associated with a particular unit. The slope is linear and must pass through the origin. The *incremental cost* slope reflects the change in cost per unit throughput over a short range. This slope is always tangential to the total cost curve at any throughput under consideration.

It can be seen that the *average cost* gives the model "greater than to be expected" incentive for changing the size of the unit, while the incremental cost curve on the other hand gives the expected incentive. The incremental cost ignores all fixed costs at the solution level and consists mainly of the expected return on investment.

The technique used in this study was to begin the solution by establishing a very nominal cost on all units. This allowed any unit to be chosen in the solution. Once the LP had selected an optimal unit configuration with those nominal costs, a recursive program for investment cost estimating was used to determine *average cost* of the units at the solution throughputs. These average costs were based on a minimum return of investment and an expected economic life calculated on a discounted cash flow basis.

These new calculated costs were then substituted for the original arbitrary cost in the model. This average costing tended to delete the very unrealistically small units that may have been chosen in the unrestricted configuration. Again, the model was optimized with these new costs.

The recursions and solutions were repeated until no further cost, configuration, or size changes were required. All the items described above were carried out in a single computer run, and this solution was saved on tape and reported. Close scrutiny of the results then followed to make sure that they were reasonable and that there was no automatically restricted unit that might have been selected had a different solution path been used.

A second step was then commenced which restored the solution of the first step based on the *average cost* to the computer. The *investment costs* for the configuration were then recalculated using the incremental cost concept. This incremental cost required no return on investment, and an infinite economic life was assumed for the units. The only costs that were recognized in this step were the incremental maintenance for each unit. Therefore, the building costs did not economically suppress the size of units or the total investment. The unit sizes and total investment were optimized on the premised product slate and available raw materials. A similar recursive step was again used, but this time it included only the incremental maintenance cost.

The model contains a variable that carries the sum total of the investment. This variable is updated at the same time as the unit costs are updated by the recursive operations described. Using this total investment variable, it was possible to step down (parameterize) on the total investment, until a feasible solution was no longer possible. An infeasible solution in this context is that in which the cash flow for the configuration becomes less than zero.

As the total investment is reduced, the unit sizes, the product slates, and the raw materials are changed within the framework of the overall premises. Therefore, by this parametric sweep, the refinery configurations (both in size and form) could now be found which would satisfy the following requirements:

- Maximum investment
- Maximum return on investment
- Maximum expected cash flow
- Minimum investment

The results of each parametric step were reported and documented.

Solution Analysis

Besides the specially designed report writing technique already discussed, the LP also has a standard number of solution reports, and these are generally of a more technical nature. Although of great value, they do not readily lend themselves to immediate and apparent interpretation. It is imperative, however, that some members of a team using an LP can read and interpret these outputs, particularly as one major use of these reports is to highlight any obvious errors that may have been

Table 24 An extract of a typical LP BI/DJ output

Status	Label	Cost	BI/DJ	Status	Label	Cost	BI/DJ
BI	FU+VIS	0.000	12.9443	BI	FU/VBR	0.000	0.0000
BI	FU/CYO	0.000	1.4567		GO–DIN	0.000	0.0574
BI	FU/HBA	0.000	0.0000	BI	GO–SPG	0.000	0.0029
	FU/HBB	0.000	0.0591		GO–XXX	−10.000	14.1623
BI	FU/HBE	0.000	0.0000	BI	GO–446	0.000	8.7949
	FU/HBF	0.000	0.0000	BI	GO–675	0.000	12.5429
	FU/HBG	0.000	0.1084	BI	GO+POR	0.000	1.9087
	FU/HBH	0.000	1.3164	BI	GO+SPG	0.000	0.0097
	FU/HBM	0.000	0.6095		GO+SUL	0.000	0.0754

Table 25 An extract of the corresponding LP primal range output

		Limits of range			
		Negative		Positive	
LP label	LP cost	Variable affected	Cost increment	Variable affected	Cost increment
MD/KER	0.000000	MD/HDF	−0.005291	MD+SUL	0.131973
FU/CYO	0.000000	HF/CYO	−0.000000	XX+VBR	0.028074
FU/HBA	0.000000	HF/HBA	−0.000000	GO/HDA	1.293871
FU/HBE	0.000000	HF/HBE	−0.000000	H3FHCE	1.085441
FU/HRB	0.000000	HF+POR	−0.000000	HF+VIS	0.000000
FU/HRE	0.000000	HF/HRE	−0.000000	HVFHBE	0.164348
FU/HRG	0.000000	HF/HRG	–0.000000	GO/HDG	1.243582
FU/HSB	0.000000	HF/HSB	–0.000003	GO/HDB	1.510931
FU/KEX	0.000000	XX+KEX	−2.541661	Slyker	19.910502

overlooked. Some of these reports used in this study were called the BI/DJ and range output. They warrant a brief explanation.

The BI/DJ output (see Table 24) gives the solution level activities (BI) for all the variables that were selected in the optimum solution. For those variables that were not selected, the cost or decrease in profit that would occur were they forcibly included in the configuration (or basis) is given by the DJ value.

The range information is a complementary report to the BI/DJ. The ranges give the incremental volume associated with the DJs and the cost ranges associated with the basis variables. The valuable use of the BI/DJ and the range files can best be expressed by an example, using the extracts shown in Tables 24, 25, and 26.

Table 26 An extract of the corresponding LP dual range output

LP label	Original activity	Limits of range	
		Variable affected	Positive volume increment
FU/HBB	0.000000	FU/HRB	0.000000
FU/HBF	0.000000	HF/HBF	0.000000
FU/HBG	0.000000	CCFHSG	0.000000
FU/HBH	0.000000	TEFCYO	0.109287
FU/HBM	0.000000	FU/CYO	0.549070
FU/HRA	0.000000	FU/VBR	0.000000
FU/HRF	0.000000	FU/VBR	0.000000
FU/HRH	0.000000	FU/VBR	0.000000
FU/HSA	0.000000	CCFHSA	0.000000

Consider the component CYO that has been selected in the configuration. (The code FU/CYO in this case indicates that the refinery stream CYO is routed to fuel.) The quantity of the stream CYO that enters the fuel blend is 1,457 BPCD. Now consider the component "HBM." This has not been selected in the basis, and this stream has a DJ value (i.e., no prefix). To route the "HBM" stream to fuel forcibly would cost \$0.6095/bbl. This information is interesting, but has no real value unless the ranges for their streams are known.

Because the FU/CYO item is selected in the basis, the range data for this is found in the primal range output (Table 26). Interpreting the statement for this stream in this output means that optimum volume levels of the solution would not have changed even if the variable had a very small *negative* incentive (less than \$0.000001). Further, the situation would not have changed even if this variable had a *positive* cost incentive of up to \$0.02807/bbl.

Let us now look at the "HBM" variable. This was not chosen in the basis and it appears in the dual range output (Table 27). Interpreting the data for this item shows that to route "HBM" to fuel would cost 60 cents/bbl for the first 549 BPCD. All that is known thereafter is that the cost per barrel over 549 BPCD would increase.

The example chosen here describes the economic analysis of two optional streams which can be logically routed to a fuel blend. It is emphasized that the BI/DJ and range outputs, however, contain similar information for *all* variables whether process units, refinery streams, product specifications, etc., contained in the model.

Computer Report Writer

The data generated by the computer contains all facts relevant to the solution. However, to all but a few highly trained people, the data in this form would be meaningless and of no practical use. The LP system used in this study contained a specially designed report writer, coded in a language called DART. This converted and assembled the computer LP output into management orientated reports that could easily be read and understood without sacrificing the relevant technical content.

Table 27 Material and economic balance

Product or feed	Price	M B/CD	M $/CD	MM $/year
Premium gasoline	–	–	–	–
Inter. gasoline	–	–	–	–
Regular gasoline	–	–	–	–
Hi. vis. Hvy. fuel	–	–	–	–
Kerosene, regular	–	–	–	–
Propane LPG	–	–	–	–
Marine diesel	–	–	–	–
Sulfur MM LBS	(Actual data has been deleted)			
Shortage and fuel	–	–	–	–
Total production	–	–	–	–
Crude	–	–	–	–
Total feedstocks	–	–	–	–
Tel. in liters	–	–	–	–
Production margin	–	–	–	–
Expenses				
Utilities chem. and royalties	–	–	−6.064	–
Operating labor, super, and lab.	–	–	−2.930	–
Maint., ins., tax, and overhead	–	–	−3.061	–
Capital recovery	–	–	−12.817	4.678
Total expenses	–	–	−24.872	–
Earnings (loss)	–	–	−4.202	−1.534
Cash flow, earning plus capital recovery	–	–	–	3.144
Investment				MM $
Plant				27.929
Offsite				–
Catalyst and royalties				–
Added offsites, wharfs, etc.				–
Total				27.929
Year to payout, inv./cash flow[a]				8.882
ROI 7 years, 3.0 %				
ROI 10 years, 10.5 %				
ROI 16 years, 15.1 %				

[a] Figures reported before income tax withdrawn

In this particular case, too, much of data, as produced by the report writing sequence, was in such a form as to be reproducible and able to be included in the final documentation. Table 27 shows an example of such a report. (Note: the actual calculated data in this example has been deleted).

For the parametric series discussed above, a special report writing technique was developed which allowed each succeeding parametric step to be repeated in a case stacking fashion. This type of report was considerably condensed from the reports described earlier.

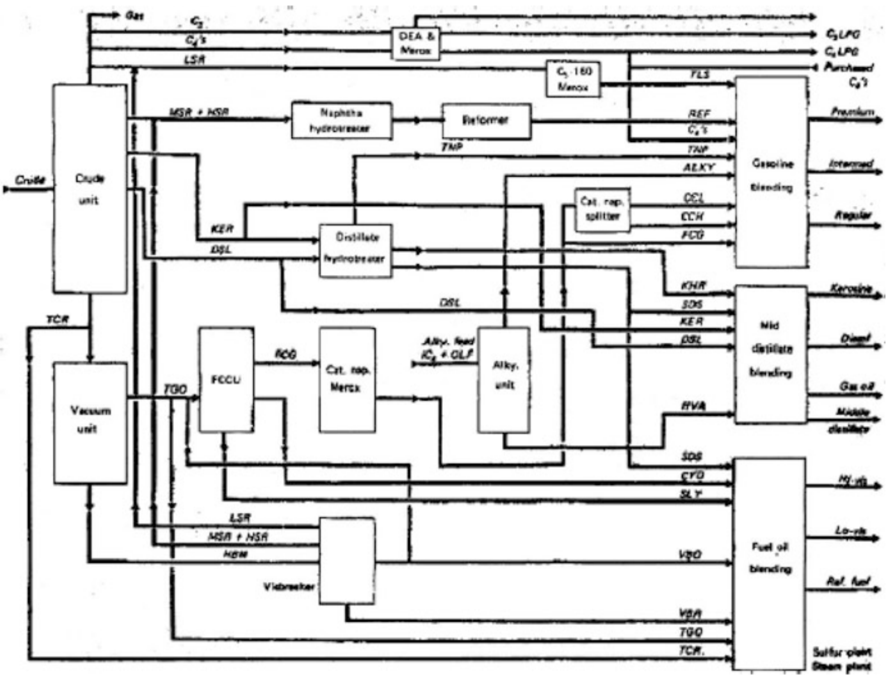


Fig. 20 Typical final optimum configuration

Final Documentation

When the solutions to the four premises of the problem had been determined, using the techniques described, they existed, hidden among the mass of tabulated data that formed the computer output. It remained now to extract the pertinent section of the output and to present it so that the objective of the study, which was to provide management with information to make a good decision, could be achieved. The most common means of doing this – and the one chosen on this occasion – is by a written report in which the data is summarized and discussed and the conclusion stated.

Although it is not proposed to discuss the general techniques of technical report writing here, some fundamental requirements of a complex presentation such as this are worth highlighting. This report had to satisfy two principal functions. The first is to present as succinctly as possible the conclusion, and the interpretation of those conclusions, for the convenience of the client's management. Secondly, it had to present all the backup data in as short a form as possible that would be necessary to enable the client's own staff to check and confirm the conclusions reached.

This second function was satisfied in this report in the form of an appendix. This included copies of the actual pertinent computer printouts complete with tabular listing of the submodels, economic balances, etc. These data were further augmented by the summary of the economic and yield output for the respective parametric runs.

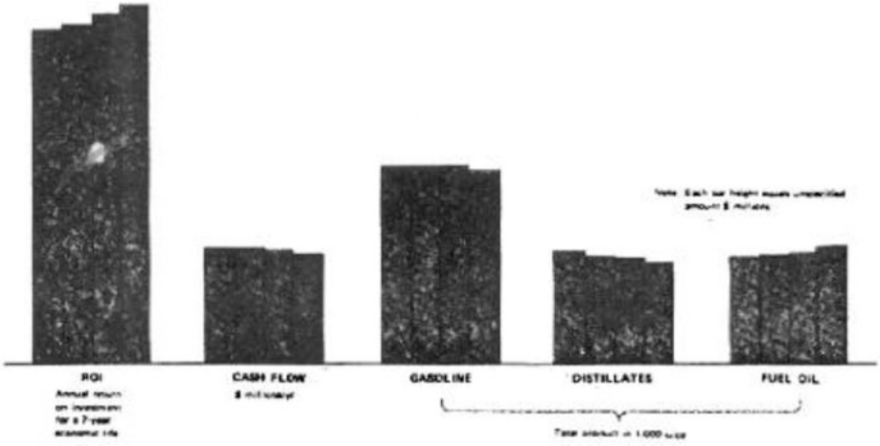


Fig. 21 Bar chart summarizing economic studies for configuration in Fig. 20

The main body of the report consisted of a short description of the study, together with discussion of the result. The results were however succinctly described by two illustrations for each of the four cases of the problem. The first illustration showed the ultimate refinery complex which satisfied the premise of the case studied, and a typical example is shown in Fig. 20. The second illustration, typified by Fig. 21, gave the basic economic trend for this configuration and also described the yields of major products for each parametric case.

The charts shown are meant only as an example and the figures are fictitious or have been purposely deleted. However, it can be seen that Fig. 20 describes the result in terms of the processes that must be built to satisfy the premise. Figure 21 shows why such a configuration is the optimum and what the ultimate product slate would look like. Such a chart also gives the client's management an opportunity to assess quickly the effect of changing a basic premise such as maximum return on investment or minimum capital investment.

References

Mukesh Sahdev, Refinery planning and optimization (2010) www.cheresources.com/content/articles/energy

J. Zhang, X.X. Zhu, G.P. Towler, A simultaneous optimization strategy for overall integration in refinery planning. Ind. Eng. Chem. Res. **40**(12), 2640–2653 (2001)

Li Wenkai, Chi-Wai Hui, AnXue Li, Integrating CDU, FCC and product blending models into refinery planning. Undated paper available online

Petroleum Processing Projects

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_29

Abstract

There are many activities carried out by a company in installing a new or revamped facility. Much of the initial work in executing a project is carried out by the company's development engineers in a series of "Front End Loading" (FEL) stages to help insure the right facility is being built with the right economics. The discussion of project economics in the handbook chapter on economics and planning meshes with the FEL efforts. Once the facility is well-defined, the company will establish a team to execute the project. This chapter details the steps in project execution starting at the FEL stage and continuing through detailed design, guarantees, and into on-stream operation.

Keywords

Refinery • Project • Front-end loading • Guarantee • Specifications • Flow diagram

Introduction to Project Execution

This chapter deals with the activities that are carried out by a refinery in installing a new or revamped facility which has been approved by the mechanism defined in the handbook chapter "▶ Petroleum Refinery Planning and Economics." Much of the initial work in executing a project is carried out by the company's development engineers. Later, during the early part of the work being executed in a selected engineering office, the company will set up a project team headed by a project manager to monitor and oversee the company's interests and requirements are met as the project is executed.

Front-End Loading

The "Petroleum Refinery Planning and Economics" chapter of this handbook describes several steps that lead to actual project execution. Today, the early project decision-making is often grouped into successively more detailed steps in an approach referred to as "front-end loading" or FEL. This process is also referred to within different companies as "pre-project planning (PPP)," "front-end engineering design (FEED)," "feasibility analysis," "conceptual planning," "programming/schematic design," and "early project planning." While the details of what deliverables a company expects at each FEL stage vary with the company, the general approach follows the pattern described here. Additional information on this approach can be found on the Construction Industry Institute website and publications. The "Best Practices" selection on the website is particularly useful. Their website is at http://construction-institute.org/.

The FEL approach entails performing a larger portion of the process engineering and some additional preliminary engineering work early in the execution than in past practice. This enables better definition of a project and its probable cost before detailed design is committed and when the value of the engineering is best leveraged. More money is spent in the development phases, with the expectation that less money will be wasted in detailed execution.

The FEL approach is broken into three or four phases, depending on a company's philosophy. There is management review at the conclusion of each phase and approval for the project to proceed to the next phase (or recycle if the next phase is not approved). The common FEL phases and the primary, typical activities in each phase are the following.

Pre-FEL-1

The initial objectives for a project along with some early economics are developed in the Pre-FEL-1 phase. This work is normally done in-house by a small team within the petroleum processing company. A large number of studies are normally done in this phase using simple spreadsheet models, often just barrel balancing the units. Potential process licensors may be contacted to obtain budgetary yield, product property, utility, and other estimates. The costs for different options are estimated based on the budgetary or capacity factored approach. Cost estimates will still have large contingencies at this point. Deliverables from this phase usually include:

- The proposed project objectives
- Block flow diagrams and technology options
- Barrel balances for several cases
- Budgetary capital cost estimates (+/−, say, 30–50 %)
- Preliminary economics
- Recommended case or cases for development in FEL-1
- Questions still to be addressed in FEL-1
- Request for approval of expenditure on FEL-1, with estimated FEL-1 cost

FEL-1

This phase narrows the options and better defines the project scope and cost. The work here may continue to be done in-house or a contractor may be engaged. Options from the Pre-FEL-1 phase will be evaluated in more detail and reduced to one primary option. The costs for the one option will be defined better, still using a factored approach usually. In some cases, vendors may be asked for study-level costs for major, high-cost, or long-lead items to improve the estimate quality.

The preliminary process flow diagram for the unit will be developed along with the heat and material balances (using licensor input if needed). A typical process flow diagram with its accompanying material balance is illustrated in Fig. 1. The initial equipment list is developed along with some preliminary duties for the equipment. Licensed technologies would be evaluated and a preliminary recommendation on the technologies would be made.

Deliverables from this phase usually would include:

- Project charter and objectives (or premises)
- Process engineering design data (utilities, location, wind loadings, etc.)
- Recommended block flow configuration
- Preliminary process flow diagram (PFD)
- Heat and material balance for the PFD
- Preliminary equipment list and rough duties
- Recommended technology (and licensor if needed) along with costs
- Capacity factored estimate (+/−, say, 20–30 %) plus major equipment budgetary quotes
- List of remaining process decisions for FEL-2
- Proposal for FEL-2 engineering
- Request for approval of expenditure on FEL-2, with estimated FEL-2 cost

FEL-2

Approval of the FEL-1 package moves the project to the FEL-2 stage. The project may also be stopped at this stage (sometimes shelved for later execution) or it may be recycled back to an earlier phase with changes in basis. An engineering

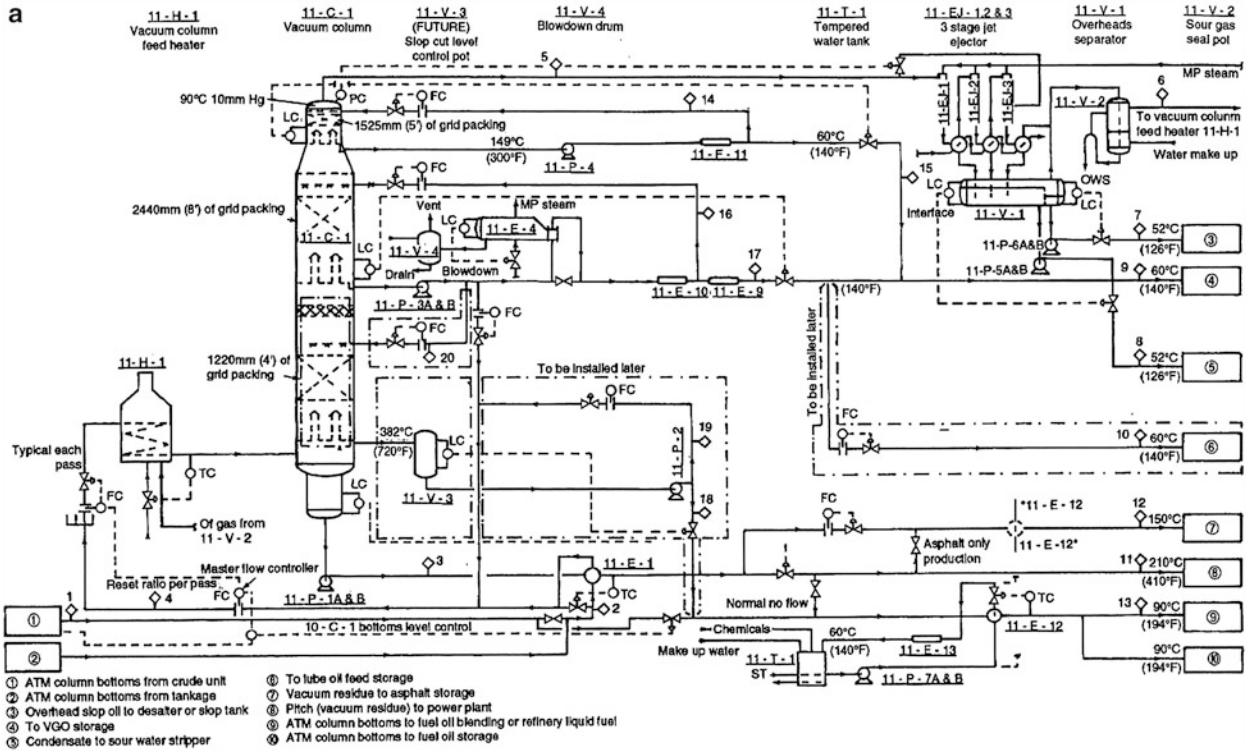
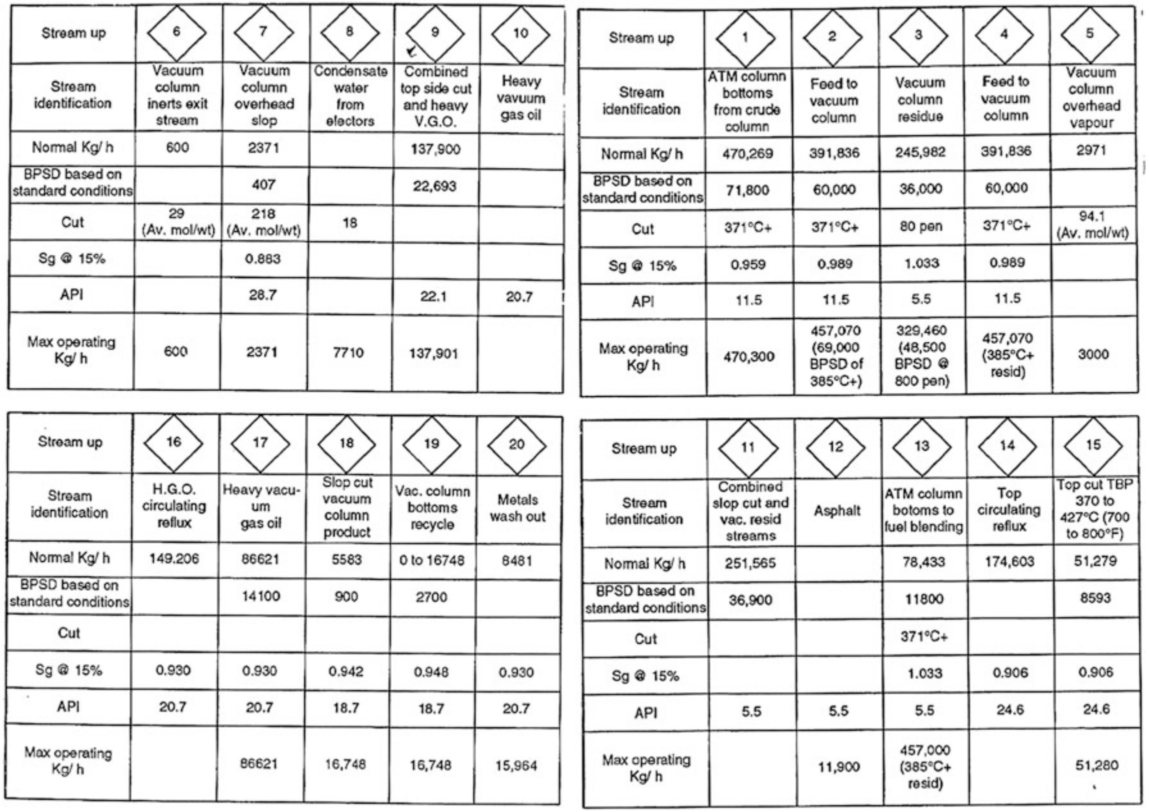


Fig. 1 (continued)

b



Stream up	6	7	8	9	10
Stream identification	Vacuum column inerts exit stream	Vacuum column overhead slop	Condensate water from electors	Combined top side cut and heavy V.G.O.	Heavy vavuum gas oil
Normal Kg/ h	600	2371		137,900	
BPSD based on standard conditions		407		22,693	
Cut	29 (Av. mol/wt)	218 (Av. mol/wt)	18		
Sg @ 15%		0.883			
API		28.7		22.1	20.7
Max operating Kg/ h	600	2371	7710	137,901	

Stream up	1	2	3	4	5
Stream identification	ATM column bottoms from crude column	Feed to vacuum column	Vacuum column residue	Feed to vacuum column	Vacuum column overhead vapour
Normal Kg/ h	470,269	391,836	245,982	391,836	2971
BPSD based on standard conditions	71,800	60,000	36,000	60,000	
Cut	371°C+	371°C+	80 pen	371°C+	94.1 (Av. mol/wt)
Sg @ 15%	0.959	0.989	1.033	0.989	
API	11.5	11.5	5.5	11.5	
Max operating Kg/ h	470,300	457,070 (69,000 BPSD of 385°C+)	329,460 (48,500 BPSD @ 800 pen)	457,070 (385°C+ resid)	3000

Stream up	16	17	18	19	20
Stream identification	H.G.O. circulating reflux	Heavy vacuum gas oil	Slop cut vacuum column product	Vac. column bottoms recycle	Metals wash out
Normal Kg/ h	149.206	86621	5583	0 to 16748	8481
BPSD based on standard conditions		14100	900	2700	
Cut					
Sg @ 15%	0.930	0.930	0.942	0.948	0.930
API	20.7	20.7	18.7	18.7	20.7
Max operating Kg/ h		86621	16,748	16,748	15,964

Stream up	11	12	13	14	15
Stream identification	Combined slop cut and vac. resid streams	Asphalt	ATM column botoms to fuel blending	Top circulating reflux	Top cut TBP 370 to 427°C (700 to 800°F)
Normal Kg/ h	251,565		78,433	174,603	51,279
BPSD based on standard conditions	36,900		11800		8593
Cut			371°C+		
Sg @ 15%			1.033	0.906	0.906
API	5.5	5.5	5.5	24.6	24.6
Max operating Kg/ h		11,900	457,000 (385°C+ resid)		51,280

Fig. 1 (**a**) A typical process flow sheet. (**b**) The associated material balance

contractor is normally engaged at this point, with the small in-house development team continuing to guide the project.

In FEL-2, detailing of the project engineering continues. The PFD is finalized. The heat and material balances are brought to near final form. A preliminary piping and instrumentation diagram (P&ID) or mechanical flow diagram (MFD) is developed. A section of a typical P&ID or MFD is shown in Fig. 2. Initial process hazards reviews, cost reduction reviews, process simplification reviews, and project risk analyses may be completed. A process licensor may be engaged at this point to supply more detailed information to complete the PFD.

Very long-lead equipment specifications may be developed in detail and prepared for purchase during FEL-3. The preliminary plot plan would be developed along with a preliminary project execution schedule. The draft equipment specifications would be developed.

With the additional engineering, a more detailed cost estimate, including operating costs, would be developed. The accuracy of the estimate continues to improve.

Deliverables from FEL-2 can include:

- Final block flow configuration
- Final process flow diagram (PFD)
- Heat and material balance for the PFD
- Preliminary P&ID
- Preliminary plot plan
- Preliminary equipment design
- Process license in place (if needed)
- Preliminary project schedule
- Equipment-factored estimate (+/−, say, 20 %) including some major equipment quotes
- Proposal for FEL-3 engineering
- List of remaining process decisions for FEL-3
- Request for approval of expenditure on FEL-3, with estimated FEL-3 cost
- Request for approval to purchase long-lead items, if necessary

FEL-3

If the FEL-2 package is approved, the project would move to FEL-3. As in the other phases, management may choose to cancel, delay, or recycle the project instead of proceeding.

In FEL-3, definition of the project continues in additional detail. By this point, an engineering contractor is normally involved and a small project team has been assembled. The team that guided the Pre-FEL-1 through FEL-2 efforts may continue to be involved, but the time and cost requirements here normally dictate use of a dedicated group with a project manager.

The equipment specifications, along with the attendant project specs, would be developed to the point of being “purchase-ready.” In the case of very long-lead

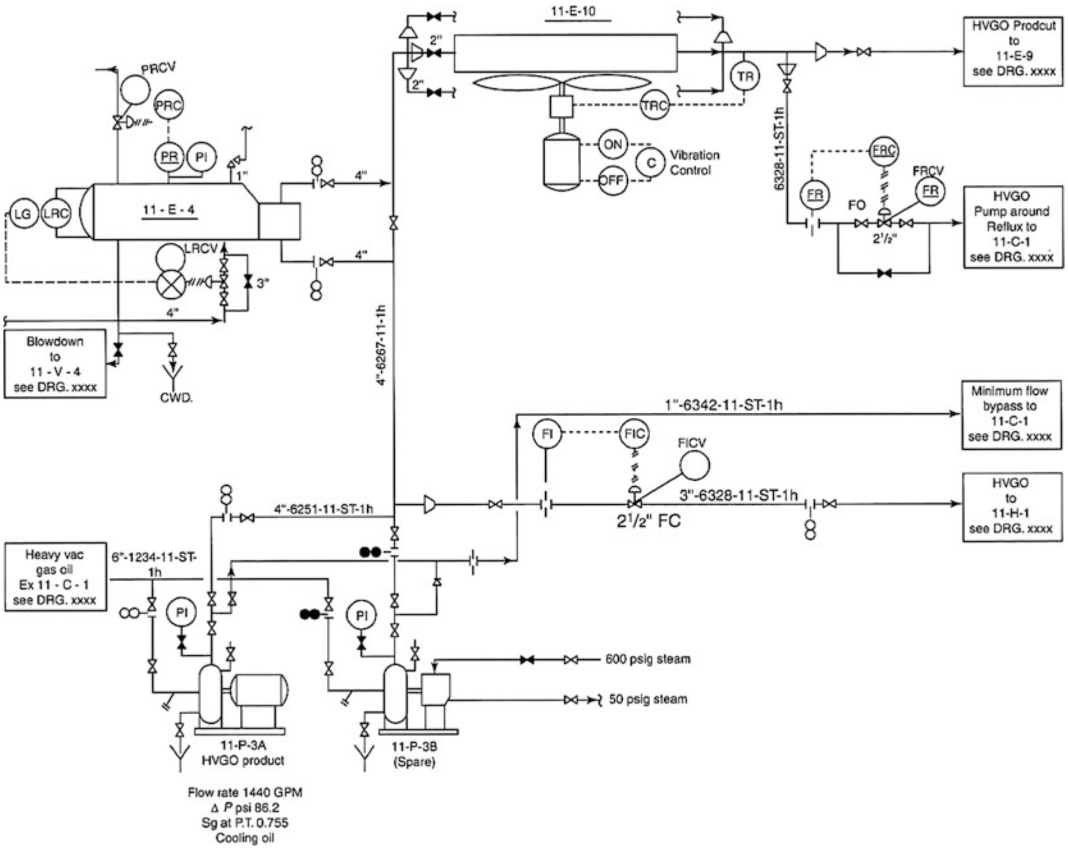


Fig. 2 A section of a typical mechanical flow sheet

equipment, those items may be purchased during this phase and preliminary information from the vendors incorporated into the design.

The process has basically already been defined. The final process decisions should be made now. The process hazards review (PHA), "layers-of-protection analysis" (LOPA), and other required process reviews would be completed and the results addressed in the design. The P&ID would be further refined to an "approved for design" level. From the P&ID, the line list would be developed along with the electrical equipment list.

Quotations are obtained for all equipment to support a semi-definitive or definitive estimate. The piping, electrical, civil, and certain other discipline estimates may still be factored at this point.

The project execution plan would be developed, with decisions on how the project would proceed. There are at least four major functions the plan needs to address:

1. Perform the detailed design engineering (E)
2. Procure the equipment, bulks, etc. (P)
3. Construct the facility (C)
4. Manage the construction (CM)

For instance, the company may choose to have the same contractor engineer, procure, and construct including field construction management (EPC). Or they may choose to have one contractor do the engineering and procurement (EP) with a second contractor doing the field construction (C) and a third contractor providing construction management (CM) or any of a number of combinations. Note that if separate contractors perform the functions, the company is assuming the responsibility of coordinating these contractors (this is a much bigger task than you might anticipate).

The deliverables from FEL-3 may include:

- Final PFD with material balances
- Detailed licensor packages
- Near-final P&IDs/MFDs
- Completed process hazards review (PHA)
- Completed layers-of-protection (LOPA) review
- Risk register
- Purchase-ready equipment specifications
- Actual purchase of long-lead equipment and initial vendor documents
- Project execution plan with contract(s) prepared to execute the plan (or requests for proposal/quotation, depending on company philosophy)
- Plot plan and preliminary 3-D model
- Materials of construction
- Line list
- Electrical equipment list
- Semi-definitive to definitive estimate (depending on company philosophy)
- Approval for expenditure for the detailed project execution ready to sign

After the FEL-3 approvals, the project moves to the detailed execution phase. Much of the balance of this chapter delves into detailed execution, with a smattering of discussion on items from the FEL levels. An attempt has been made to indicate where the discussion applies to an FEL level.

Developing the Duty Specification

There are many approaches to defining and executing a project. The approach discussed in the following sections meshes into the FEL approach discussed in the section "Front-End Loading" of this chapter but may not be an exact match. Each company executes a project slightly differently.

Among the first activities in a refinery project is the development of the "project duty specification" or the equivalent. This effort is often accomplished through the front-end loading approach described in section "Front-End Loading" of this chapter. If we look at the FEL levels, the deliverables by the end of FEL-2 essentially comprise the project duty specification. The process major input to this important document is usually supplied by the company's process development engineers or equivalent, with help from licensors and contractors where needed.

Once a project and the initial funds have been approved for implementation, work must begin to appoint an engineering and construction contractor to do the detailed design work. Before this can be accomplished however, it is necessary to complete the following:

1. Prepare the duty specification for the plant.
2. Develop the contractor's scope of work.
3. Develop the contractual terms and the contract itself.
4. Assemble the document inviting contractor bids.
5. Decide on the selection procedure for the contractor appointment.

Normally the operating company will assemble a team of people who will be dedicated to carry out these activities. This team may be supplemented by contracted services. The team will usually be headed by a member of the company's middle management who will be responsible for these pre-contract activities. The team itself will consist of senior personnel from its engineering disciplines and other parties such as the company's purchasing and legal departments.

The development engineer will almost invariably participate in some or all of the activities listed above. His/her main participation however will be in the development of the duty specification or the equivalent. The importance of this document is that it forms the basis of the selected contractor's scope of work. It also establishes the standard of quality required by the operating company as the client. A well-drafted project duty specification will contain at least the following sections and/or information:

- The process specification
- General design criteria

- Any preliminary flow sheets (duly labeled “Preliminary”)
- Utilities specification
- Basis for economic evaluations
- Materials of construction
- Equipment standards required
- Instrument standards required

A company following the FEL approach in section “Front-End Loading” will have developed all these items by the conclusion of FEL-3.

The specific items within the project duty specification are discussed in the following paragraphs.

The Process Specification

This document is developed by the senior development engineer assigned to the project team, with help from a contractor and other company resources. It gives, in precise terms, the plant required, the number of units, its throughput, the product yields and quality, the required test standards, and any salient process requirements. An example of a typical process specification is given in Appendix 1 of this chapter.

The process specification is essentially completed by the end of FEL-2 of the front-end loading approach.

General Design Criteria

This section of the project duty specification is usually compiled by the refinery’s project engineers assigned to the team with help from a contractor. Some input is required from the development engineer to ensure that technical documents and data developed by others will conform to the company’s usual format. This section, as the name implies, supplies the general data associated with any work done in the company’s plant site. This document is normally completed by the end of FEL-1 or FEL-2.

The following topics are included in this section:

Scope

This is a brief statement covering the objective of the project. This is followed by a list of the company’s standards that are to be used in the implementation of the work.

Climatic Data

A list of the following data is given here. These are the data that will be used in the various specifications and calculations developed during the course of the project, such as:

- Dry and wet bulb temperatures
- Winter design dry bulb temperature

- Temperature extremes
- Barometric pressure

General Design Considerations

This section lists *all* of the legislative criteria associated with the building of an industrial plant in the area. It will include the environmental requirements and safety and quality standards to be adhered to by contractors and licensors.

Units of Measurement

The units of measurement that will be used in all calculations, flow sheets, and specifications are given in this item. It begins by stating the units in terms of:

- English units
- SI units
- Any others

The next section then defines these units in more detail such as:

Linear – millimeters (mm)
Mass – kilograms (kg)
Flow gas – normal cubic meters per hour (Nm^3/h)
Flow liquid – (large) cubic meters per hour (m^3/h)
– (small) liters per minute (l/min)

There follows then a list of conversion units that should be used on the project.

Engineering Flow Diagrams

Many companies include those flow diagrams they have developed during the appropriate stage of the project. These are usually the process flow diagram and the mechanical or piping and instrumentation flow diagrams (see Figs. 1 and 2). Their inclusion adds to the description of the work scope supporting the process specification. In most contracts however the client company will expect the contractor and/or the licensor to take responsibility for the process performance and to guarantee it. Under this circumstance these engineering diagrams are released into the project duty specification as "preliminary" issues. The contractor is expected to check and, if necessary, revise them. Thereafter, the contractor must accept responsibility for the technical content of the diagrams as a basis for future normal design development.

Utilities Specification

Full details of the utility streams available in the plant are given in this item. This item is generally prepared by the process engineers and must include data concerning all steam and condensate systems, water systems, air, and fuel. Such data will include at least the temperature and pressure of these streams. In the case of circulating systems, such as fuel oil and cooling water, both supply and return conditions will be required. Raw water available should also have a complete analysis of its impurities. The analyses of the normal fuel oil and fuel gas should be included. These would contain, for example, the following:

Fuel oil: supply temperature
  - SG @ supply temp
  - Visc @ 120 °F cSt
  - Visc @ 210 °F cSt
  - Supply and return pressure

Fuel gas: supply temperature and pressure
  - Molecular weight
  - Approximate molar analysis

The dew point of instrument air required at the air supply header must be stated. If the client has any preference as to the type of desiccant to be used in the drying of the air, this too must be stated.

All other preferences or standards that the client company requires to be utilized in the utilities design must be given in this section. For example, most companies have a standard burner control system for their plants. This should be fully described here together with some appropriate sketches.

The electrical engineers usually add details of the plant power supply and distribution in this section. If some existing switchboards and substations are to be utilized, this should be noted together with a list of drawings that should be referenced.

Other systems, although not strictly utilities, may be included here. Among these would be:

- The fire main
- The flare(s)
- Water effluent treating, disposal, and environmental regulations
- Other environmental protection systems
- Boiler blowdown systems

The preliminary utilities flow diagrams (UFDs, e.g., Fig. 3) may also be attached if they were developed during the FEL phases. Otherwise, the UFDs will be developed during detailed design.

Basis for Economic Evaluations

The process engineer completes this section with the criteria used in the evaluation studies and the preliminary design. The section should begin with a statement that contractors are encouraged to review all flow and equipment arrangements so that all possible alternatives are considered. The incremental cost of any alternative arrangements must however yield a minimum of the company's stipulated return on investment. This return on investment is stated here.

This section continues with the detail costs of labor, utilities, feedstock, and products to be used for any such economic analysis.

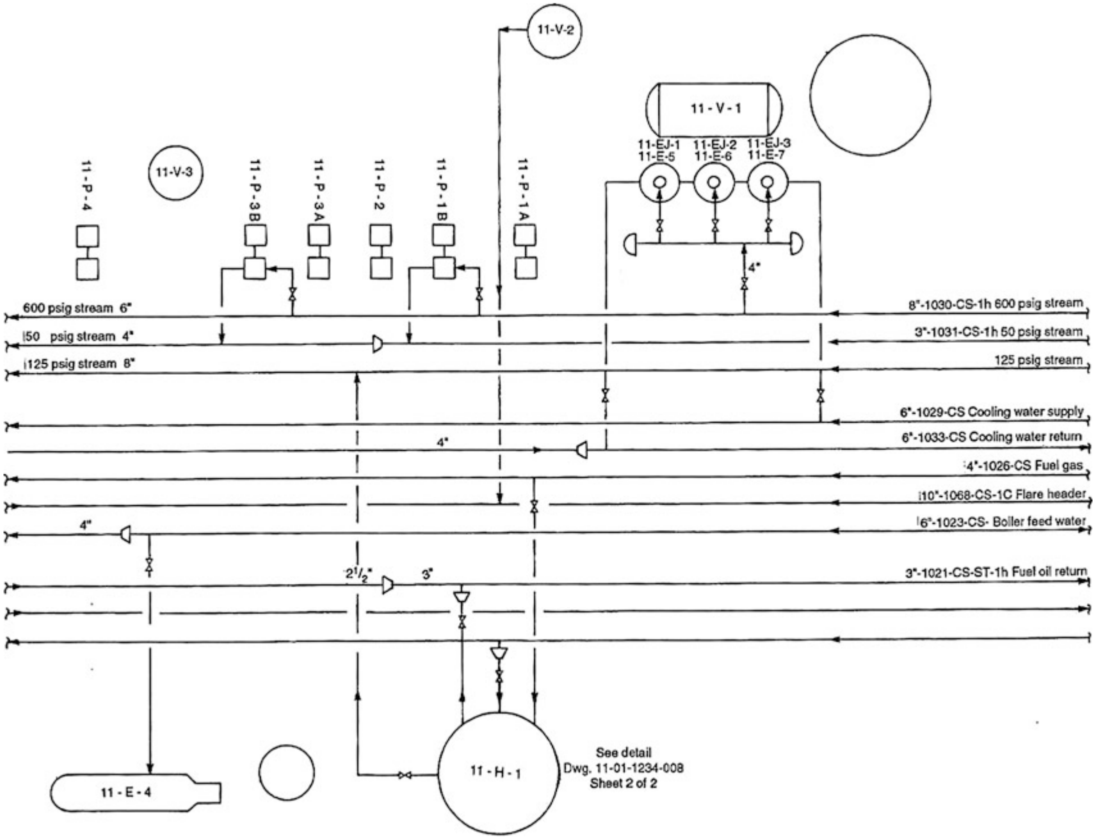


Fig. 3 A section of a typical utility flow sheet

Materials of Construction

This section is usually compiled by the team's project and metallurgical engineers with some input by the process engineers. It should begin with a paragraph on the references to be used in selecting the materials used in handling the corrosive streams. For example:

- Selection of steels exposed to hydrogen service shall be based on "API-941."
- Corrosion allowances for steels subject to hydrogen sulfide environment shall be in accordance with Couper, A.S., and Gorman, J.W (1971), Article: Computer correlations to estimate corrosion of steels, Materials Protection and Performance 10, pp. 31–37.

The next paragraph or subsection should detail the client's requirement for corrosion allowances in terms of equipment life. For example:

Equipment	Life in years
Columns, drums, and reactors	20
Heat exchanger-shell	20
Heat exchanger-tubes	5
Pumps	10
Compressors	10
Heater tubes	100,000 h
Atmospheric tankage	20
Piping material	10

These data may also be supplemented by a table giving the company's accepted minimum corrosion allowance in mm or inches (mils) for the various equipment items.

Equipment Standards to Be Used for Sizing and Design

There follows in this section data to be used for the sizing and the specifying of the major equipment items, which are:

- Vessels and columns
- Heat exchangers
- Pumps
- Compressors
- Heaters

Examples of such data included in this section are as follows:

Vessels and Columns

Columns to be sized on a specified type of tray (e.g., valve trays).

Design for a percentage of flood (usually 80 %).

Design pressure and temperature criteria for all vessels.

Minimum diameter for trayed columns.

Heat Exchangers

Design standards to be used (e.g., TEMA, ASME, etc.).

Rating procedures.

General design criteria (e.g., use of fixed and floating head tube bundles, expansion bellows, tube side flows where special considerations are required, use of kettle or thermosiphon reboilers, etc.).

Tube sizes and pitch relative to fouling factors.

Table of fouling factors to be used.

Allowable velocities and pressure drops.

Approach temperatures to be used.

Design temperature and pressures.

Pumps

The standard to which the pumps are to be designed. For example, API 610 "Centrifugal Pumps for General Refinery Services."

Rated capacity of the pump over normal. For example:

	Rated capacity over normal %.	
Service	Flow control	Level or temp control
Feed	5	10
Product	10	15
O/hd reflux	15	20
Inter reflux	20	20
Reboiler feed	15	20

The following additional information should also be included:

- Sparing requirements and philosophy
- NPSH calculation criteria
  - Source pressure
  - Rate for suction line losses
  - Level for static head (e.g., bottom tangent line for columns)
  - Pump center line elevations,
- Pump selection preferences
- Minimum flow criteria
- Casing design conditions
- Types of drivers
- Piping configurations (company standard)

Compressors

Standard to be used for the design of compressors

(e.g., centrifugal compressors designed to API-617)

Compressor-type selection preferences

Rating of compressors. Includes % over normal capacity

Sparing requirements and philosophy
Mode of control
Types of drivers
Type of cooling
Piping configurations

Fired Heaters

Types and selection preferences
Any company standards for heaters or safety systems
Heater design criteria, such as:

- Burners and flues to be designed to 125 % of normal heat release
- Environmental constraints
- Acceptable average flux, coil pressure drops, and mass velocities
- Surge volumes and acceptable % vaporization for fired reboilers
- The rated duty of the heater as a % of normal duty

Allowable maximum coil film temperature (where coking is a problem)
Coil design temperature and pressure criteria
Fuel system details (company standard)
Burner types preferred and burner control (company standards)

Instrument Standards Required

This section of the specification is usually compiled by the instrument and the process engineers. Its objective is to convey to the contractors the instrument, safety, and control philosophy required for the company's plants. It may begin with the sizing criteria for control and relief valves that the company wishes to use. For example:

- Criteria to set the control valve pressure drop, such as a % of line losses
- Design capacities for control valves
- Design standards required for relief valve sizing (e.g., API-520 and 521)

This item should then continue to define the company's preferences in piping design for control valve manifold configuration, relief valve venting, and relief valve locations. Some basic criteria concerning the relief header and its condition should be described. Finally, the section should give a list of instrument drawing symbols that the company prefers or, in the case of a plant being built in an existing complex, the symbols already in use.

This completes a review of a typical project duty specification. This document which usually forms part of a request for contractor's quotes may be smaller and less detailed than described here. Sometimes the client company may wish to depend solely on the contractor's standards and criteria. However to ensure good competitive quotations, a document such as described here or even more detailed is desirable.

The Project Team

Fairly early in the development and approval phases of a project (usually about FEL-1 or 2), the company usually appoints a project manager to look after the execution of the project as a whole. The project manager is typically chosen from senior engineers in the company or a dedicated group of project engineers. He or she will usually be a person with wide experience in the management of engineering and installation of petroleum processing facilities and, ideally, will be very familiar with his company's procedures, practices, codes, and standards.

One of the first activities of the project manager will be to form a team of experienced people who will assist him in directing the effort of his company and third parties who will be engaged in executing the project. In the early stages of the project (FEL-1 through FEL-3), the team will be relatively small, consisting of a process or development engineer, a scheduler, and a cost estimator. Later a contracts specialist, discipline specialists, operations specialist(s), and a legal advisor will join the team on a part-time basis. As the project continues with the selection of the engineering and construction company, the team will include additional development/process engineers, discipline specialists, procurement or purchasing specialists, operations specialist(s), and one or more assistant project engineers. This team will probably move into the contractor's offices once detailed design begins, so that a day-by-day interface with the contractor is established.

Once in detailed design, the team structure will likely change. The senior development engineer and some of the assisting process, discipline, and project engineers will move to other assignments. They will still participate in addressing any process or other problems that may arise. Their place on the team will be taken up by one or more experienced construction supervisors who will assist in monitoring progress both with respect to time and to budget during the construction period. A dedicated operations specialist will normally be assigned to the field to help coordinate field work, such as tie-ins, if the project is being built in an operating plant.

Many oil refining companies carry their own commissioning and start-up specialists, but most pull people from the facility staffs and operator ranks for commissioning and start-up to form a commissioning and start-up team.

The duties of the commissioning and start-up team commence before the facilities or part of the facilities have been declared by the contractor to be complete. Their initial effort is to develop the commissioning and start-up plans and the appropriate procedures. They will also develop the operating procedures for the new facility.

Once parts of the facilities near completion, they will begin checking the plant for completeness and that it conforms to P&IDs and the company's standards and requirements. In doing this they develop a "punch list"' of those items that do not conform or require more work. After the contractor has worked through the "punch list" and the work has been accepted, the plant is handed over to the "care, custody, and control" (CCC) of the company. At this point, the company has "bought" the plant. There may still be outstanding punch list items, but these will be on an action items list with completion dates and assigned completion responsibilities. Not all paunch list items may actually be addressed, especially if they are minor deviations.

Now commissioning of the facilities can commence with the "lead" specialist taking charge. Part of the duties of the commissioning specialist is to orientate and/or train plant operating personnel to run the facilities. The senior commissioning specialist usually remains on site to monitor the guarantee test run and interpret its results.

Primary Activities of the Project Team

The function of the project team has been touched on in the last few sections. The activities that satisfy these functions are listed as follows:

Precontract Award

- Preparation of the project specification (FEL-2)
- Determining the type of contract (FEL-3)
- Preparing the inquiry document (FEL-3)
- Issuing the inquiry document (FEL-3 or just after)
- Tender evaluation (FEL-3 or just after)
- Recommendation of the award contract (post evaluation)

The first of these activities "Preparation of the project specification" has already been discussed earlier in this chapter.

Determining the Type of Contract

Types of contracts fall into three main categories. These are:

"Lump Sum." With this type of contract the contractor undertakes to provide the complete plant ready for operation for a fixed, lump sum of money.

"Fixed Fee." Here the contractor undertakes to execute some of the services associated with the plant installation for a fixed sum of money. All the other costs would be reimbursable at net cost to the contractor. For example: The contract may require the contractor to fix his "home office" engineering cost plus his profit fee with all other costs being reimbursable (this is called an Omnibus Fee contract). Other forms of this type of contract may require the contractor to fix just his profit fee or perhaps part of the office engineering cost.

"Cost Plus." In this type of contract, the contractor is reimbursed for all costs applicable to the work plus a percentage of these costs as the contractor's profit fee and overheads. There are several factors that determine the choice of these types of contracts. Among the more important of these are the following considerations:

- Is the project subject to process design changes?
- Can the scope of work be accurately defined?

- Is time an essential factor?
- The current and anticipated trend in material and labor prices.
- The amount of competition among the contracting organizations.

A “Lump Sum” contract would be the preferable type of contract if the scope of work can be accurately described in the project specification and it was certain there would not be any major changes to the process. However, contractors would require a reasonable time to respond to the request for a “Lump Sum” bid. After all, they would require the time to properly analyze the project specification, obtain equipment quotes, and make preliminary layouts, design, and material takeoff for cost estimating. The standard of the cost estimate in this case would need to be at least a semi-definitive type (see the chapter on “▶ Petroleum Refinery Planning and Economics” in this handbook).

The advantage of the “Lump Sum” contract is that the owner knows from day 1 the cost of the project. However, the owner is also faced with the need to closely monitor the project to ensure the contractor does not realize savings at the expense of quality to increase his, the contractor’s, profitability.

Inquiry documents for “Fixed Fee” contracts can be prepared in a much shorter time and with less definition than for “Lump Sum” contracts. If time is an all important element and the project itself is so complicated that even a fairly accurate scope of work cannot be made, then a “Cost Plus”-type contract is preferable. In both these types of contracts, the owner has complete control over material and labor costs. This is a big advantage when material prices and labor costs are falling, but it imposes a significant onus on the owner.

The types of contracts described here are the “basic” types. There are many variations or small changes to these that are often used. For example, a contract may call for a “Cost Plus” up to, say, the stages where a semi-definitive estimate can be developed. It may then require the contract to be converted to “Lump Sum” for the remainder of the project.

Preparing the Inquiry Document (AKA Request for Proposal (RFP) or Request for Quotation (RFQ))

The “project specification” is the instruction to the contractor as to what facility is required to be built and to what standards and codes. The inquiry document must now include the exact scope of the work that has to be undertaken by the contractor and what work has to be provided by the owner. It is this scope of work that will become the basis for the contractor’s program and ultimately his master control plan for executing the work. It will also be the basis for negotiations with respect to changes and the cost/schedule implication of such changes.

The next important item in the inquiry document must define in clear terms the type of contract. This is most important in the case of “Fixed Fee”-type contract. Contractors bidding the work must understand fully what is included as a fixed portion and what is to be reimbursed. As mentioned earlier the contract type may be a variation of the three major categories. Such terms must be clearly defined and, if changes are to be made during the project, such as conversion to a different type or an addition of target pricing, this too has to be clearly defined. If there is a time element for completion, a bonus/penalty clause is often included, in particular if "time is of the essence" terms are invoked.

The inquiry document must include information regarding the procedures to be adhered to during the life of the project and toward the latter part when the plant is considered ready for operation. Such instructions, which may affect the contractor's bid, are as follows:

- List of approvals required by the owner
- Attendance by the owner at critical reviews and conferences
- Correspondence and communication to/from the owner
- Preferred vendors list (particularly in the case of "Lump Sum" contracts)
- Guarantees: process and mechanical
- Environmental considerations
- Site data (such as: elevation, location, ambient conditions, etc.)
- Obtaining building licenses
- Hand over procedures

Finally, the inquiry document gives instructions as to how the contractor's bid is to be submitted. This includes the number of copies required and when and in what form the bids are presented.

Issuing the Inquiry Document

Prior to issuing the inquiry document and in the time span in which the document is compiled, the owner's company should review the contractor market. This review should include a limited number of suitable engineering companies. Preparing bids with the subsequent follow-up work does cost contracting companies a significant amount of time and money; therefore, the selection of contractors to be invited to bid should be carefully made. Do not invite a contractor to bid if you would not be willing to award the contract to them.

In this task the first question to be resolved is: Which contractors are qualified to undertake this work? For example, if the project requires engineering, design, and installation of a hydrocracker, then ideally the qualifying contractor should have installed a hydrocracker or a similarly complex unit before. It would not be appropriate, for example, to solicit a bid from a civil contractor for this kind of project or, indeed, a contractor who had only installed smaller petroleum plants.

The next task is to meet with potential contractors at their respective establishments. The purpose here is to determine the extent of their home office facilities for engineering and to establish the method they use for executing a project. The other factor during this meeting would be to determine the spare capacity they have available for undertaking the work and their program for growth or completing their existing “in-house” work.

Finally, and during this meeting at the potential contractors’ offices, the owner should meet the key people the contractor would assign to the project. Certainly, meeting the proposed project manager is a must. In the case of a major refinery project, meeting the lead process engineer is equally as important. Present-day contractor evaluation must include the extent of this company’s computer application experience. This will be a significant factor in the selection.

The prescreening meetings may be conducted during FEL-3, in preparation for inquiry and award shortly after approval to proceed to detailed design.

Normally three to four bidders should be selected from this pre-inquiry review to receive the invitation to bid. These selected bidders should be informed by phone or fax and confirmed by letter. In this way the bidders are asked if they are interested in receiving the bid documents and subsequently submitting a bid. The bid documents, when complete, should be delivered by hand, if possible, or by courier at a predetermined date.

Contractors Bid Evaluation and Recommendation

The first activity after receipt of the bids is to carefully review their contents to ensure that they comply with the inquiry documents. In the case of Lump Sum bids, careful review of the equipment offered is made to ensure they meet the owner’s vendor list and approval. The bids are reviewed regarding the commercial offer. The selection is never made on price alone but on the complete offer. While the price at first glance may seem very attractive, in some cases, an evaluation of the other contractual offers may prove more advantageous at the end. Often, a very low bidder will end up inflating the final cost with “change orders,” so that minimal final costs savings are actually realized.

In most companies approval of major contracts is made by an executive group or person. It is usually the duty of the project team to compile the bidders’ offers into a succinct form for review by the approval board. The project manager of the team should include a recommendation for approval in the report to the company’s approval executive.

A suggested content of a “Contractors’ Bid Summary” for a Lump Sum Contract includes:

Contractor’s name
Total price $
Engineering $
Design $
Procurement $
Home office overheads $

Materials
Equipment $
Piping $
Instruments $
Electrical $
Civil/structural $
Others $

Construction
Direct field costs $
Indirect field costs $
Total construction $

Deviations from and exceptions to the duty specification
Compliance with and exceptions to contractual terms
Completion time

There may be further items depending on the inquiry content:

Project manager's recommendation
Project manager's notes and justification

The bid summary is given top priority and early completion is usually of major importance. Most bids do carry a limit on the time that the quotes are valid. It is in the owner's interest to make the award within those validity dates, if possible. Many owner companies prefer to short-list the bids to two or three and to interview the companies so listed to discuss their bids (bid conditioning) before making the final selection. This is very common in the case of Lump Sum- or Fixed Fee-type contracts. Such reviews certainly help to minimize "change order" negotiations further down the line.

Monitoring the Execution of New Projects

The discussion here applies to the detailed design and execution of a project post-FEL.

Project Initiation

As soon as possible after the award of the project, the owner's project team moves into the successful contractor's offices. The content and size of the team will vary with the type of contract and the status of the work in the contractor's home office. In general though the project team has more responsibility when administrating a Cost Plus contract than either of the other two types. The major activities of the team in this section of the work refer to those required for the Cost Plus contract. Initially the team should consist of the project manager, the senior process or development engineer, one or two project engineers, possibly a procurement (purchasing) specialist, and a cost/scheduling engineer. The activities of this team during the initial stages of the work will be:

- Conduct the client's "kickoff" meeting.
- Review and approve preliminary schedules and budgets for the project.
- Review and comment on the contractor's project procedure manual.

These are described in some detail in the following paragraphs.

The Kickoff Meetings

One of the most important conferences held during the course of the project life is the "kickoff" meeting. This takes place as soon as possible after the award of the project by the client to the contractor. As the name implies this meeting formally releases the contractor to begin work on the client's plant and describes again in detail the client's requirements. Its purpose is to communicate to the contractor's project team, the scope of work, the time span required, the budget (approximate or firm), and details of quality requirements and specifications as outlined in the client's "project specification." Discussion should then follow on the project management aspect of the work. The completion date required for the project is tabled together with major milestones to be met with during the project life. These milestones usually indicate when cost estimates (and schedules) are to be updated or when critical overall project decisions are to be made.

This first or formal "kickoff meeting" conducted usually by the client's project manager is invariably followed by a second, less formal, meeting of the contractor's project team. The client's team may or may not be invited to attend this meeting. However at the end of both these kickoff meetings, each key member of the client's and the contractor's project teams should be absolutely sure of what the project requirements are and what role they are to play in achieving them.

Preliminary Schedule and Budget

Soon after the "kickoff" meetings, a preliminary schedule for the engineering work and a budget will be developed by the contractor. The contractor will be able to produce a fairly accurate schedule for the early work based on their experience in similar projects. The remainder of the schedule to "job end" will be far less accurate. Much of this forward scheduling will depend on equipment vendor quotes and, if applicable, licensor data and later subcontractor quotations. The same applies to the accuracy of this first budget. However, both this schedule and budget will form the first control parameter for the project execution plan. On "Cost Plus" projects the client's approval for these items is usually mandatory.

Review and Comment on the Contractor's Project Procedure Manual

Most contractor project managers develop a procedure manual for major projects on which they work. This project manual contains details of the particular lists, directory of the project team, and specific procedures that will be adopted on the project. This eliminates the need for a great amount of correspondence defining instructions during the course of the project. Although this is a contractor's internal document, the client's project team is always invited to review and often participate in its development.

A typical project procedure manual is divided into several sections. An example of these sections is as follows:

- Introduction
- Project organization and directory
- The master schedule
- Man-hour budgets (restricted issue)
- The cost code of accounts
- Project control procedures
- Correspondence and communication
- Conferences and meetings
- Filing index
- Individual engineering, procurement, and design interface procedures
- Drawing index
- Field organization and directory
- Hand over procedures, and close out reports

The items given above may be increased or decreased depending on the wishes of the contractor's project manager. After all, this is the project manager's document although it is compiled by the members of the contractor's project team. A brief description of the contents of some of these sections follows:

Introduction

This section begins with the general information as to who the client is, the official address of the client and the phone, fax, or telex numbers, e-mail addresses, etc. It continues with a short history of the project up to the award and concludes with a synopsis of the process(es) involved. This section should not be more than three or four pages in length.

Project Organization and Directory

The project organization chart for the project is included in this section. Following the chart is a table of the key positions (and those of the client's project team) with the individual's name and office phone number or extension, and e-mail addresses.

The Master Schedule

This is the master schedule in bar chart form which shows the scheduled progress by discipline and activity. Initially, and of necessity, this will be preliminary but will indicate critical milestone dated clearly. It may be followed by a list of these milestone dates with explanatory notes. This will be subject to updates as the project progresses.

Man-Hour Budgets

This includes the allocated man-hour budgets by discipline for the project. This item is restricted to the copies of the manual issued to key personnel who are responsible for their discipline's budget control. As in the case of the master schedule, initially these man-hour estimates will be preliminary and will be subject to updates as the project proceeds.

The Cost Code of Accounts

This is a summary of the cost coding that will be used on the project to identify all the various cost centers. This coding will also be used to identify and code such items as purchase orders, client billing, change orders, and the like. More often than not the contractor's normal cost codes are used for this purpose.

Project Control Procedures

This section outlines the reporting procedures the project manager will adopt to control the project in terms of progress and budget. It will detail the data required from the key members of the project and the timing of the data for each reporting period.

Correspondence and Communication

All correspondence leaving the project does so under the project manager's signature. Similarly all correspondence originating outside the project is addressed to the project manager. All correspondences are given a coded reference number, and this coded reference number also identifies the origin of the correspondence. This reference code is given in this section, together with instructions on the routing of the correspondence. Detailed procedures as to the communication by other means, such as telephone, e-mail, and fax, are also given here. A list giving the required distribution of all correspondence to the project team personnel and possibly others outside the project is given in this section.

Conferences and Meetings

Routine meetings and conferences are scheduled in this section. This will also include a list of permanent attendees to these meetings. As time taken up in meetings is a large consumer of man-hours, the project manager may elect to outline certain recommended procedures for unscheduled meetings in this section. Minutes from all meetings on the project are recorded; and the minutes are distributed within the team and other interested parties according to the project's correspondence distribution list.

The Filing Index

The project secretary organizes the project filing system. The files generated on the project often become legal documents which may be used for such purposes as "job closeout" negotiations, any possible litigation, or inquiries at later dates into industrial accidents and the like. Maintaining the filing therefore is an important function on the project, and to accomplish this effectively a filing index is initiated and developed. This is given in the manual to enable members of the project team to utilize the files effectively when required. There is generally a document control specialist or lead who coordinates the filing and distribution of all project documents.

Individual Engineering, Procurement, and Design Interface Procedures

During the life of a project, there will be a considerable amount of data and information generated and distributed to the various disciplines in the project team. To ensure the correct movement of these data, each discipline develops its interface procedures. For example, in the case of a process engineer who has now completed the data sheet for a pump, he needs to ensure that this document is sent to the correct discipline for further work and ultimately purchasing. In this particular project the mechanical engineer is designated to be the interface between process and the purchasing department. Then this section of the procedure manual will detail such interface with instructions as to how the transmittal of the data sheet is to be done.

Drawing Index

This is initiated and maintained by the design coordinator. In developing the index as a list of all the drawings, he also demonstrates what the items in the drawing reference numbers signify. This is updated as the project proceeds.

The remaining items of the manual are self-explanatory. These are usually added only in later editions of the manual, for example, just before or immediately after field "move in".

Monitoring the Engineering, Procurement, and Design Phase

With the project now underway, the work continues in the home office of the contractor to detail the engineering of the plants, to purchase the equipment and materials to be installed, and to arrange the "layout" of the facility on the site provided by the client. Each of the various disciplines proceeds with their function to meet the progress milestones defined by the "master schedule." Some of these milestones are finalized by conferences of all the contractor's participants and the client's project team. The first of these and perhaps the most important is the mechanical flow sheet conference.

The Mechanical or Piping and Instrumentation Flow Sheet Conference and Approval

One of the major objectives of the process engineering's early activities is to provide sufficient data to enable other disciplines to commence effective work as early as possible. A major milestone in achieving this objective is to conference the MFD (mechanical flow diagram) or P&ID (Process and Instrumentation Flow Diagram) and have it approved by the client. This approval allows a considerable amount of design work (which is the major man-hour user on most projects) to commence. The development of the equipment data sheets has already allowed the mechanical engineering and the procurement functions to commence work, but it is the release of the approved mechanical flow diagram that really puts the activities of the project into top gear.

Participation of the client company in the flow sheet conference depends on the type of contract and the relative location of the client's offices to that of the contractor. In the case of a Cost Plus contract, however, participation by the client is mandatory. Whether there is client participation or not, the flow sheet conference follows some basic guidelines, and these are described in the following paragraphs:

- *Preparing for the conference*. The contractor's lead process engineer is responsible for organizing and conducting the flow sheet conference. The flow sheet that will be used in the conference will be "clean" and free from any pencil or other marks on the diagram itself. It will be given the revision number "0" and clearly marked "FLOW SHEET CONFERENCE MASTER."

  The diagram will be complete with all lines sized and specified. Instrumentation will be correctly shown with control valves sized; relief valves will also be shown but not necessarily sized at this time. All equipment will be properly titled and labeled in accordance with the agreed format for flow sheet production.

  Accompanying the "FLOW SHEET CONFERENCE MASTER" will be the current revision of the process flow diagram. This will also be "clean" with no pencil marks other than the label "Flow Sheet Conference Copy." The lead process engineer will also ensure that copies of all the equipment data sheets pertaining to the equipment shown on the flow sheet are available at the conference. The current equipment list will also be made available at the conference. Finally, the lead process engineer, or the process engineer he has assigned to the particular process that is to be part of the conference, should have available a copy of the process calculations developed. This often helps to resolve minor issues that may arise.
- *Attendees*. After notice of the conference has been issued by the lead engineer, the project manager or his assignee will designate the location where the conference is to be held. He will also issue directives to attendees giving the date, time, and location of the conference. In cases of major conferences where client representatives are present, professional secretaries may be employed to take notes at the meeting. Otherwise project engineers will be assigned this task. The notes taken at this meeting are most important to the final approval mechanism. The attendees are usually:
  - Client's representatives (if applicable)
  - Project manager (usually part time)
  - Lead process engineer (meeting leader and convener)
  - Responsible process engineer(s)
  - Engineering manager

  - Area project engineer(s)
  - Lead discipline engineers (except civil and structural – called for as required)
  - Design coordinator
  - Design section heads (piping, instruments, electrical)
  - Others as required, such as environmental engineer, cost and schedule control engineers, etc.
- Conducting the conference. The process engineer conducting the conference commences with a brief outline of the process and its objective. He proceeds to describe the process using the process flow sheet to illustrate the process flow and the equipment. He then commences with the description of the MFD/P&ID which is attached to a wall or suitable frame from which it can be easily read by the attendees. Many modern reviews use electronic displays. Now most companies have a color code depicting "additions to," "deletions from," etc. Colored pencils are used therefore to cover all such points made during the conference by marking up the flow sheet as the conference proceeds. Assume the color coding in this case is as follows:
  - Yellow – Shows all items that have been conferenced (i.e., discussed at the conference).
  - Red – All changes and additions.
  - Blue – All deletions.
  - Green – Numbers in green refer to note items taken during the conference.

The process engineer conducting the conference starts at a suitable point on the left of the flow sheet. He selects a major line, checks and "yellows out" the source label, and traces the line using the yellow highlighter pen to the first equipment item. In tracing the line, he highlights the line number, size, and specification shown on the line. The design coordinator or piping designer checks this against his line list. It must match exactly or it is marked as requiring further review. All valves and instrumentation along the line are similarly checked against piping lists or the instrument register.

The equipment item into which the line is connected is checked for correct labeling and data. Those shown on the flow sheet are compared with the equipment list, data sheets, and the process flow diagram for an exact match. The process engineer continues with a second line in a similar manner. He may elect to go back to the left side of the flow sheet to select this line or take a line leaving the equipment item. However, the same exercise is carried out for all lines and equipment until the flow diagram is completely yellowed out with the discussed notes marked and with all deletion and changes shown.

This flow sheet conference is a necessary activity but is nevertheless a high consumer of man-hours. The process engineer should therefore use his experience and knowledge to minimize the time taken in this activity. For example: where there is some considerable contention or where there is an area of concern to the client highlighted in the conference, the process engineer should attempt to defer a solution until after the conference. Don't design in the meeting. Appropriate note should be made however of the problem and the item clearly marked with a

"HOLD" sign. Clients will normally approve flow sheets with some "HOLDS" providing there are not too many. In further development of the flow diagram, priority is given to resolving the issue(s) and removal of the "HOLD."

Immediately after the conference, the lead process engineer and the project manager formally solicit the client's approval and the release of the project to detail design work. The approved flow sheet is marked as Rev 1, "Approved for Construction."

Approval of Equipment Selection

On a Cost Plus contract, the client's project manager must approve the selection of all pieces of equipment that will be purchased and installed. Next to the approval of the mechanical flow sheet, the commitment to purchase equipment is certainly the next most important. Certified equipment vendor data are essential for updating the budget and schedule. It is also important in obtaining correct outline drawings for certain items to initiate piping layout and also plot plan development. This certified and guaranteed data will only be made available to the project after the issue of the purchase order.

In addition to releasing the project to essential design work in piping, civil (foundations), and electrical engineering, it also enables the contractor's process engineers to build an accurate utility balance. This in turn initiates the engineering of the utility facilities if this is part of the project.

The contractor's process engineers initiate this function by developing data sheets that define each equipment item. The data in these sheets define the equipment size and performance required to meet the facilities' heat and material balances. Mechanical and other disciplines add their requirements to the sheets. On completion of these data sheets, the contractor's procurement department completes the commercial conditions associated with the purchase and sends these documents to a small number of vendors for each type of equipment soliciting their quotes for supplying the items.

The receipt of the quotations initiates the selection process. Usually the contractor's procurement department develops a bid summary list of the quotes from each vendor for a specific equipment item. They enter all the associated price and delivery, and together with the actual quotations, this bid summary is then sent to the process and other engineering disciplines who analyze the technical content of the quotes giving their comments on the bid summary. The summary is then reviewed by the cost/scheduling engineers who compare the offers against the control budget and the master schedule. They add their comments and route the summary to the contractor's project manager for recommended selection. Finally, the client's project manager receives the package and the recommended selection. He usually solicits input from his project team before approving the selection.

If the approval mechanism meets with some problems, the client's project team through the project manager may request a conference of members of the contractor's team to resolve the problem. This is sometimes requested for major equipment; after all, the equipment cost is a significant portion of the total budget, and, besides, an incorrect or poor selection could adversely affect the detail design work that depends on it and even, much later, the construction effort (e.g., late deliveries to the field).

Purchase Orders

With the selection of the equipment vendors, the contractor's procurement team develops the purchase orders for the client's approval (for Cost Plus or Omnibus Fee contracts). Prior to this activity usually the successful vendor is invited to the contractor's offices for a pre-award meeting to discuss his or her offer in detail. The contractor's purchasing department prepares the purchase order for the approval signature of the contractor's project manager and, when appropriate, the client's project manager.

Plot Plan Development and Approval

Shortly after the commitment of the major equipment purchase orders, certified vendor data in the form of outline drawings, completed data sheets, and the like will begin to be received by the contractor. These data are received by the purchasing department whose duty is then to route the data to all the engineering and design departments for checking and data acquisition. The receipt of equipment dimensioned outline drawings enables the design department to initiate the plot layout, showing the exact location of the items relative to one another. This is a combined operation involving most of the engineering and design disciplines. The key members of this group will be the process engineer and the lead piping designer. Some contractors will conduct this activity using small-scale wooden or plastic models of the items on a scaled board representing the total site. Computerized piping isometrics and 3D visualizations can be of great help at this stage and have become common.

When satisfied with a reasonable layout, the contractor's project manager will arrange a conference with all interested parties, including the client's project team, to view the layout. Comments made at this review will be incorporated and the layout will be the basis for the plot plan drawing. This plot plan and 3D model will then become the basic tools for routing pipe ways, electrical and underground piping, and the civil foundation and structural design.

On Cost Plus and Fixed Fee contracts, the plot plan requires client approval before use is made of it for further design work.

Routine Progress Meetings and Conferences

Although there is a continual interface between the two project managers during this phase, there need to be formal meetings between the two teams. This is usually on a set weekly basis where key members of both teams sit down together and solve the problems that have arisen or are anticipated to occur in the near future. Minutes of these routine meetings are recorded in and become part of the project record, although they may be conducted in an informal manner.

A more formal meeting takes place once per month. Again the participants are the two project managers and their key staff members. Very often senior executives of both companies may attend, particularly if there is a question affecting either company policy. This monthly meeting is convened primarily to discuss and review progress and expenditures. Obviously these topics more often than not involve some technical interface. Minutes of this meeting form the basis of the contractor's project manager's monthly written progress report. The distribution of this report includes the client's project manager, and members of his/her home office senior management, and the contractor's home office senior management.

The Master Construction Plan

At some point toward the end of the engineering phase and when all equipment is defined, and the bulk of material quantities are known, the master plan for the construction is developed. As in the case of the project master plan, this item is detailed both in terms of time and in terms of cash flow. In all contracts where the field cost is reimbursable, the client's project team, including a representative of their field specialist, must be involved. In all projects, field costs (and, of necessity, schedule) are significant items in the overall project cost. Indeed, in many parts of the world where climatic conditions or accessibility to the site are a problem, field costs are the major item in the overall project cost.

Among the first items in the plan that have to be decided is: What method of construction is to be adopted? Some of these options are:

- Subcontracts
- Direct hire
- Field erected
- Remote modularization

There can be a mixture of these options in the overall plan for the construction, but the decision has to be made in plenty of time for a smooth field move in.

Monitoring the Construction Phase

With the development of an approved construction plan, the client's project team in the contractor's home office can be substantially reduced. Most of the engineering work should be close to completion at this stage. There will still be some design work, such as detail pipe spooling, electrical, and instrument hookup details, to be completed. These do not require the monitoring and input from the client's team however. The primary remaining major engineering items at this stage that will require client input and approval will be:

- The operating instruction manual
- The mechanical catalog compilation
- Plant guarantees

These items continue to be developed through most of the construction phase by a small contractor's team consisting of one or two process engineers, a mechanical engineer, document control, and/or a project engineer. These will be discussed later.

The Field Move In

The extent of the field "move in" will depend on the type of construction decided on, the location of the site, and the proximity of the labor source to site. The most extensive effort in this respect is the situation where it is decided to utilize direct labor, and this labor source is a considerable distance from site. In this case the contractor must set up a camp for the labor and field staff complete with canteen, social facilities, and the like. Developing labor contracts also becomes a major activity for both the contractor and the client in approving these contracts. In this situation there would be a definite advantage in totally subcontracting the work. This field aspect of the "move in" would become part of the subcontract.

Monitoring the Field Activities

The activities of the client's project team during the construction phase are reduced to monitoring the cost and schedule with respect to the master construction plan. The team itself will probably be reduced to the project manager and possibly a project engineer with the process engineer on a part-time basis. It is also likely that this smaller project team will remain in the contractor's office rather than move permanently to site. Usually monthly site meetings are conducted and the project manager among others would attend these meetings. During such meetings physical review of progress in the field would accompany an in-depth written and verbal report on the schedule and the cost aspects.

Although the project manager would not be present full time on site, there would be a client presence there continually. Heading this team would be the client's construction specialist, with some project engineering assistance. As the construction work progresses, this team would expand to include specialists in all disciplines who will follow the installation and testing of equipment relating to the various disciplines. These would include mechanical, electrical, and instrument engineers. The follow-up for the piping installation would usually be undertaken by piping specialists (to check such details as piping layout conforming to plan, pipe stress analysis, and the like). Most clients also include the proposed permanent operators and maintenance staff of the facility in this team. Process licensors will also be present as provided by their respective companies.

Final Activities of the Project Team-Mechanical Completion

The erection of the facilities is considered complete when all the equipment, piping, cables, and buildings (if any) have been installed, and such testing that is necessary (such as line and vessel pressure testing) has been done. The contractor is also responsible for completing all insulation, such refractory lining as may be required, and the disposal of debris from the site. Most vessels may be left open for final inspection by the client. When satisfied that all activities required to be done according to contract have been completed, the contractor will issue a formal notice to the client that the facilities are "Mechanically Complete." (Note: Be certain you are clear about the definition of "Mechanically Complete" – this does not necessarily mean the plant is ready for commissioning or operation or even insulated.) With the receipt of such a notice, the client usually has a fixed period according to contract to check the plant out and to inform the contractor of any defects or omissions to the plant. The field contractor will remedy these items notified by the client and then issue a formal notice handing over the plant to the client in terms of "Transfer of Custody and Control." On acceptance of this notice, the client takes over the facilities and prepares to commission them.

Developing the Operating Manual, Procedures, and Plant Commissioning

The development of the operating manual and procedures occurs toward the end of the engineering and design phase. It may occur in the contractor's home office or at the plant, depending on company practices. It may be compiled by the contractor's process engineers, but more commonly it is developed by the client's operating staff.

Normally, the process engineers who have been most closely associated with particular process plant(s) on the project may be required to assist in the punch listing and commissioning of those plants. The following sections describe the activities associated with these functions.

Developing the Operating Manual and Procedures

The operating manual is a compilation of instructions and data reflecting recommended procedures for:

- Prestart-up conditioning of the plant
- Plant start-up
- Normal operation and troubleshooting
- Emergency action and shutdown

- Normal shutdown
- Catalyst regeneration and decoking (where applicable)

These procedures include equipment manufacturers' recommended handling, conditioning, and operation of their items of equipment and the experience of the process engineer who designed the plant. To the process engineer, the writing of the operating manual provides him or her with the final "in-depth" review of the mechanical flow diagram of the plant. During the course of writing the manual, he/she will use the P&ID/MFD continually to make reference to the operating procedures he/she proposes. Anomalies or missing valves and piping become obvious as the process engineer develops the procedure logic.

The operating manual is normally translated into detailed, step-by-step operating procedures using a specific format defined by the operating facility. These procedures are normally in much more detail than the manual.

A typical operating manual may include the following table of contents.

Introduction and Process Description

This will include a brief statement as to the contents of the manual and its purpose. This will be followed by a process description which will include the "Approved for Construction" revision of the process flow diagram as reference.

Prestart-Up Conditioning

This item describes the cleaning out of the plant after construction and its reassembly following the cleanout. For example, this item will designate those lines and equipment that will be flushed out by water and those that will be blown out by air. It will also describe the equipment and materials that will be used for this cleanout such as piping spool pieces to replace control valves and nozzles and lines that will be blanked off during this activity. Finally, this item will draw attention to the manufacturer's requirements for the various equipment cleanout and conditioning procedures. Copies of the actual manufacturer's documents relating to this activity should be included in the appendices of the manual. It is important, in order to maintain the warranties that accompany most equipment, that the manufacturer's instructions be carefully followed.

Plant Start-Up

This section of the manual presupposes that the plant has been properly cleaned, all utilities to the plant have been commissioned, all equipment is ready for operation, all drains are free, and firefighting equipment and procedures are in place. The process engineer then begins his detailed description of the activities to be carried out in their proper sequence to bring the plant on line and producing the products intended. To accomplish this he refers to the MFD/P&ID. Using this document he describes each action in the start-up sequence by referring to line numbers, control valve numbers, equipment item numbers, and titles as they appear on the diagram.

Normally all these actions start with introducing the cold feed. For example, in the case of a Thermal Cracker project, cold feed from storage would be used for start-up. Sufficient lines and valves would be provided for this purpose and the manual text would be somewhat as follows:

> Open block valves at tank TK 101 and at the plant battery limits on line 1234 CS 12″ ST. Open the suction valves on pump P 106 A and start the pump [Editors note: Only the term "Start the pump" need be made as instructions on how to start the pump are included in the manufacturer's documents found in the appendices.]. Set the flow control valves 106 FRCV 1 A, B, and C to full open. Set back pressure controller 300 PRCV 1 at the outlet of heater H 301 to 250 psig. Commission the level control indicator 301 LCI 1 and when the desired level in the bottom of the fractionator is reached (NLL) open the suction valves to bottoms pump P304 A on line 1235 10″ Cr ST. Control discharge flow from pump P304 by activating control valve 301 LCIV 1 on line 1236 8″ Cr ST, etc.

Normal Operation

This section carries on from the end of "start-up" with the unit lined out and in stable operation. It then describes a series of procedures during normal operation to fine-tune certain parameters and to maintain the plant on set conditions when minor changes in feed composition, temperature changes, etc. occur. It must be noted here that in modern control systems associated with plant operation, these types of adjustments are made automatically with very little need for operator intervention.

The other adjustments that may still require operator action are those associated with changing the product grade or specification. This section therefore still includes a selected list of operating changes that may be required to be made under normal operating conditions and the procedures used to make these changes.

Normal Shutdown Procedures

Normal shutdown procedures are usually divided into two forms, which are:

- Short-duration shutdown
- Shutdown for an extended period

The short-duration shutdown is that associated with a minor mechanical problem, or temporary loss of feed, or a minor instrumentation problem and the like. In these cases the feed to the plant is diverted, but some or all of the product streams are rerouted back to take the place of the normal feed. The feed heater, if it is a fired heater, may continue to be fired on a lower level of operation but sufficient to enable a quick resumption to normal operation when the fault causing the shutdown has been rectified. The unit under these conditions is said to be "boxed in" or "blocked in."

The second type of normal shut down occurs when a major fault has occurred requiring equipment to be taken out of service for repair. This type of shutdown is also placed on a predefined schedule for routine maintenance. Such a shutdown requires the unit feed to be withdrawn and the unit itself allowed to cool down to ambient temperature, be depressured, be cleaned out (usually by steam or nitrogen), and drained free of any hazardous material.

This section of the manual describes both these procedures in the same detail as described earlier for “normal start-up.” Again the MFD/P&ID is used as a reference in these detail procedures.

Emergency Procedures

This section is the most important in the manual and requires careful development and presentation. Its importance is reflected in the fact that very often the preparation of this section becomes a combined effort of both the client process engineers and the contractor’s process engineer. Its obvious importance to the safety of all personnel working on the plant is often coupled with the requirements of insurance underwriters and, in the case of a major mishap, its legal significance.

The section should contain at least the following subsections:

- Emergency shutdown
- Emergency action by personnel
- Plan showing location of firefighting equipment
- Emergency telephone numbers (by client)
- Location and setting of pressure relief valves

The contractor’s process engineer is primarily concerned with the writing of the recommended emergency shutdown procedures. In most process units, this follows the same basic principles (although detailed process hazards analysis of these procedures will actually dictate the specific recommendations), which are:

1. If there is a fired heater (either as a feed preheater or reboiler), shut down the burners immediately.
2. Again, in the case of fired heaters, take out the fresh feed and recycle products through the coil until the coil is cool enough not to be damaged. Use vendor data to fix this temperature.
3. Cool down fractionating towers by increasing reflux flow and wherever possible reducing return temperatures.
4. In the case of reactors, remove the feed stream immediately and purge with inert gas such as nitrogen. In the case of reactors in exothermic service and where there is a coolant, increase the coolant duty.
5. Divert all product streams to slop, but maintain any cooling cycle until safe conditions are reached.
6. Depressurize all pressure vessels to flare or to atmosphere at a safe location. Note: The process engineer must make sure that there exists a depressuring system on all these vessels and that they are clearly shown on the MFD/P&ID.

7. As soon as conditions allow, introduce purge steam or inert gas into all vessels, towers, and, where applicable, reactors. In some cases steam would be injurious to catalysts in reactors; under these circumstances the reactors should be purged with inert gas.
8. If the emergency is the result of a fire in a heater firebox due to a ruptured coil, shut down the burners and take out the feed immediately. Introduce snuffing steam into the firebox (once the combustible source is eliminated), and do not recycle product or introduce steam into the leaking coil.

As in the case of start-up and normal shutdown procedures, the same kind of detail covering the basic actions given above would be written for the emergency shutdown. Again the P&ID/MFD would be used as the reference document.

In practice, the documents and instructions developed by an engineering contractor or licensor are considered to be recommended. It is always the final responsibility of the operating facility to translate the instructions into usable, detailed, safe procedures. The translation of the manual is normally done by the operations group, with help from the engineers.

Appendices to the Operating Manual

The appendices to the manual should contain as much data as possible to assist the operator of the plant in the safe operation of the plant. As a minimum the appendices should contain:

- The “As Built Revision” of the MFD/P&ID
- An up-to-date equipment list
- Equipment manufacturers operating instructions and data
- A list of hazardous materials used in the process, with a summary of recommended handling procedures

Plant Commissioning

Process engineers from the contractor’s organization are often called upon to assist in plant commissioning. Process engineers from the client’s organization are invariably called to help with commissioning. This task begins at the point where the contractor’s field organization has completed all their installation activities and has handed the units over to the client’s “care, custody, and control.” At this point all contractor’s debris has been removed, pressure testing has been completed, and the unit has been reassembled after the initial flushing.

Sometimes, on large projects, the turnover and commissioning occurs in stages as parts of the facility are completed. In these cases, things like utilities may be started up while the contractor employees are still working in the plant.

Careful procedures and extensive labeling of live systems have to be followed to ensure contractor safety.

The commissioning activities fall into the following general sequence of events:

- Pre-energizing activities
- Energizing the plant
- Conditioning equipment, calibrating instruments, and setting relief valves
- Final checkout and closing of all vessels
- Preparation for "start-up"
- Start-up
- Lining out
- Performance test runs and guarantee test run

Much of this work is carried out by the future operators of the plant to enhance their familiarity with the process, and, as mentioned earlier, the team is often supervised and the activities planned by the responsible startup coordinator (often process engineer(s) or a senior operations specialist). Further description of the major commissioning activities follows.

Pre-energizing Activities

When the plant is handed over by the contractor to the client, no hazardous material such as fuel oil, fuel gas, or permanent electrical power has been introduced into the plant area. Before much of the work to check out and condition equipment, utility services must be established, and that will be the objective of this phase of the work. Normally while the plant is in this "safe" condition, many client companies take advantage of this to carry out their final physical check of the plant on a line-by-line, item-by-item basis.

Although the contractor has flushed the plant out before hand-over, a further and more thorough flush out is advisable before start-up. This is done at this "safe plant" stage when utility lines and underground lines can also be flushed out. If the plant is a unit in an existing complex, oily or chemical drains would at this point be blocked off from the complex's main drain systems. Immediately prior to the plant being energized, these drain systems must be unplugged and checked that they are free of any obstruction.

Energizing the Plant

As soon as the responsible startup coordinator is satisfied that all pre-energizing activities are complete, he will instruct that the utility systems be commissioned. Normally this starts with the introduction of permanent power and the checking of the circuits by the electrical technicians. When this has been completed to the startup coordinator's satisfaction, instructions for commissioning the steam, condensate, and fuel systems will follow. Note: The water system is usually commissioned before the final flush out and the system used for this flushing activity.

The commissioning of the fuel systems indicates that the plant is now a "hazardous area" and all regulations pertaining to this type of area come into effect.

Conditioning Equipment

Certain new process equipment will require conditioning before being used in the process. Some of these are:

Reactors: In some processes these will have refractory lining which will need to be "cured." Curing is the subjection of the refractory to a controlled increasing temperature environment until the curing temperature is reached. The refractory is held at this temperature for a prescribed period of time, before cooling back to ambient temperature. The cooling is also undertaken in a controlled fashion. Many reactors and reactor systems also require drying out. This too is accomplished during this period using heated air or inert gas through the recycle gas compressor, if there is one in the circuit.

Heaters: All heaters will have refractory lining, and these will need to be "cured" as described above. If the heater contains coils that are to be used in steam generation service, these coils need to be treated with hot caustic soda or other cleaning solutions to remove all traces of grease or other undesirable contaminants.

Fractionating columns and vessels generally: These usually need to be dried. This is usually done at the same time that the associated heaters are being conditioned. The hot air or inert gas stream passing through the heater coils to protect them during the refractory curing is routed to the vessels and used for the drying activity.

Piping in sour service: Piping and vessels in high H_2S and hydrogen concentration service are sometimes treated to protect them against local corrosion or embrittlement under these conditions. This is called "pickling" and is usually accomplished by setting up a temporary system. This contains a reservoir for the fresh acid, one or two small skid mounted reciprocating pumps, and a receptacle for the used acid. The pumps deliver the acid through the piping and equipment for a prescribed period of time.

All of these conditioning procedures are provided by the respective equipment manufacturers and would be included as part of the operating manual.

The opportunity is normally taken at this time to calibrate as much instrumentation as possible. Flow meter orifice plates are installed and, where possible, flow meters and control valves are used in these procedures. Relief valves are set (this is always done by the client's organization) and the settings certified.

Final Checkout and Closing Up of All Vessels

This will be the last opportunity to check such items as the internals of towers, fractionation trays, condition of refractory and other linings, holdup grids, distributors, and the bottom of the tower baffling system (to and from the reboiler). A final checkout of the piping layout also needs to be carried out at this point.

When satisfied that all is satisfactory, the startup coordinator will authorize the following final prestart-up activities to be completed:

- Catalyst loaded into the respective reactors. This is often supervised by the licensor's representative. The reactor is closed up by installing the correct operating gaskets. This latter point is made because during the prestart-up activities and conditioning temporary gaskets are used on manways, nozzle connections, and the like. These are replaced by the correctly specified gaskets for the operating conditions. The temporary gaskets are never used again and are thrown away.
- All towers containing random packing are loaded with the packing and closed up. Permanent specified gaskets are used to replace temporary gaskets as described above.
- All other vessels and towers are closed up using the permanent specified gaskets.
- In cases where equipment has been subject to a caustic wash, the temporary silica level gauges used during the wash are replaced by the specified operational ones.

With the completion of these final checks and vessel close-up, the plant is now ready for start-up.

Start-Up and Lining Out

The activities and their sequence for starting up the plant are carried out as described in the operating manual. In the case of an oil refining plant, for example, the first activity is to eliminate air from the plant systems. This is done by using water or steam or inert gas or a combination of all three. The use of steam or water is prohibited for most reactor systems where the catalyst would be irreparably damaged by such contact. Inert gas is circulated using the recycle compressor for this purging. Thus the recycle compressor is commissioned and will then continue to function until the plant shuts down. In the case of the fractionating units of the crude distillation and thermal cracking systems, water and steam are used for purging. The water is used to purge the heaters and tower bottom systems, and steam is used for purging the upper sections of the fractionating towers.

After the purging comes the introduction of the cold feeds. In the case of units that contain reactors and use hydrogen under pressure, a leak testing program is required. First of all the plant is subject to leak testing at operating pressure using the inert gas. Then as the inert gas is replaced by hydrogen, further leak tests are required. All leaks must be repaired before start-up of these units can begin.

Where water has been used for purging, the water is replaced by the oil feed. This is termed the "oil squeeze." The steam is not replaced by anything. It continues to flow through the tower until after start-up where it may then be replaced by the vapor phase of fractionation.

Start-up may be defined as beginning when the purge program shows conditions to be safe to apply heat into the plant. In the case of catalytic plants using a hydrogen stream, the hydrogen stream is circulated and heated up to its operating temperature first. Catalyst activation is normally accomplished during the heatup. When the plant operating conditions are right and the catalyst has been activated, the oil feed may be introduced and heated to process conditions. In some cases, oil may have been introduced during activation, depending on the catalyst.

In the case of non-catalytic units where only fractionation is being carried out, heat may be applied to the oil feed directly. This is done when the oil squeeze is complete and the water content of the oil flowing out of the plant is at an acceptable level. The plant conditions are obtained in accordance with the procedures described in the operating manual by adjusting heat input, reflux rates, pressures, and respective circulating rates in the case of the catalytic plants. Up to the point when the operating conditions have been reached, the total products have been routed to slop. They may be returned later as feed or used in the refinery fuel system. As soon as the plant has reached its operating conditions, product streams are required to be diverted to storage. This is done however only after the product quality has been confirmed by laboratory tests.

Performance and Guarantee Test Runs

Often, as soon as possible after the plant has been lined out and is in production, a performance test run may be carried out. The purpose of this test run would be to establish, as far as possible, the limits of the various systems included in the process. Normal feedstock would be used and the performance of the plant(s) under various operating conditions examined. The other objective of this exercise is to familiarize the operators with the plant control responses to the various changes.

The guarantee test run is a more formal requirement. At the end of the test run carried out over a fixed period and under specific conditions, the client will accept the plant completely or require remedial work and further test runs to meet the guarantees. More details on this test run are given in the next section of this chapter.

An example of a commissioning plan used in the commissioning of a “grassroots” refinery on site facilities is given in Fig. 4. This plan reflects the program for the on-site units and tank farm only. All the utility plants had already been commissioned and started up before this plan begins. The program was successful, and apart from some minor problems, the refinery was brought on stream in the time span predicted.

Process Guarantees and the Guarantee Test Run

Among the last activities that a contractor’s process engineer performs on a project is the preparation of the process guarantees that are usually required by the client and the procedure for testing the plant to meet the guarantees. The process guarantees may begin to be developed as soon as a firm process has been established and

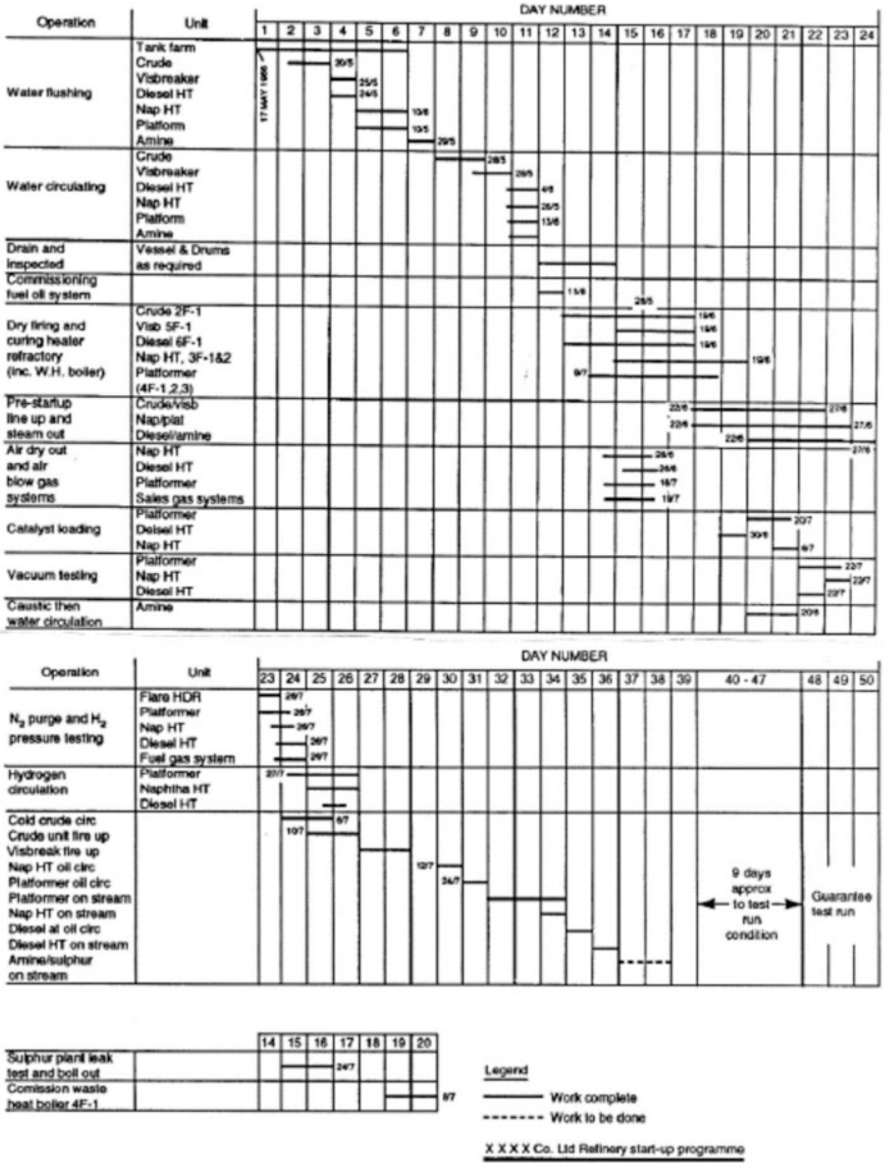


Fig. 4 A typical commissioning plan

manufacturer's guarantees obtained for the performance of the various manufactured items of equipment. The process engineer may be required to guarantee the performance of any plant that he has calculated and specified equipment, piping, instruments, etc. for. He will not be expected to guarantee the performance of any item of plant or piece of equipment he has not specifically designed. He will also not be expected to guarantee any criteria that cannot be measured during a test run. Thus if a process engineer calculates a fractionating unit to meet a specified separation, he will be expected to guarantee that the design will make the separation at the design feed rate and composition. He will not, however, be expected to guarantee the performance of individual items of equipment contained in the unit and which have been properly specified by him. This guarantee is carried by the respective manufacturers who have designed and fabricated the items.

The process performance is tied also to a guarantee of its efficiency. This will be in terms of a guarantee of the utility consumption in the plant while operating on the design throughput and conditions. Of course the guarantees as written will differ from process to process but will usually follow a similar pattern or format. This is as follows:

- Description of the feed in terms of throughput, composition, or source (e.g., in the case of crude oil).
- Design operating conditions and the guarantee of the product specification at these conditions. Alternatively, a guarantee of the fractionation or separation performance of the process in terms of key component separation.
- A guarantee of the hydraulic capacity of the process system. This would only be in the terms that the process system will handle a design quantity per unit time. Note that this hydraulic guarantee would not normally be combined with the stream composition specification guarantee. This is discussed later.
- The utility consumption guarantees. These are usually taken for the total plants in the new or revamped complex. Rarely are utility guarantees written for individual units making up the new or revamped complex.
- A list of the accepted test procedures that will be used.
- The guarantee test run procedures that are written in some detail. Provision is normally made in them for the contractor's process engineer to instruct operating changes to be made as necessary before or during the test run.
- Description of the notices to be given in event that:
  1. The test run was successful and met all the requirements of the guarantee.
  2. The test run was not successful and must be run again.
  3. Some or all of the guarantee requirements cannot be met and a limited liability clause is invoked.

The following paragraphs describe and discuss the contents of a performance guarantee in more detail.

Description of the Design Feedstock

Although the plant may have been designed on the basis of handling more than one feedstock of slightly differing composition, the test run is conducted using one of the design feedstocks as a parameter. This practice is more common in the oil refining industry than in the production of chemicals or even petrochemicals. This is so because most refineries handle crude oil from various sources around the world, and these can vary considerably in composition. The intermediate products from the various crude oils therefore can also vary in composition.

The choice and proper definition of the test run feedstock is absolutely basic in developing the guarantees and assessing the result of the guarantee test run(s). This begins by providing a statement of the design feed throughput. This should be as simple as possible and preferably in the units of measurement used in the client's original "duty specification." If the measurement units used in the design or the units of measurement used in the operation of the process differ from that in the "duty specification," then the conversion factors used to convert from one unit of measurement to the others must be noted here. There must be no ambiguity concerning this quantity.

The second item of importance in this section is the composition of the design feedstock. Where possible this should be a breakdown in the quantity of each component in either weight or molar terms. Occasionally volume composition may be used; however, the composition and the units it is quoted *must* be able to be measured using accepted normal test equipment and/or reagents.

When it is not possible to give the feed composition as described above, other acceptable criteria for establishing the feed quality may be used. For example, in defining the quality or composition of a crude oil or the products of crude oil, distillation boiling points and boiling curves are used (see *Elements of Petroleum Processing* by David Jones, John Wiley & Sons Ltd.). Again however these characteristics of the feedstock must be measurable by accepted means. The test methods to be used in evaluating the guarantee test run results are listed in this document. This item is discussed later.

Test Run Conditions and the Guarantee of Product Quality

Following the description covering the design feedstock comes the heart of the performance guarantee – the guarantee of the end products. This guarantee is always tied to the feedstock and to the conditions that the plant is operated under to meet the product specifications. Where there is a catalytic or any other type of reactor involved in the process, this guarantee may extend to cover the yield of product promised by the contractor or the licensor.

The pertinent process conditions to obtain the guarantee with respect to the end products are defined here. Obviously, these conditions will reflect the basic parameters used in the design of the facility. The process engineer developing the guarantee document must be sure that the conditions described here *are pertinent* to meeting the end product specifications and yield. Over or incomplete definition of the process conditions may lead to ambiguity and conflict in operating the plant under test run conditions.

The product specifications, and product yields under certain circumstances, should reflect exactly those given in the client's "duty specification." Yields and/or product quality which have been left open or to be confirmed by a licensor's pilot plant tests during the compiling of the "duty specification" must be included here. These should be qualified however with reference to the client's acceptance of them and his approval for their use in the plant design. They become part of the client's licensor agreement. The contractor may then develop the remaining process guarantees on the design carried out by him or her based on this approved licensor data.

Performance of the plant may also be judged by the performance of some engineering principle used in the design. For example, in oil refining, the performance of some of the complex fractionators used (e.g., the atmospheric crude distillation unit) is most often defined in terms of fractionating efficiency. This is measured by the difference in the ASTM distillation temperature reading between a 95 vol.% recovery of a light product and the 5 vol.% reading of the adjacent heavier product. The test used to determine these readings is the accepted ASTM distillation test carried out routinely in all refineries. The measure of these test temperatures indicates how much of the lighter product is contained in the heavier one and vice versa. This of course is also a measure of the respective products compositions and the contaminants they contain.

The Hydraulic Guarantee

Although this is tied to the plant design and its ability to handle the feed and product streams as stated earlier, it is guaranteed separately to the performance guarantee described above. This is so because very often it is not possible for a contractor to guarantee the quantity of product that the plant will make. An example of this is again seen in the oil industry. When a contractor's process engineer designs the unlicensed units of an oil refinery, he/she does so using the design crude's assay data. All the product yields and compositions therefore are based on the assay data which the contractor could not have developed – he/she is therefore not expected to guarantee it. From this design calculation however, he/she has sized the various systems in terms of piping instruments and of course specified the various pumps. He/she is expected to guarantee these based on the design flows that were used.

Thus, the hydraulic guarantee should start with the following example statement:

"When the unit is operated on the design feedstock and at the design feed rate, the following systems shall be capable of handling:

- Stream one 450 gpm measured at 60 °F
- Stream two 600 gpm measured at 60 °F. And so on for all guaranteed streams."

Utility Consumption Guarantees

Normally contractors offer utility guarantees as a summation of the cost of all utilities consumed by the process. These are also determined as a summary of the utilities consumed by all the plants considered in the test run. The utility guarantee figure is developed from the utility balances compiled during the process design. Many of these figures are based on manufacturers' guaranteed equipment efficiencies for electric motors and turbines. Others are based on the process heat and material balances. The calculated utility consumption for each utility is multiplied by the respective utility unit cost as provided by the client in his "duty specification." The utility guarantee figure is then quoted as the sum of all these cost items as a single cost figure.

In preparing the utility guarantee, the following should appear in the statement of the guarantee:

- Unit cost of each utility
- Expected normal consumption of each utility
- Either the *guaranteed* total daily cost of all the utilities as one figure (this would include a contingency factor agreed to by the client) or a guaranteed daily cost of all the utilities as a percentage of the expected normal consumption

The descriptions of the remaining items that make up the guarantee document are self-explanatory and are illustrated in the example of a typical process guarantee given in Appendix 2 of this chapter. This example is based on the study case for a thermal cracker illustrated in the various sections of the chapter "▶ Petroleum Refinery Planning and Economics" of this handbook.

In this example, it is assumed that the contract has been awarded on a lump sum basis for engineering, all other home office functions, and the contractor's profit fee. The other costs such as equipment, materials, and the installation of the plant are on a cost payable directly by the client basis.

Appendix 1: An Example of a Process Specification

XYZ Refinery Project

Process Specification for a Thermal Cracker

Number of units. One

Capacity. The unit shall have an input capacity of 34,500 barrels per stream day of a residue from the atmospheric distillation of Kuwait crude oil.

Charge. The normal feedstock will be an atmospheric residuum boiling above 700 °F TBP cut point on Kuwait crude.

Duty. The duty required from this unit will be to thermally crack the feedstock to produce gas, naphtha distillate, gas oil, and fuel oil.

Yields. The unit shall be designed to make the required products in the following relative proportions from the feedstock specified above. The process licensor shall confirm these proportions by pilot plant tests on samples of the feedstock provided by the owner.

	Wt% on feed
Conversion to 340 °F TBP cut point	25.0
Products:	
Gas to C_5	9.0
Naphtha distillate to 390 °F TBP cut point	20.3
Gas oil 390–622 °F cut points	24.7
Fuel oil +622 ° F cut point	46.0

Products

1. The gas shall include C_3s and C_4s and shall be routed to the crude unit overhead distillate drum.
2. The overhead naphtha distillate product shall also be routed to the crude unit overhead naphtha drum. The naphtha product shall have an ASTM distillation end point of not more than 387 °F.
3. The gas oil side stream product shall have an ASTM 90 vol.% distilled at a temperature no higher than 645 °F.
4. The fuel oil as residue from the cracker primary tower shall have a minimum Pensky-Martens flash point of 200 °F and shall be thermally stable.

Process conditions

1. *Thermal cracker furnace*

   It is required that the furnace and transfer line be capable of effecting a crack of 25 wt.% on feed of gas and naphtha to a TBP cut point of 340 °F. The transfer line outlet temperature from the furnace shall not be higher than 920 °F at a pressure of 250 psig. The injection of HP steam into the furnace coils may be considered to increase turbulence and minimize the laydown of coke. Should steam be used, its volume under the furnace conditions must be accounted for in the design of the furnace coil(s). The temperature of the feed to the inlet of the furnace soaking section must be controllable.
2. *The main fractionator*

   The feed to the fractionator from the furnace must be quenched to a suitable temperature to meet the residue cut point requirement. This temperature must also be sufficient to produce enough over flash for proper fractionation between the distillate streams.

   The column will be operated at a pressure in the overhead distillate drum of 50 psig. Naphtha distillate stream shall be maximized, and steam stripping of the gas oil side stream should be considered in this respect. Fractionation criteria in terms of gaps (and overlaps) between the distillate streams shall be:
   ASTM Dist 95 % temp of naphtha and 5 % temp of gas oil to be not less than +15 °F.

   The residue leaving the bottom of the tower shall be steam stripped for flash point control. It shall also be quenched in the well of the tower to prevent further cracking. A cold residue stream is recommended for this quench.

Appendix 2: An Example of a Process Guarantee

XYZ Refinery Project Contract 1234

The process performance guarantees are handled on an individual process unit basis as set forth in subsequent sections of this exhibit. The utility guarantee covers all of the process units associated with this contract and is lumped into an aggregate utility cost as set forth in this exhibit.

Where licensed or proprietary processes not owned by the contractor are involved or proprietary catalysts are supplied by others, such as in the case of the thermal cracker, naphtha hydrotreater, diesel hydrotreater, and catalytic reformer, contractor offers only the guarantees set forth herein and identified as the responsibility of the contractor. Any other guarantees shall be negotiable between client and licensors and are not part of this exhibit.

Thermal Cracker

Feed

The thermal cracking unit shall be designed to process 34,320 BPSD of Kuwait reduced crude to produce gas to C_5, gasoline, gas oil, and fuel oil as residue. The feedstock shall be material boiling above 700 °F TBP cut point from an atmospheric crude distillation unit. The feedstock shall be substantially in accordance with the Kuwait assay titled "Assay of Kuwait 31.2° API Crude Dated xxxxx" and shall have the following properties:

Gravity °API	15.8
ASTM D-1,160, °F	
IBP	650
5 %	750
10 %	775
20 %	800
30 %	850
Pour point (max) °F	85
Viscosity. cSt @ 122 °F	55
Flash point (Pensky-Martens)	>250 °F

Performance Guarantees

1. When owner operates the thermal cracker at conditions defined by the contractor with the feedstock and rates given in section "Feed" above, the estimated (but not guaranteed) yield structure will be as set forth in Table 1 attached.

2. The thermal cracker will be designed so that it will have the hydraulic capacity to process 34,320 BPSD of the feedstock defined in section "Feed" above, with the design yield structure defined in item 1.

Table 1 Design yield structure

	wt% on feed
Conversion to 340 °F TBP in furnace and transfer line	25.0
Products:	
Gas to C_5	9.0
Naphtha to 390 °F cut point	20.3
Gas oil 390–622 °F cut point	24.7
Fuel oil +622 °F cut point	46.0

3. Based on the yield structure defined in item 1, the contractor guarantees that the fractionation section of the unit shall be designed so that the numerical difference between the 5 % point of the thermal cracker gas oil and the 95 % point of the thermal cracked naphtha, expressed as ASTM gap, shall be no less than 10 °F, as measured by ASTM D-86.

4. If the feedstock does not meet the assay defined in item 1 or if the thermal cracker is not operated in accordance with contractor's instructions, then the performance guarantees set forth herein will be modified in accordance with sound engineering practice, as appropriate, based on actual conditions during the test run and using the same data sources and calculation methods as used in the design so as to obtain a true measure of the unit's performance.

5. The test methods that shall be used in evaluating all aspects of this guarantee shall be as listed below:

Feed flash point – ASTM D-93
Feed distillation – ASTM D-1,160
Product distillation – ASTM D-86
Feed viscosity – ASTM D-445
Feed pour point
Gravity – ASTM D-287

Utilities

1. The process units will be designed so that the daily aggregate cost of utilities consumed for all facilities covered in item 2 below shall not exceed $xxxxxxxxx when the process units are operated at the rates and conditions summarized in item 2 and with the individual unit utility costs as summarized in item 3 below.

2. The utility guarantee is based on operating the process units at the rate and conditions summarized below and defined in more detail in the other sections of this exhibit:

New naphtha hydrotreater	13,500 BPSD fresh feed
New naphtha splitter	13,500 BPSD fresh feed
New thermal cracker	34,320 BPSD fresh feed
New light ends unit	3,830 BPSD C_4s, C_3, C_2 mixed feed
New diesel hydrotreater	9,000 BPSD fresh feed
New catalytic reformer	9,000 BPSD fresh feed

This utility guarantee covers only those units listed above and does not include the utilities of any revamped units (such as the existing debutanizer). All conditions regarding feedstock composition and operating conditions defined in this exhibit shall extend to the utility guarantee.

3. The following unit costs for the individual utilities shall be used in computing the daily aggregate cost of utilities:

Fuel gas	$0.47 per MMBtu, LHV
Fuel oil	$0.23 per BPSD
Power	$0.042 per KWH
Water	$0.5/1,000 US Gals
Steam	$0.83/1,000 lb

4. In the event that the daily aggregate cost quoted herein is exceeded, contractor shall have the right to make any alterations it deems necessary in order that the utility guarantee can be met in a subsequent test run. Contractor shall make alterations or pay a penalty as defined herein at his/her sole option.

5. The penalty that the contractor shall pay in the event that the utility guarantee is not met, and the contractor elects not to modify the plant, shall be the difference between the average daily aggregate cost of utilities for the best test run made and the guaranteed daily cost of utilities in herein multiplied by 700.

Qualifications for Guarantees

1. Notwithstanding any other sections or statements in this exhibit, the guarantees in all sections above are subject to change if licensor information, data, or designs for the licensed units should be revised at any time so as to differ from the licensor's information, data, or designs in the contractor's possession on – date – or if licensed units require more utilities than specified by the aforesaid licensor information, data, or designs.

2. In no event shall the contractor be liable for contingent or consequential damages, including damages for loss of products or profit or for plant downtime.

Performance Test Procedures

To determine whether the guarantees defined above are met, the following test run procedure will be used:

1. The contractor will notify the owner in writing when the plant or any portion thereof is ready for initial operation. Within 30 days thereafter, the owner will perform a series of test runs unless delays are caused by deficiencies that are the contractor's responsibility. If the performance test run for the plants or any portion thereof is not conducted by the owner within 30 days after notification by the contractor to owner of availability for test run, it shall be conclusively presumed that the performance guarantees have been met and that contractor's obligations covered herein have been satisfied and owner agrees to pay any sums due to the contractor as if the test runs had been successfully met. The time of these test runs may be initiated at any hour of day or night. Test periods shall be of 72 h duration or less as mutually agreed upon by owner and contractor and may be interrupted as follows:
   a. For minor alterations, repairs, failure of feedstock, utility supply, or other conditions beyond the contractor's reasonable control, each of which does not exceed 24 h, the test run shall proceed promptly after the interruption and as soon as the contractor deems the plant operation has leveled out. The sum of normal operating periods before, between, and after such interruption shall be considered the required test period when it totals 72 h.
2. Owner shall be responsible for supplying all the necessary operating labor, feedstocks, utilities, catalysts, chemicals, sampling laboratory analyses, and other supplies for operating and testing the process units. Owner shall maintain the process units in accordance with good practice, and all catalysts shall be in essentially new condition to the end that the process units will be in proper condition for the performance tests provided for herein.
3. The contractor shall furnish observers and test engineers, excluding licensor personnel, to technically advise owner during the performance tests. Contractor's observers shall have the right to issue instructions regarding the manner in which the plant is to be operated during the test run. Owner shall comply with these instructions unless the instructions are contrary to generally accepted safety practices or expose equipment conditions of temperature, pressure, or stress greater than their maximum allowable operating conditions.
4. Analyses of the streams and products for these tests shall be determined by methods mutually agreed to by owner and contractor. Analysis will be conducted by owner and may be observed or witnessed by contractor. In case of disagreement, a referee laboratory may be selected by approval of both parties and paid for by the owner.
5. Samples shall be spot and/or composite, and sampling procedure shall be by methods as mutually agreed upon by owner and contractor. Samples shall be taken at uniform intervals. Elapsed time between samples or sample increments

shall not exceed 4 h, and composite samples increments shall be of equal volume when flow rate is essentially uniform. All flow rates, product rates, and analysis shall be averaged over the test period. Where possible, tanks shall be gauged at frequent intervals to substantiate meter readings.

6. The performance guarantees shall be considered satisfactorily met when the average of the performance results during the period meets or exceeds the performance specified in this exhibit. Owner shall be responsible for the security of the unit operating log sheets, charts, laboratory test results, gauging records, and other pertinent information for the test period. Within 10 days after the completion of each performance test, owner shall submit a written statement for each unit indicating whether the guarantee has been met. If the test is not acceptable to the owner, then the owner shall specify in writing to the contractor in what respect the performance has not been met. On request the owner shall submit to contractor all records and calculations for review.
7. A performance test run shall be stopped when, in the judgment of the contractor, alterations, adjustments, repairs, and/or replacements which cannot be made safely with the equipment in operation must be made to enable the plant to meet and fulfill the performance guarantees, or the data obtained during the test will not be sufficient to establish the actual performance of the unit within desired limits of error, or it becomes obvious that such performance test cannot be satisfactorily concluded in the current attempt.
8. If a performance test is stopped as provided above, or if the unit or units do not meet their guaranteed performance during the test run, owner, when requested, shall make the unit or units available to the contractor as soon as possible to make such alterations or additions thereto as, in the contractor’s judgment, is required to enable the plant to fulfill the aforesaid guarantees. If the owner does not make the unit or units available within 3 months, the performance guarantee will be considered to have been met in its entirety. Contractor will make such alterations as it shall deem necessary to make the unit or units perform as guaranteed and a further performance test shall be conducted in accordance with the above procedure.
9. Process performance tests for the units described in this exhibit along with the appropriate pro rata of the utility guarantee as set forth above in all of this exhibit, may be carried out collectively and/or on an individual basis as may be mutually agreed to by owner and contractor. If a test run involving more than one process unit or section of a process unit indicates that any unit or section meets its guarantees as set forth in this exhibit, then that unit or section shall be accepted.
10. Notwithstanding any other provision hereof, contractor’s liability for making the changes to units to make them perform as guaranteed in this exhibit shall be limited to $xxxxxx. In determining the total cost expended by contractor, there shall be included the engineering costs to the contractor of making the necessary design changes and the labor and material costs of implementing these changes.

Part II

Variations

Non-energy Refineries in Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

Abstract

Not all refineries are aimed at producing fuels. This chapter focuses on two significant types of non-energy facilities: (1) lube oil refineries and (2) petrochemical refineries. In the lube oil discussion, we explore the nature of lubes and the various process routes used to make them. Routes include conventional deasphalting and extraction, hydroprocessing, Fisher-Tropsch synthesis, and

---

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_9

oligomerization. Related to lubes, we explore the production of asphalt, with a process discussion and an example design. In petrochemicals, an aromatics complex is described, along with the processes used to make the typical BTX streams.

Keywords
Lube oil • Refinery • Petrochemical • Asphalt • Dewaxing

Introduction

Non-energy refineries refer to those plants that produce non-energy products from crude oil. These fall into two categories:

Lube oil refineries
Petrochemical refineries

Both of these types of refineries have already been mentioned earlier in this handbook. This chapter provides further details on these two important refining aspects of crude oil.

Lube Oil Refineries

A lube oil refinery is often included as part of a conventional energy refinery, but may also be a separate facility, depending on the chosen process route. Often the lube oil section of the facility will take its feed from the atmospheric distillation tower in the form of an atmospheric residue stream. The balance of the crude oil not used in the lube complex is processed through the conventional refinery units – hence the normal incorporation of a lube complex along with a refinery.

Traditional, conventional lube refining uses solvent extraction processes to separate undesirable materials from the natural desirable ones present in the crude oil. About half the lube oil supply today comes from these solvent processes. However, many of the world's crude oils do not have enough of these desirable molecules in them to justify the cost of elaborate extraction processes, and therefore lube oil refining leans toward processing the "desirable" lube oil crude oils. An example of desirable lube oils is those from Venezuela (i.e., Tia Juana and the heavy Bachaquero crude). This restriction on lube oil production often leads to large refineries dedicating a separate atmospheric distillation unit to provide the necessary lube complex feed.

The problem of lube oil selective crude oils has diminished with the development of alternative processes that produce much higher-quality lube stocks from lower-quality crudes. These processes virtually eliminate the need for solvent extraction and dewaxing of the lube oil stock. Processes are also being employed to make lubes from feedstocks other than conventional crude oils.

In one common alternative, hydrotreating of light vacuum distillates to make lube oil specification has been in commercial use since the mid-1960s, but with the advancement of this technology, the heavier lube oil stock can also be treated in a similar manner. Lube base oil production by severe hydrotreating, hydrocracking, and hydrodewaxing/hydrofinishing also improves color and stability, but each crude source of the lube oil stock requires different processing conditions in these hydroprocesses. This in turn leads to different yields of the various cuts to meet their specified viscosity. This production approach is quite common today for making high-quality lube base oils, accounting for about half of base lube oil production in 2004.

Even higher-quality base oils can be produced by gas-to-liquids (GTL) technology. The GTL process makes pure paraffins, which can be hydrocracked and isomerized to very pure, clean, stable lube stocks. This approach has been commercialized in a few locations. These locations can be independent of a refinery, since they do not depend on crude oil.

Another type of lube stock commonly produced is the mixed poly-alpha-olefins or PAOs. These are the product of chemical oligomerization or polymerization of specific alpha (or primary) olefins to make high molecular weight branched molecules. Development of these materials was an outgrowth of plastics manufacturing. PAOs make very high-quality lube base oils, but they are expensive. This is another type of lube stock which is not normally tied directly to a refinery.

There are numerous other types of lube base oils that can be derived from hydrocarbons. These include organic esters and polyesters, polyphenyl ethers, silicate esters, phosphate esters, polyalkene glycols, and various fluorocarbons. These specialty products are low-volume materials that are not normally made in a refinery and will not be discussed in any detail here.

Finished lubricating oils are actually blends of various “base oils” with additives to meet a specific set of specifications. There are hundreds, if not thousands, of lubricants blended from the various components available. The primary refined products are really just the base oils that go into the blends. Normally, separate lubes compounding or blending and packaging plants produce the final lube oil products. We will not be dealing with these compounding plants in detail in this reference.

The following discussion will provide an overview of lube base stocks, their important properties, and the most common processes used to make them. We will start by discussing some of the basic background for lube oils.

Definitions and Specifications

Lube oil refining has developed its own series of definitions quite separate from those of the conventional energy refineries. Some of the key definitions are:

- *Lube Base Stock*
  This refers to a lube product that meets all lube specifications and is suitable for blending to meet performance specifications.
- *Lube Slate*
  A lube slate is the set of lube base stocks produced by the refinery. This is usually a set of 4–6 base stocks.

- *Neutral Lubes*
  These are obtained from straight-run cuts of the vacuum tower.
- *Bright Stock Lubes*
  These are processed from the raffinate of the vacuum residue deasphalting unit.
- *Virgin Base Lube Oils*
  These are those base stocks obtained by processing straight-run distillates from crude.
- *Re-refined Base Stocks*
  These are those processed from used or recycled lube oils. Refer to the chapter on "▶ Unconventional Crudes and Feedstocks in Petroleum Processing" in this handbook for a more detailed discussion of re-refining.
- *Finished Lube Oil*
  This is a lube oil that has been blended to meet a final specification.
- *Paraffinic Lube Oils*
  These are all grades of lube oils, from both neutral and bright stocks, that have a finished viscosity index (VI) greater than 75.
- *Naphthenic Lube Oils*
  These are lubricants with a VI less than 75.

There are two important specification definitions for lube oils. These are:

- The quality specification
- The performance specification

Quality Specifications

Quality specifications include those for kinematic viscosity, viscosity index, pour point, color, and flash point. These specifications are determined by standard tests from organizations such as the ASTM, SAE, or API. The specifications generally detail the characteristics considered important to the application of the specific lube oil. For example, one very well-known motor oil specification is SAE viscosity, established by the Society of Automotive Engineers, an organization that also carries out research and publishes specifications on a wide range of automotive topics. Figure 1 gives a range of viscosities versus temperature for a family of motor crankcase oils.

Although the kinematic viscosity is measured in centistokes, specifications may be labeled in Saybolt seconds universal (SSU).

Performance Specifications

Finished lube oil products are usually certified or qualified against performance specification requirements established by equipment and vehicle manufacturers, government bodies, and industrial organizations such as the SAE. These qualifications usually require extensive performance testing using specialized apparatus and engines (including road tests). These tests refer only to those base oils produced in a specific manner and from specific crudes. Significantly altering the process scheme or the crude source could violate the intent and validity of the performance qualification certificate.

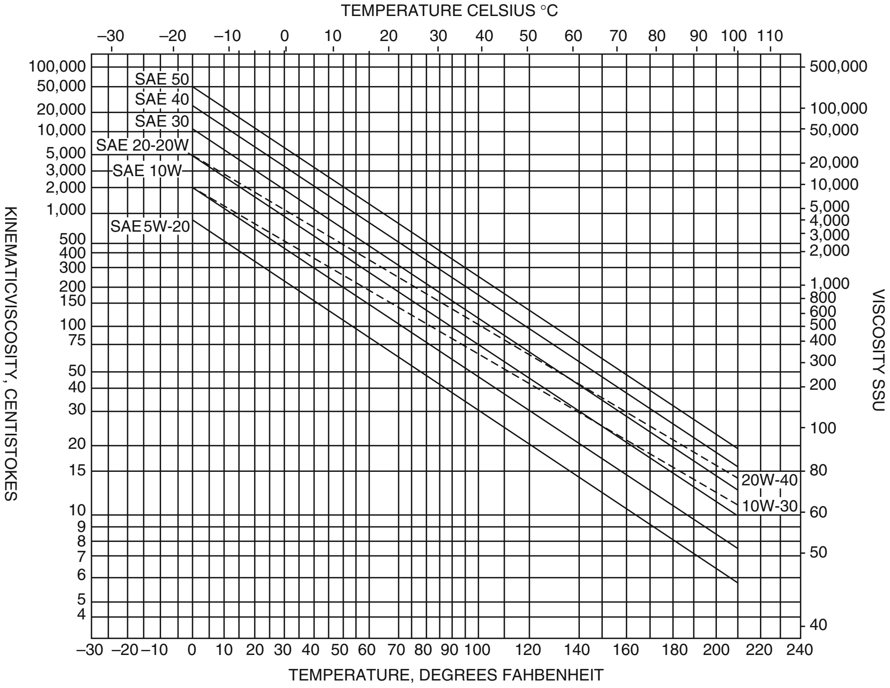


Fig. 1 Viscosity versus temperature of crankcase oil

The performance of the lube base oils in service cannot be measured until after the production sequences are long completed. Manufacturing lube base oils therefore requires good correlations between measured properties at each stage of production and the final product performance quality. Developing these operating guidelines and correlations for plant units usually requires pilot plant and full plant test runs for each crude oil feedstock and finished products.

Lube Oil Properties

The important properties that are recognized in lube oil production are:

- Viscosity
- Viscosity index
- Pour point
- Oxidation stability
- Flash point
- Thermal stability
- Volatility
- Color

These are discussed in the following paragraphs.

Viscosity

This is the single most important characteristic of any lube oil. At its service temperature, it is balanced to prevent wear and to enhance fuel economy. Most bearings operate with a hydrodynamic wedge-shaped film of lubricant between the bearing surfaces. This mechanism minimizes wear of the surfaces under the operating conditions of the machinery. To accomplish this, the lube oil must have adequate viscosity for the operating load, bearing speed, and the bearing surface smoothness to allow the hydrodynamic head to form and remain between the surfaces. Too high a viscosity will cause extra friction and heat, while too low a viscosity will allow the surfaces to touch. A bearing may operate over a wide temperature range, as in an engine or automatic transmission, and the lube oil has to have adequate viscosity over the entire temperature range to be effective.

Viscosity Index

This is a measure of the amount the viscosity of a lube oil will change with temperature. A high viscosity index denotes less change of viscosity with temperature. A high viscosity index is necessary for lube oils that are to be used for services with a large temperature operating ranges.

Pour Point

This property is important for any application in cold climates. Too high a pour point will result in the oil being gelatinous or even solid at ambient temperatures.

Oxidation Stability

This is also an important requirement for a lube oil that is to operate under severe high-temperature conditions. If the oil has a tendency to oxidize, the product of oxidation is often hard granules (similar to coke) which will damage bearing surfaces and block up the lube oil system filters and ports.

Flash Point

The flash point of a lube oil must be high enough to be safe under any of the temperature conditions that the lube oil will be required to operate.

Thermal Stability

This property requirement is similar to that for oxidation stability. In the case of thermal stability, the lube oil must be able to operate within its specified temperature range without the danger of the oil cracking or breaking down and giving rise to harmful polymers, acids, or other compounds.

Volatility

This property is important for ensuring minimum vaporization of the oil and thus maintaining the lowest oil consumption.

Color

Unusually dark coloring in a lube oil is indicative of the presence of olefins. These are undesirable in lube oils as they are thermally unstable. Lube oils are often filtered through a clay bed (usually bauxite) to improve color. Hydroprocessing always results in lube stocks with good color.

Lube Base Oil Group Classifications

The base oils used to blend finished lubes are divided into five classifications or "groups" by the API. The groups are distinguished from each other by their sulfur contents, saturate molecule content, and viscosity index. The categories and the typical processes used to produce the stocks are in Table 1.

In general, the higher the group number, the more valuable the product and the more difficult it is to produce. Groups II+ and III+ are not officially defined grades; but these terms are in common use for oils that are more toward the premium VI range of Groups II and III, respectively.

The trend today is toward the use of more lube oils in Groups II or above. This trend is driven by increasingly severe performance requirements which are, in turn, driven by demands for smaller, more efficient engines with higher stresses and higher temperatures. The high viscosity indices and high stability of oils in Groups II through IV fit well with the engine demands.

A Description of Major Processes in Lube Oil Refining

Figure 2 provides block flow diagrams for the general refining routes to lube oil stocks that meet the requirements of the primary base oil groups. In the discussion that follows, we will describe the primary processes used to perform solvent refining in some detail and will discuss the hydroprocessing, gas-to-liquids, and poly-alpha-olefins routes briefly.

The major processes described here are:

- Traditional solvent-based lube production
  - The propane deasphalting process
  - An aromatic extraction – furfural
  - A dewaxing process – MEK

Table 1 API base oil classifications

Group	Sulfur, wt%	And/or	Saturates, wt%	Viscosity index (VI)	Typical processes
I	>0.03	And/or	<90	80–120	Conventional solvents
II	≤0.03	And	≥90	80–120	Solvent with specific crudes, hydroprocessing, GTL
(II+)	≤0.03	And	≥90	110–119	Hydroprocessing, GTL, specific crudes
III	≤0.03	And	≥90	≥120	Hydroprocessing, GTL
(III+)	≤0.03	And	≥90	130–150	Hydroprocessing, GTL, specific crudes
IV	~0	And	>99	≥140	Poly-alpha-olefins
V	All others (esters, naphthene-based (<75 VI), polyglycols, poly-internal-olefins, etc.)				

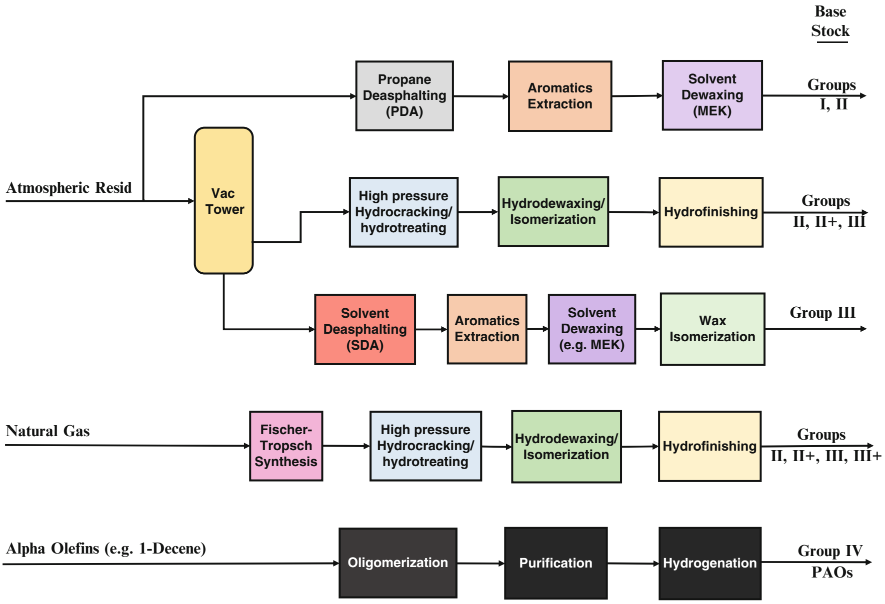


Fig. 2 Some of the lube oil production process options

- Hydroprocessing route
  - Hydrotreating/hydrocracking
  - Hydrodewaxing/isomerization
  - Hydrofinishing
- Gas-to-liquids route
- Poly-alpha-olefins production

Traditional Solvent-Based Lube Production

Propane Deasphalting Process

Deasphalting the heavy end of crude, that is, the vacuum residue, is not entirely reserved for the production of lube oils. In energy refineries, it is used to remove the asphaltene portion of the residue to prepare a suitable feedstock for catalytic conversion units. In most of these conversion units, the performance of the catalyst is greatly impaired by the presence of heavy metals and the high Conradson carbon content of the residue feed. Most of the metals are contained in the asphaltene compounds which make up most of the asphalt portion of the residue. These asphaltenes are also high in Conradson carbon content, so the removal of these serves to eliminate both the heavy metal content and the high Conradson carbon.

In the case of lube oil production, the light liquid phase resulting from the extraction of the asphalt makes excellent lube base oil. This deasphalted oil is termed “bright stock” and can now be further refined in the same way as neutral

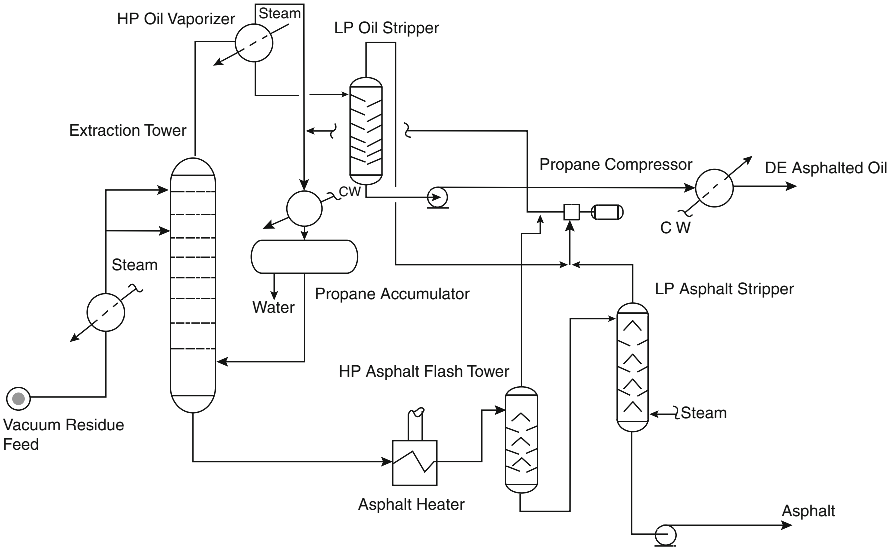


Fig. 3 Propane deasphalting process

base stocks which are vacuum distillates to meet the specifications for blend stocks. The process configuration is shown as Fig. 3.

The configuration shown here is that for a propane deasphalting unit. Vacuum residue feed enters the unit directly from the vacuum distillation tower and is heated to an inlet temperature of around 140 °F before entering the top section of a trayed extraction tower at a pressure of 485 psig. Liquid propane is introduced into the bottom of the tower below the bottom tray.

The propane solvent moves up the tower countercurrent to the precipitated asphalt. The extracted asphalt is removed from the bottom of the tower and is routed through a fired heater to enter the top tray of a baffle-trayed separator. Some of the propane entrained in the asphalt phase is removed from the overhead of the flash tower. The asphalt phase leaves the bottom of the flash tower and is reduced in pressure before entering the asphalt stripper tower above the top row of baffles. Steam is introduced to the bottom of the tower, and the remaining entrained propane is stripped out of the asphalt. The stripped asphalt leaves the bottom of the tower, is cooled to battery conditions, and is routed to storage or the asphalt blending plant. The propane stripout enters the suction side of a propane compressor and on discharge routed to the propane accumulator.

The deasphalted oil phase from the extraction tower overhead enters a high-pressure oil vaporizer which removes most of the entrained propane. The propane stream leaves the vaporizer to be cooled and enters the propane accumulator. On leaving the vaporizer, the oil phase enters the top row of baffles in a low-pressure stripper tower. Steam is introduced to the bottom trays of the tower and moves up the tower countercurrent to the oil phase. The residual propane is stripped out of the

Table 2 Product yield and properties – propane deasphalting

	Feed	Deasphalted oil	Extract
Yield vol%	100	52	48
Gravity °API	11	21	1.5
Viscosity, SSU at 210 °F	1,150	175	–
Viscosity, SSU at 275 °F	–	–	250
Con. carb. wt%	10	2.7	–
Color TR dilute	–	9	–
Softening pt, R&B, °F	–	–	135

oil phase and leaves the top of the stripper tower with the steam. This overhead vapor stream joins the stream from the low-pressure asphalt stripper at the suction of the propane compressor.

The compressed propane is cooled and drained free of the water from the stripping steam in the accumulator. The dry propane is then recycled to enter the extraction tower.

Typical data on deasphalting Aramco crude residuum for lube oil with a propane treat of 600 % volume on feed are as follows (Table 2).

The salient operating conditions for this unit are as follows:

Treater tower	
Top temperature	140 °F
Bottom temperature	105 °F
Tower pressure	485 psig
Deasphalted oil vaporizer	315 °F
Deasphalted oil stripper	310 °F
Vaporizer pressure	220 psig
Stripper pressure	5 psig
Asphalt flash tower	525 °F
Asphalt stripper	515 °F
Flash tower pressure	220 psig
Stripper pressure	5 psig

Lube Oil Extraction Process: Furfural Extraction

The furfural extraction process described here is designed to produce lube oil base oils (before dewaxing) having high viscosity indices and other desirable lube oil qualities, such as color and stability. The furfural process is one of a few means of removing aromatic and naphthenic compounds from both neutral feedstocks and the bright oil feedstocks (deasphalted oils) by extracting them using furfural as solvent. The other most common processes to attain this are extraction using liquid SO_2 as solvent and a process using phenol as solvent. The furfural process configuration is shown below as Fig. 4.

Either straight-run distillate feed or bright stock oils (or a blend of both) enter a trayed extraction tower below the bottom tray. A dry furfural stream enters

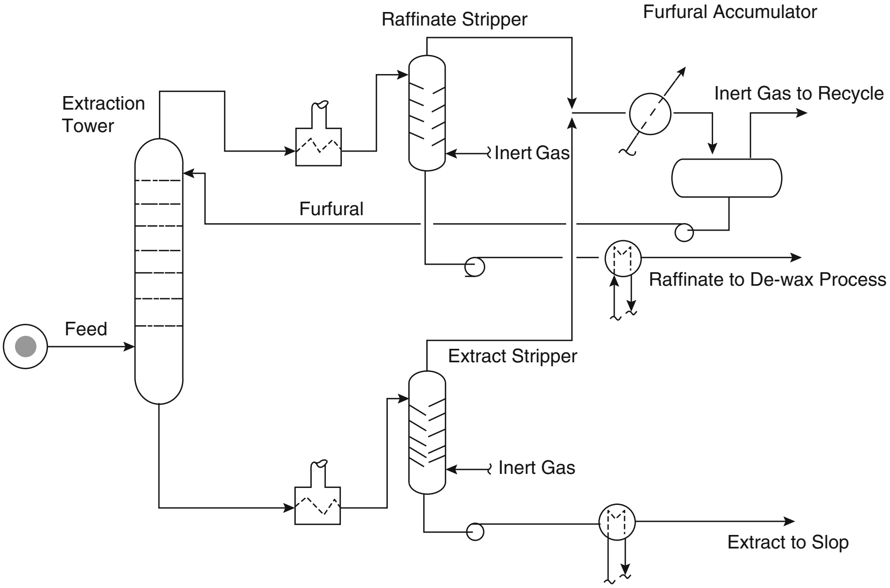


Fig. 4 A furfural lube oil extraction process

above the top tray to move countercurrent to the oil feed. The undesirable compounds are removed from the lube oil feed to leave the bottom of the tower as a rich furfural stream. This stream is heated in a fired heater before entering an extract stripper. The furfural is stripped off and leaves the top of the stripper to be cooled and enters the furfural accumulator vessel. Stripping of the furfural is achieved using an inert gas stripping stream introduced below the bottom row of trays in the stripper. Inert gas is used as the stripping medium because furfural is highly susceptible to polymerizing upon exposure to steam or air. The extract leaves the bottom of the tower to be cooled and is routed to refinery fuel or the fuel oil pool.

The raffinate oil, essentially free of aromatic and naphthene compounds, leaves the top of the extraction tower to be heated in a fired heater before entering the raffinate stripper. The entrained furfural is again stripped out using an inert gas as the stripping medium leaving the raffinate to be routed from the bottom of the stripper to a dewaxing plant. The stripped furfural stream leaves the top of the stripper to be cooled and collected in the furfural accumulator.

The entrained inert gas from the stripping is flashed off the furfural collected in the accumulator to be either vented to the atmosphere or returned to the refinery's inert gas system.

Some data on this process is given in Table 3. These data are based on two typical feedstocks A and B which cover the usual range of feedstock parameters.

The extraction tower operates at between 150 and 200 psig and at a top/bottom temperature of between 190/140 °F and 195/135 °F.

Dewaxing Process: MEK Dewaxing

There are several dewaxing processes in use today. Among them are the propane dewaxer, Edeleanu's SO_2/benzoyl combination of extraction and dewaxing, the MIBK (methyl isobutyl ketone), and the more common MEK (methyl ethyl ketone) process. These processes, except the Edeleanu process, have a similar process configuration. The one based on MEK is shown in Fig. 5. More modern processes include catalytic dewaxing.

Either neutral base oil or bright stock from the extraction unit is mixed with MEK before entering a tubular chilling unit. During the chilling of the mixture, the wax content in the oil forms crystals in the presence of the MEK. The chiller tubes are furnished with internal chain scrapers which collect the oily slurry. This stream is then introduced to the bottom trough of a rotary filter. The outer drum of the filter is covered by a filter cloth. The drum in turn is divided into two or sometimes three

Table 3 Product yields and properties – furfural extraction

Untreated oil	Feed A	Feed B
Viscosity index	70	89
Gravity °API	25	28
Viscosity, SSU at 210 °F	55	44
Treated oil		
Yield vol%	69	55
Viscosity index (dewaxed)	102	113

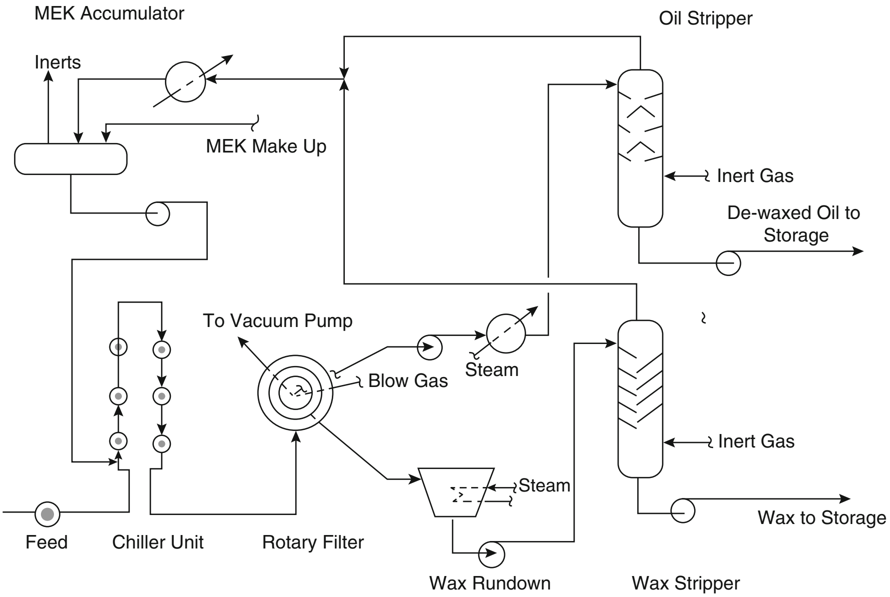


Fig. 5 Configuration of a MEK dewaxing process

chambers. The first is under vacuum and draws the oily slurry in the trough through the filter cloth. The oil phase, free of wax crystals, flows though the cloth to the inner section of the drum. The wax is retained firmly on the cloth. In some processes, a stream of the dewaxed oil is returned as a wash to the wax cake. As the drum rotates, it enters the second phase of its operation. Here a positive pressure in the form of an inert gas stream is applied to the rear of the wax cake. This lifts the cake off the filter cloth sufficient for a disengaging scraper to remove the cake and deliver it to a heated trough where the wax is melted. The molten wax is pumped from the trough to the top row of baffles in a wax stripper tower. Here the wax is stripped free of MEK using a stream of inert gas passing upwards through several rows of baffle trays countercurrent to the wax stream. The stripped wax is pumped from the bottom of the stripper to storage and further treating.

The dewaxed oil phase from the filter is pumped from the inner chamber of the filter to a steam heater and then to the top row of disk and donut trays in the oil stripper tower. Inert gas flows upwards through several rows of trays countercurrent to the oil flowing downward. The oil is stripped free of MEK and leaves the bottom of the tower to storage and use as blend stock.

The MEK from both strippers is collected, cooled, and routed to an accumulator drum. Here the absorbed inert gas and the blow gas are flashed off to be recycled or vented. The MEK is returned to the system by a pump to join the waxy oil feed at the chillers. Table 4 lists some typical yields and product properties from MEK dewaxing.

Hydroprocessing Route to Lube Oil

With the demand for higher-purity, higher-VI lube oils, a hydroprocessing route to lubes was developed in the 1960s. There are several locations employing this route to make Group II, II+, and III base oils. The processes will be briefly described here. These same processes are also employed in converting raw GTL feed to base oils.

The overall process block flow for the hydroprocessing route is shown was Fig. 2 as the second string from the top of the figure.

Table 4 Product yields and properties – MEK dewaxing process

	Feed A	Feed B	Feed C
Feedstock			
Viscosity, SSU at 210 °F	41	58	126
Pour point, °F	95	110	125
Flash point, °F	400	450	540
Products			
Dewaxed oil, vol%	70	77	80
Pour point, °F	15	15	10
Cloud point, °F	20	18	12
Slack wax (wax product)			
Yield, vol%	30	23	20
Oil content, wt%	25	20	15

Hydrotreating/Hydrocracking

The primary objectives of the hydrotreating/hydrocracking portion of the hydro route are:

- Eliminate sulfur, nitrogen, olefins, metals, and other contaminants from the stock via hydrotreating. This improves the stability of the resulting base oil.
- Saturate aromatics as completely as possible.
- Increase product yield through mild hydrocracking of the heavy vacuum gas oil feed.

Early lube oil hydrocrackers operated more as hydrotreaters at relatively mild conditions. Newer units operate at much more severe conditions and tend to use high-activity hydrotreating catalysts combined with mild hydrocracking catalyst at very high pressures (2,500 psig and higher). The high pressure promotes aromatic saturation and allows operation at relatively low temperatures which also help saturation. Because the conditions tend to center around aromatic saturation, the hetero-compounds (S, N, O, etc.) and olefins are easily eliminated. Metals are absorbed quantitatively onto metals traps in the reactors. Hydrocracking is also easy at the elevated pressure.

Process conditions in these units and the details of their operation are proprietary. The resulting hydroprocessed gas oil product is extremely clean and stable with low contaminant levels. It is, however, heavily “waxy” with a high pour point that is undesirable. The hydrocracked product can be dewaxed and finished using the solvent methods previously described; but, the product using the solvent approach is inferior to continuing the hydroprocessing approach with the following processes.

Byproducts from this process include ultralow sulfur distillates and naphthas which become valuable products for a refinery tied to the lubes complex. These materials are vacuum fractionated out of the “waxy lube stock” (WLS), before the gas oil boiling range WLS is sent to further processing.

Hydrodewaxing/Isomerization

The second step in the hydro route to lubes involves dewaxing the hydrotreated/hydrocracked product. This step also uses severe hydroprocessing conditions at high pressures. The proprietary catalysts used primarily promote mild hydrocracking and/or isomerization of the heavy paraffins.

Hydrofinishing

The final step is hydrofinishing where the last vestiges of contaminants and olefins are removed and aromatic saturation is taken as far as possible. The resulting lube stock goes through final distillation to produce the desired base oil cuts.

Base Stock Properties from the Hydroprocessing Route

Table 5 presents typical properties from various stages in the hydroprocessing route to base oils. Note how the properties vary between steps. The resulting base oil can

Table 5 Hydro route product property examples

	Example changes through process steps				Typical product properties	
Process point	Fresh feed VGO	After hydrocracking	After hydrodewaxing	After hydrofinishing	Group II product	Group III product
Viscosity index	70–85	<130	>120	>120	100–103	>120
Sulfur	2–3 wt%	<10 wppm	<5 wppm	<1 wppm	<1 wppm	<1 wppm
Aromatics	40–60 %	<10 %	<2 %	<1 %	<1 %	<1 %
Pour point, °C	+25 to +50	+30 to +40	<−15	<−15	−13 to −15	<−15
Color	L3.0 to L4.0	L0.5 to L2.0	~+20	+30	L 0.5	+30

Source: Hilbert et al. (2013)

be either Group II/II+ or Group III/III+ depending on the severity of the process conditions. There is necessarily a balance between yield and product quality that must be considered.

Hydro Route Technology Sources

It has been noted that the processes involved in the hydro route are proprietary. The primary suppliers of these technologies (all or portions) include:

- ExxonMobil
- Chevron Lummus Global (CLG)
- Shell Oil Company
- UOP, A Honeywell Company

Gas-to-Liquids (GTL) Route to Lube Oil

Improvements in the late 1990s and 2000s along with low natural gas prices have made it more economical to produce paraffin liquids from natural gas using Fischer-Tropsch (F-T) synthesis. These are essentially pure wax, with very little branching. The paraffin chain length ranges can be predicted fairly accurately. This wax makes a clean feedstock that can be converted to lube oils. A few plants have been built to use this route to high-value products. Please refer to the chapter concerning unconventional crudes and feedstocks for additional details about the GTL process itself.

In lube production, after the Fischer-Tropsch synthesis step, the process path generally follows the same route as the hydroprocessing route to lubes. The dewaxing/isomerization step is particularly important because of the high wax content. Since the F-T product is so pure, it is possible to make premium Group II, II+, III, and III+ base oils via the GTL route.

Some lube base stock properties from GTL are compared with typical Group III and Group IV stocks in Table 6.

The GTL route to lubes is currently (2014) in production by the Shell Oil Company. Licensors for the technologies include Shell and ExxonMobil.

Poly-Alpha-Olefins (PAOs) Production for Lube Oil

Poly-alpha-olefins (poly-α-olefins or PAOs) as applied to lube base stocks are produced by catalytic oligomerization of primary or alpha olefins, normally something like 1-decene. The reactions are carried out in a continuous-stirred tank

Table 6 Comparison of GTL products with other lube base oils

Property	Typical group III	GTL base oil	Typical group IV
Viscosity index	120	140–155	120–140
cSt at 100 °C	4.2	4.0–9.0	4.0
Volatility, wt%	15	<10	12.7
Pour point, °C	−15	−21	−64
Sulfur, wppm	<300	<1	<1

Source: Silvy et al. (2010)

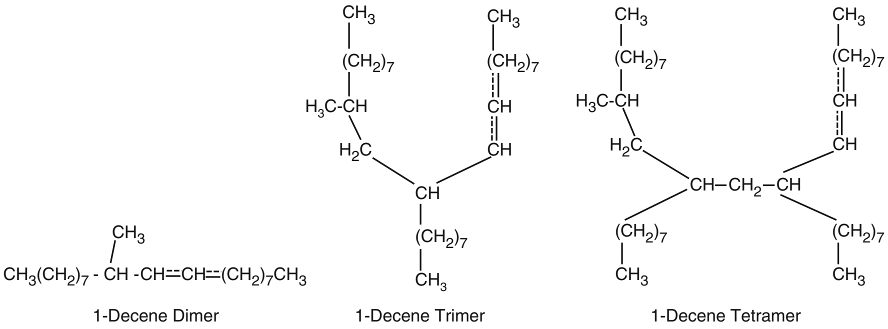


Fig. 6 Oligomers of 1-decene (typical poly-alpha-olefins)

Table 7 Typical poly-alpha-olefin base oil

Property	Typical group IV PAO
Viscosity index	120–140
cSt at 100 °C	4.0
Volatility, wt%	12.7
Pour point, °C	−64
Sulfur, wppm	<1

Source: Silvy et al. (2010)

reactor. The resulting dimers, trimers, tetramers, etc. have VIs in the neighborhood of 140 or higher and a good range of viscosity for lube base stocks.

As an example, typical oligomers from the 1-decene reactions are shown in Fig. 6.

Note that the oligomers contain some remaining double bonds that require a final hydrogenation step to stabilize them.

Typical PAO base lube oil properties are in Table 7.

Lube Oil Conclusion

Approximately 850,000 BPD of lubricating oils were produced worldwide in 2009. Of this total, the breakdown by base stock group looked something like:

Group I (solvent extraction)	61 %
Group II (hydrocracking)	30 %
Group III (hydrocracking, others)	6 %
Group IV (PAOs)	2 %
Group V (all others)	1 %

The proportion of Group I stocks has been declining for decades, even as lube demand has risen slowly. In 1990, Group I oils accounted for almost 99 % of the base stock supply. Groups II and III are growing fairly rapidly, and that trend is expected to continue as the demand for better, more stable lube oils increases.

Asphalt Production

Almost invariably associated with the lube oil refinery are facilities for the production of asphalt. It is a popular belief, even among engineers, that asphalt can be made from the heavy end of any crude oil. Unfortunately this belief is far from being correct. The asphalt product must have a series of properties which meet the specifications for the different grades. Since many of these properties are interrelated, it is difficult to meet all the specifications at the same time. The penetration/softening point relationship is probably the most important property to be considered from this standpoint.

The ideal crude for asphalt production should be heavy; should have a high, good-quality asphalt yield; and, of course, should be inexpensive. The oxidizing properties of the asphalt must also be considered. Some crudes will produce fine paving stock, but will not be good feed for air blowing, when the specification of the product calls for an “oxidized” asphalt.

Types of Asphalt Products

There are two major categories of asphalt products. These are:

- Paving and liquid asphalt
- Roofing asphalt

The Paving and Liquid Asphalt

The paving and liquid asphalt products are again subdivided into five paving grades and three liquid grades. The paving grades will have a penetration specification of 300 or less at 77 °F and 100 g weight, while the softer liquid grades will have a penetration of 300 and higher. The five paving grades fall into the following categories based on their penetration:

$$40-50, 60-70, 85-100, 120-150, 200-300.$$

The liquid asphalt grades are typified as RC (rapid curing), MC (medium curing), and SC (slow curing). Each of these grades will also have four viscosity grades as given below:

70 grade – RC/MC/SC	70–140 cSt at 140 °F
250 grade – RC/MC/SC	250–500 cSt
800 grade – RC/MC/SC	800–1,600 cSt
3,000 grade – RC/MC/SC	3,000–6,000 cSt

Rapid-curing cutbacks are penetration asphalt and naphtha blends having a viscosity range from 75 SSF at 77 °F to 600 SSF at 180 °F. The naphtha content may be as high as 75 vol%. Cutbacks are hot sprayed onto existing roads as a binding medium for new wearing surfaces.

Medium-curing cutbacks are penetration grade asphalt and kerosene blends with four grades having the same viscosities as the RC cutbacks. These are used in road building in the same way as the RC cutbacks.

Slow-curing cutbacks are penetration asphalt and gas oil blends normally produced directly from the crude oil atmospheric or vacuum distillation. The volume produced is small and they are used mainly as a gravel dust layer or mixed with aggregates for cold patching of asphalt surfaces.

Roofing Asphalt

The second largest asphalt use is that for roofing. Most of these asphalts are produced by air blowing. There are three major roofing grades that may be classified by penetration and softening points. These are:

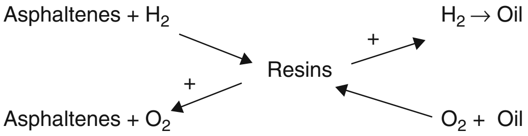
	Pen at 77 °F	Softening point °F
Type 1	25–50	140–150
Type 2	20–30	166–175
Type 3	15–25	190–205

Type 1 grade is used on “dead flat” roofs while the other two are used on intermediate and steep-slope roofs, respectively.

Asphalt Oxidizing Mechanism

Asphalt is basically a colloidal dispersion of asphaltenes in oil with resins as the stabilizing agent. The quantities of these can vary widely with the type of crude.

Asphaltenes can be hydrogenated to resins and resins to oils. Resins can be oxidized to asphaltenes and oil to resins. Thus:



Oxidation is really a misnomer, as air-blown asphalt has essentially the same oxygen content as the charge. Air blowing in asphalt increases the asphaltene content, hardens it, decreases penetration, increases softening, and reduces ductility. Basically air blowing is a polymerization process following the route below:

1. Addition of O_2 to form unstable compounds from which H_2O is eliminated leaving unsaturated compounds which polymerize
2. Addition of O_2 to form carboxyl derivatives from which CO_2 is eliminated followed again by polymerization

3. Formation and elimination of volatile oxidation products other than H_2O and CO_2 followed again by polymerization

It is worth noting that the best crudes for asphalt air blowing are those with high percentage of asphaltene fraction and low in paraffin hydrocarbons and waxes. Resins can be oxidized to asphaltenes relatively easily, so crudes rich in resin are good raw materials for asphalt manufacture. Oils can also be oxidized to asphaltenes, but they must be oxidized to resins first, which requires a more severe operation. Cracked residua simply do not make good asphalt.

Asphalt Yields

In general heavier crudes contain a higher content of asphalt or asphaltic material and this is demonstrated in Fig. 7.

The actual yield of these materials depends mainly on the composition of the crude itself in terms of the paraffinic, olefinic, asphaltenic, and naphthenic fractions it contains. Good reliable crude oil assays provide such data for specific crude oils. However, if such data are absent, then a reasonably close estimate of the asphalt yield can be obtained using a method by S. Patel (Oil and Gas Journal, Feb 1964).

This predicting method correlates asphalt yield versus "asphalt factor," a parameter obtained by Patel's formula, which is

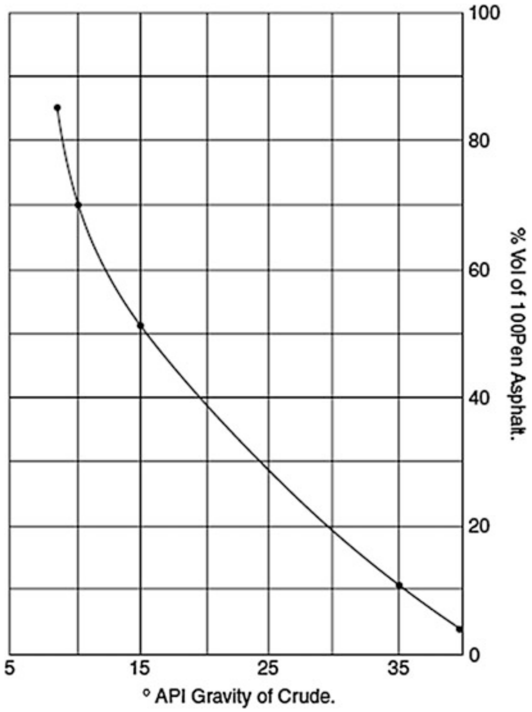


Fig. 7 Asphalt in average crudes (approximate)

$$F = \frac{(A)(CC)^n}{(B/C)(K - 10.4)} \tag{1}$$

where:

F = asphalt factor

A = the slope between 400 °F and the temperature at which 100-penetration asphalt starts to boil (see Fig. 8)

CC = Conradson carbon of 750 °F plus residue

B = slope of high-boiling material (see Fig. 8)

C = slope of lower boiling material (see Fig. 8)

K = characterization factor at 750 °F (Watson K value)

n = empirical exponent, normally 1.0

Figure 9 shows the relationship between the F factor and the approximate yield of 100-penetration asphalt.

The calculation is by trial and error, and this is given in the example for the design of an asphalt air-blowing process in the Appendix of this chapter.

Asphalt Blowing Process

Blowing air into a vessel containing asphalt from vacuum distillation or the deasphalting process will change its penetration and softening properties. Among the variables that affect the manufacture of air-blown asphalt are:

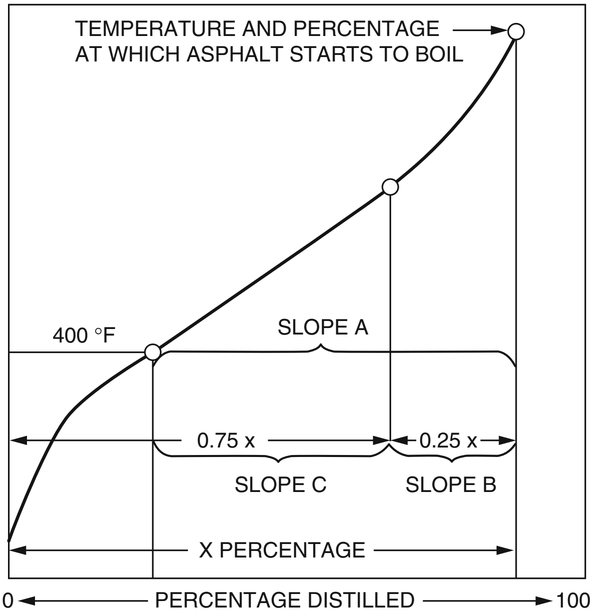


Fig. 8 How to obtain crude oil slopes for use in Patel's equation

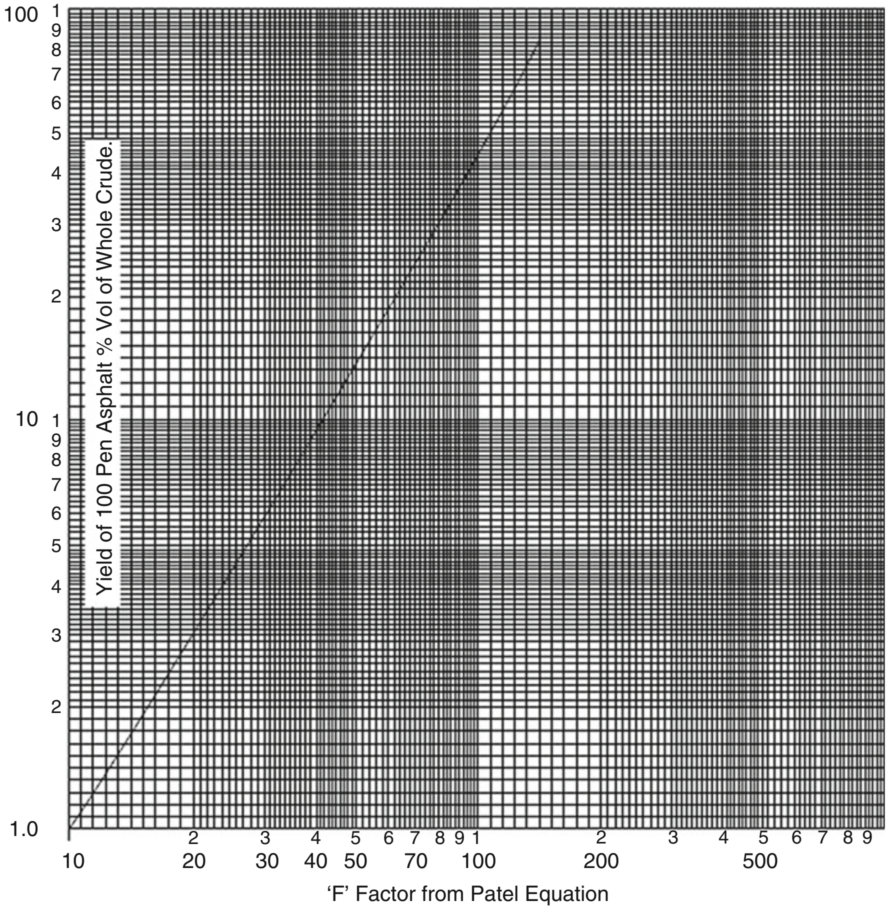


Fig. 9 Correlation of *F* factor versus yield of bitumen

- The rate of the air injected
- The temperature of the asphalt
- Retention time of the asphalt
- The system pressure

These variables and their effect on the process are discussed below.

The Rate of Air Injected

This is the most important variable in the process. If the temperature, pressure, and residence time are kept constant in the oxidizer, the softening point of the asphalt (the ring and ball) can be remarkably increased by increasing the air rate. This increase is larger at low air rates than higher values. A point is reached where the increase in air rate has little effect on the softening point and this is shown in Fig. 10.

The penetration properties of the asphalt are also affected by the air rate and this is shown in Fig. 11.

For continuous operation, normal air rates will be between 0.3 SCFM/BPSD of oil and 1.0 SCFM/BPSD. For batch processes, this rate will be between 1.5 SCFM/Bbl and 9.5 SCFM/Bbl. This will depend on the length of each batch and the number of cycles to be processed each day. The air supply must not contain free

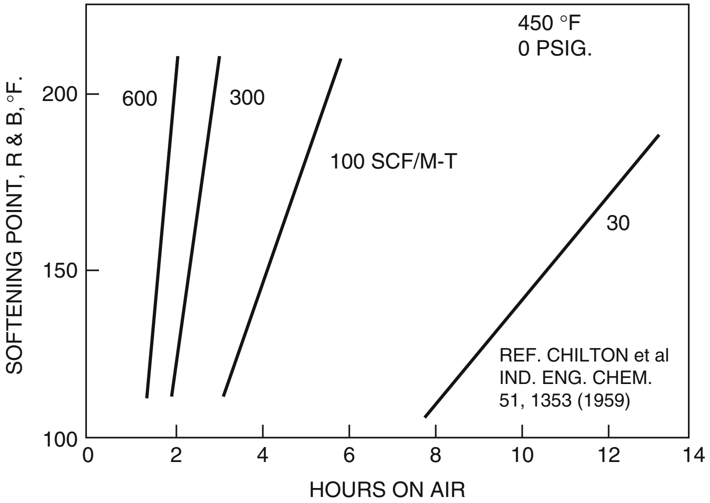


Fig. 10 Effect of air rates on softening point

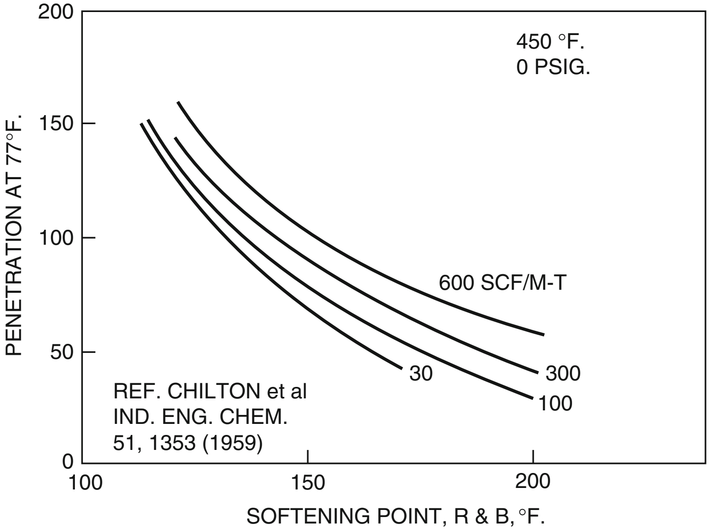


Fig. 11 Effect of air rates on softening point/penetration ratio

water but need not be dried. If the air is delivered by a reciprocating compressor, then a well-designed knockout pot is sufficient to remove the free water.

The Reaction Temperature

If the other variables are kept constant, increase in the temperature of the oxidizer increases the softening point of the asphalt. The effect of temperature increase on the softening point is larger at the lower temperature levels than when the temperature is already high. A point is reached when the increase in temperature has little effect on the softening point. Figure 12 shows this effect. The ratio of softening point and penetration increases by decreasing the temperature. To increase the softening point without affecting the penetration, it is necessary to reduce the reaction temperature, blow air for a longer period, or increase the residence time of the asphalt. Figure 13 shows this behavior.

There are certain limitations to the temperatures at which the oxidizer can be designed or operated. The design of the oxidizer should not be higher than 50 °F below the flash point of the feedstock or any of its components. It must however be recognized that effective oxidizing reaction does not occur at temperatures below 420 °F. Generally speaking, batch processes operate at a temperature between 430 °F and 475 °F, while continuous processes operate at between 500 °F and 550 °F. The asphalt oxidizing reaction is exothermic and as such must be controlled by some form of cooling. The most common means of cooling in continuous processes is to recycle a portion of the reacting feed through a cooler and returning it to the reactor mixed with the feed. Another method is to install cooling coils into

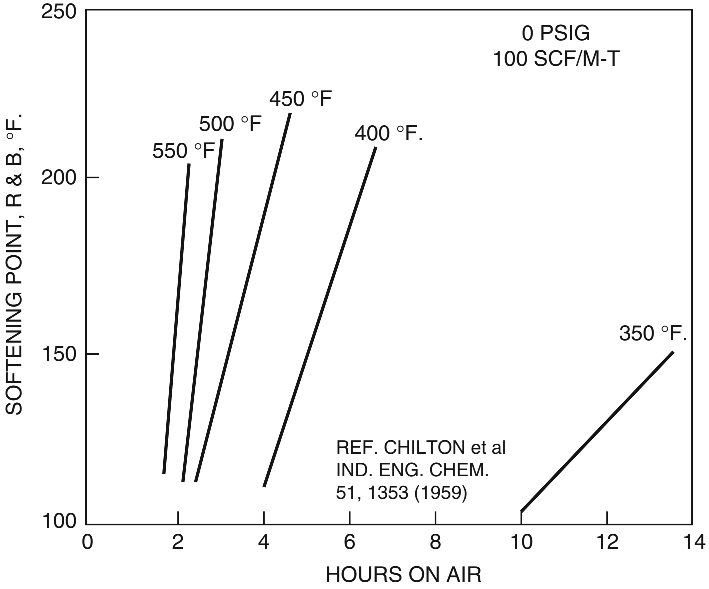


Fig. 12 Effect of temperature on softening point (or hardness)

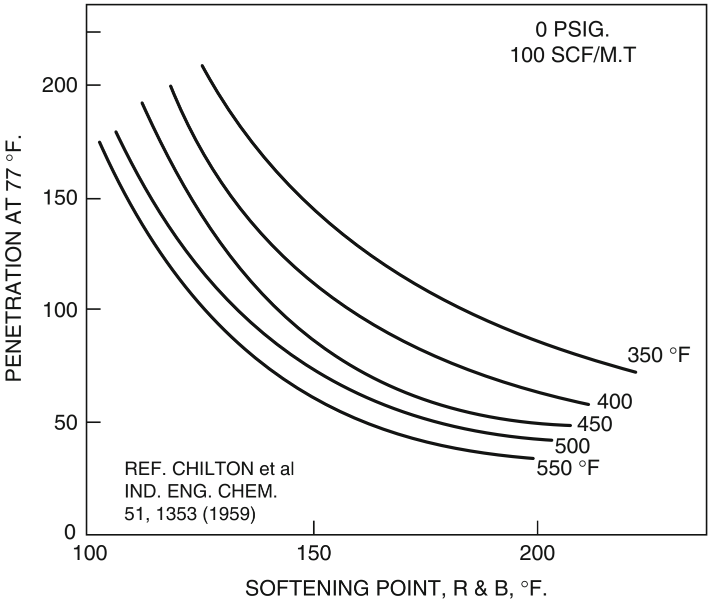


Fig. 13 Effect of temperature on softening point/penetration ratio

the reactor itself. This method is used mostly for batch processes. Steam is injected above the oil level in the reactor. The main purpose of this steam is to act as snuffing steam to avoid explosion in the air/oil atmosphere existing in this zone.

Retention and Contact Time

If all other variables are kept constant, the softening point can be remarkably increased by increasing the retention time of the asphalt in contact with air in the oxidizer. In the case of continuous processes, this is achieved by varying the throughput or by increasing the volume of asphalt (depth) in the oxidizer. In the case of the batch process, this is achieved by varying the batch residence time. Figures 14, 15, 16, and 17 show the effect of the changing retention time.

The retention time or residence time required for oxidation is different in every case depending on how much change in softening point or penetration is required. A good rule of thumb is to calculate retention time assuming it takes 1 h to increase 12 °F in the softening point of the asphalt. For example, to increase the softening point of 100 °F asphalt to a 220 °F product will require a residence time of $\frac{220-100}{12} = 10\,\text{h}$.

A second rough rule for batch processes is that it takes approximately 4–8 h of blowing, using 15 SCFM of air per ton of asphalt. That is, if 25 SCFM of air is used, the residence time would be around 2.4–4.8 h since the effect of residence time is proportional to the oxidation rate. A continuous process usually requires less time, about one-half that of a batch process.

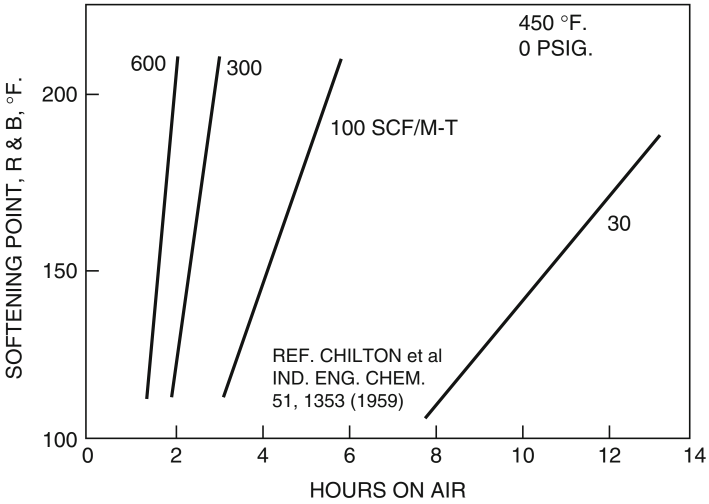


Fig. 14 Effect of retention time on softening point (or hardness) at different air rates

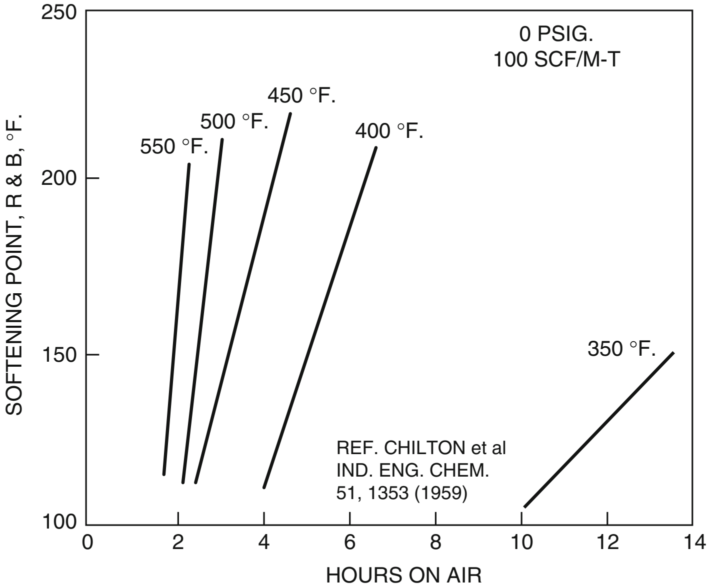
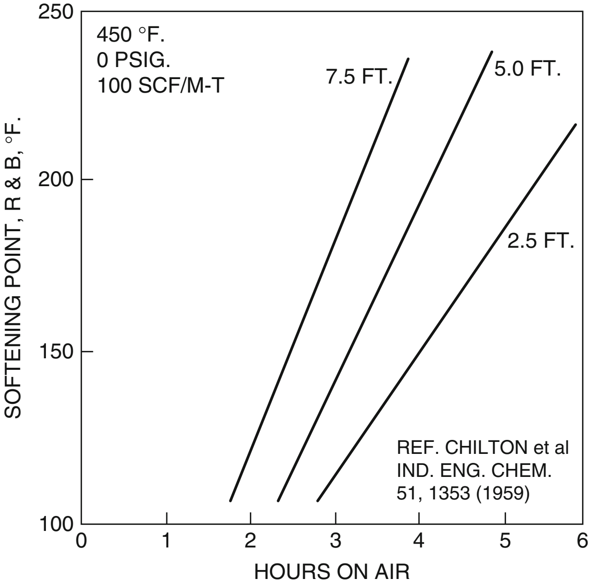


Fig. 15 Effect of retention time on softening point (or hardness) at different temperatures

Increasing the contact time or the depth of the asphalt level in the oxidizer vessel will increase the softening point of the asphalt if all other variables remain constant. In this case the softening point is changed without altering the softening point/penetration ratio. The effect of this variable is the same as increasing the residence time of the asphalt. Figure 18 shows this effect.

Fig. 16 Effect of retention time on softening point (or hardness) at different liquid depths in oxidizer



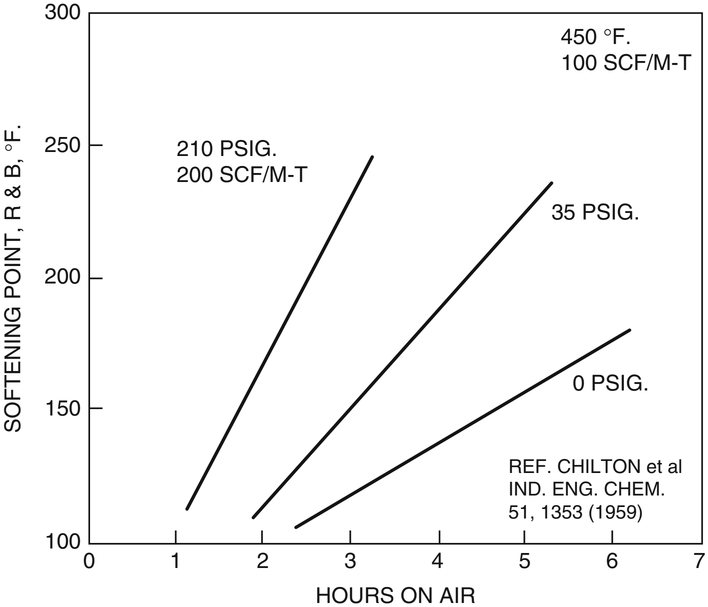
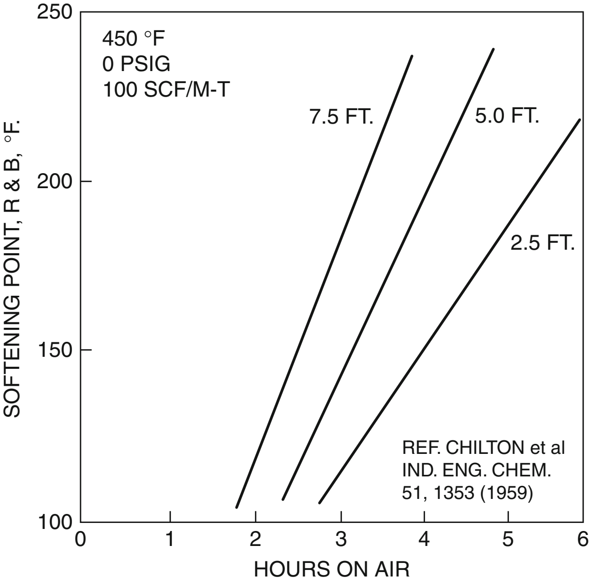


Fig. 17 Effect of retention time on softening point (or hardness) at different oxidizer pressures

Fig. 18 Effect of oil level in oxidizer on softening point (or hardness)



Although the height of the liquid and the residence time of the air are closely related, they do not exactly have the same effect on the oxidizing process. The higher the liquid level, the more efficient is the oxidizing process. This is so because the same amount of air is better utilized by remaining in contact with the oil for a longer period. Since the air is not completely used by the time it leaves the oxidizer, asphalt can be oxidized faster with the same air rate in a tall small-diameter oxidizer than one of a larger diameter but shorter, even though the residence time will be the same in both cases.

Normally height to diameter ratios of between 3.5/1 and 5/1 are used in the design of continuous process oxidizers and a somewhat lower 2.5/1 for batch processes. The liquid level in the oxidizer is usually no more than 2/3 of the total height of the vessel. At least 10 f. must remain free of liquid above the high liquid level. This is to allow for liquid disengaging and foaming.

The System Pressure

With all other variables constant, increasing the pressure of the oxidizer will increase the asphalt softening point. The effect of increasing pressure however is not as great as the effect of increasing any of the other variables. Perhaps the more significant change in increasing the oxidizer pressure is in the ratio of softening point to penetration of the asphalt. Usually it is not economical to operate at high pressure since the gains on hardening rates are small relative to the effect of the other variables. For practical purposes, pressure is not considered a design variable, and most oxidizers operate at near atmospheric pressure. A positive pressure of 5 psig is the more usual.

A flow sheet of a typical asphalt blowing plant is given in Fig. 19.

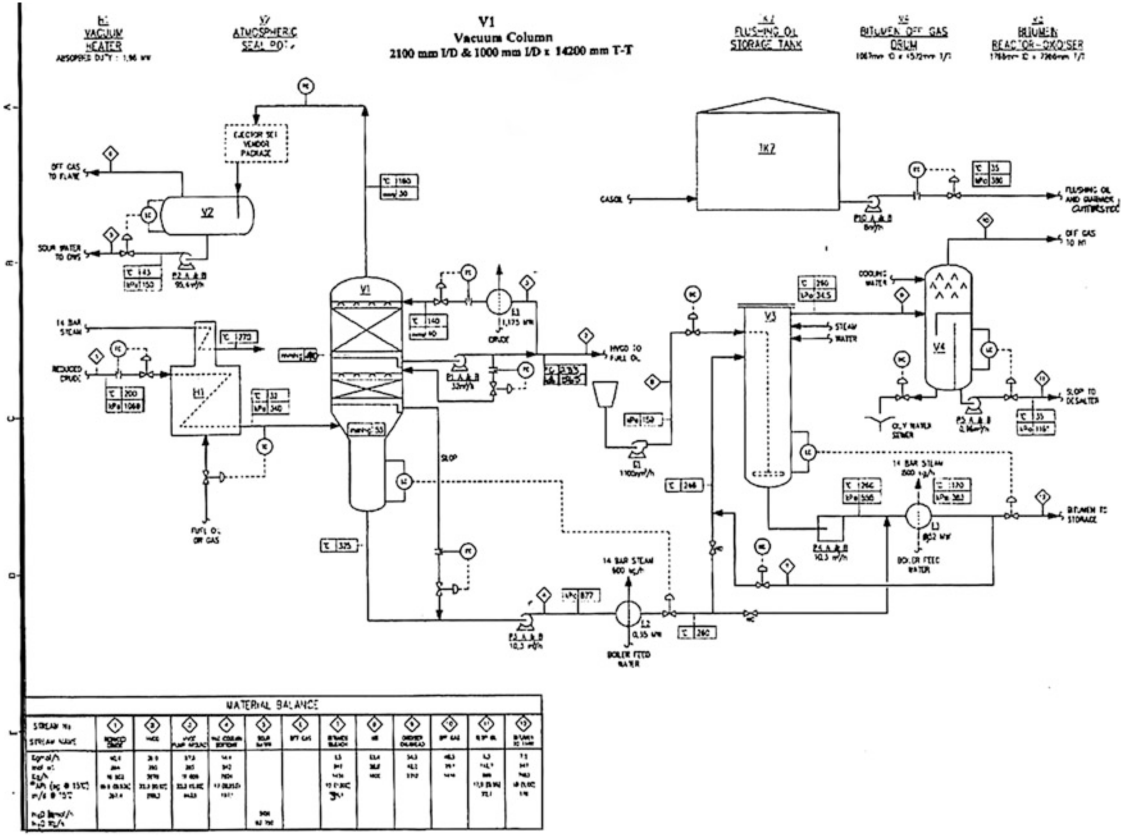


Fig. 19 A process flow diagram of a typical bitumen manufacturing plant

The Petrochemical Refinery

The petrochemical refinery processes crude oil to produce feedstock for chemical plants. The two most important processes are:

- The production of aromatics
- The production of olefins

Both of these types of petrochemical refineries have been described briefly elsewhere in this handbook. In a related process topic, although not strictly petroleum processing, you will also find a chapter on "▶ Chemicals from Natural Gas and Coal" in this handbook. It is not proposed to describe these types of refineries further here. This chapter will deal with a typical example of the process configuration for the production of aromatics only. This is probably the more common integration of the petrochemical refinery because a normal energy refinery is more easily adapted to aromatics with the minimum of additional processes.

The Production of Aromatics

The aromatics referred to here are:

- Benzene
- Toluene
- Ethylbenzene
- Para-xylene
- Meta-xylene
- Ortho-xylene

The configuration described here begins with a mixed aromatic stream which has been obtained by catalytic reforming of a high naphthene content naphtha. This naphtha would probably have been a product of a hydrocracker producing energy products from a heavy waxy distillate. There are refineries that do hydrocrack heavy distillates to extinction to produce this kind of high naphthene naphtha only. The more common though is the energy hydrocracker producing a range of products, of which the naphtha is just one of them. The reformate from this high naphthene feed is very rich in the aromatics listed above. To increase the aromatic content as feed to the aromatic complex, the aromatics are separated from the remaining paraffins by an extraction process.

The aromatics recovery complex which takes as feed the mixed aromatic stream is shown in Fig. 20.

In this particular scheme, the objective is to produce and maximize the benzene product and the ortho-xylene products only. Many aromatic complexes also produce para-xylene as product via a crystallization or adsorption step. A description of these units and the process flow of the complex follows.

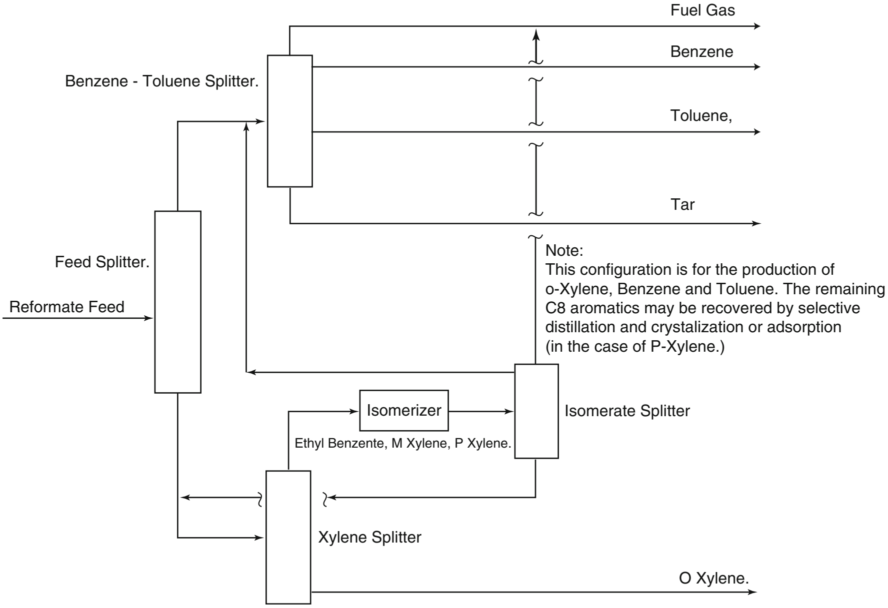


Fig. 20 A block flow diagram of an aromatic production complex

Feed Fractionation

The fresh mixed aromatics stream is delivered from off-plot to enter a 35-tray splitter tower. Benzene and toluene are removed as overhead product, while the mixed xylene streams leave as the bottom product.

Xylene Splitter and Isomerization Process

The mixed xylene stream leaves the splitter and is routed to a xylene splitter. This is a super-fractionating tower containing at least 135 fractionating trays. The fractionation split is between the meta- and ortho-xylene components. A recycle stream from an isomerization plant rich in ortho-xylene is also fed to this xylene splitter. The overhead, rich in ethylbenzene and the para- and meta-xylenes, is routed from the splitter to an isomerization plant. These C_8 aromatics are isomerized over a catalyst and in the presence of a hydrogen-rich stream to a product rich in ortho-xylene but containing also benzene, toluene, and some ethylbenzene with some light hydrocarbons and hydrogen in equilibrium. This isomerate enters a fractionator in which the light hydrocarbons and some ethylbenzene are removed as overheads, while the bottom product, containing mostly ortho-xylene, with the other C_8s in equilibrium is returned to the xylene splitter. The light isomerate overhead product from the fractionator is stabilized in a separate stabilizing column before being routed to the benzene recovery section. The bottom product from the xylene splitter enters an ortho-xylene rerun tower from which commercially pure ortho-xylene leaves as the overhead product. The bottom product leaving this tower contains heavy aromatics (heavier than C_8s) and is routed to fuel or, in some cases, to transalkylation with toluene to yield more C_8s.

Dealkylation and Benzene Recovery

The overhead from the feed fractionator and the bottom product from the light isomerate stabilizer combine to form the fresh feed to a benzene fractionator. This feed stream will contain mostly benzene and toluene. A recycle stream from the toluene dealkylation plant, if present, containing a high proportion of benzene joins the fresh feed to enter the benzene fractionator. Benzene is removed from this fractionator as an overhead product, while toluene is removed as a reboiled stripped side-stream product. A small bottom make of polymer and tar is removed as a bottom product. The toluene stream may be routed to a dealkylation unit in which about 98 mol% of the toluene is converted to benzene. This dealkylated product forms the recycle stream to join the fresh feed to the benzene fractionator.

The configuration given in the block flow diagram, Figure 20, is based on processing the following mixed aromatic feeds to the complex:

Benzene	20,000 long tons/year
Toluene	50,000 long tons/year
Ethylbenzene	9,000 long tons/year
Para-xylene	11,400 long tons/year
Meta-xylene	27,000 long tons/year
Ortho-xylene	12,600 long tons/year

Make-up gas to the isomerization unit and the dealkylation unit has the following composition:

H_2	81.5 mol%
C_1	12.2 mol%
C_2	5.2 mol%
C_3+	1.1 mol%

The products required to be maximized are:

High-purity benzene to a specific gravity of 0.882 (min) and 0.886 (max), all at 60 °F. Ortho-xylene will contain not less than 99.0 wt% of ortho-xylene

Process Discussion

Feed Fractionation and Xylene Splitter

Good separation of the light aromatics and the xylenes can be achieved in a 35-trayed column operating at about 35 psig in the reflux drum. At this pressure, the tower overhead is at a temperature high enough to offer some preheating of the tower feed by the overhead condensers. Splitting the xylenes however requires a tower of about 136–140 trays. A reasonable economic overhead pressure (in the reflux drum) is about 98 psig. Again at this pressure, as in the case of the feed fractionator, the overhead temperature offers some opportunity for feed preheat from the overhead condensers and reboil of the ortho-xylene rerun tower.

The Isomerization Unit

This is a licensed process which converts the xylene streams to approach an equilibrium xylene composition. Some isomerization units convert ethylbenzene to xylenes while others essentially dealkylate the ethylbenzene. By removing one or more of the components (ortho-xylene in this case), the remaining xylenes in the feed are isomerized to recover the equilibrium distribution lost by removal. The unselected isomers in the fresh feed are recycled to extinction by this method. The process shown here uses around 1.2 MMscf/day of 81.5 mol% hydrogen.

The Dealkylation Unit

This unit is also a licensed process. Its purpose is to dealkylate the toluene component in the feed to produce benzene.

This process utilizes a separate polymer reactor to increase benzene selectivity. It also uses a hydrogenation reactor to control impurities in the benzene such as unsaturates and sulfur products. The yield of benzene in this process is about 98.2 mol% on toluene in the feed. Except for very small units, a cryogenic step is applied to remove the reaction products of methane and heavier. Where hydrogen from a catalytic reformer is used as make-up, the C_3s and heavier paraffins and any H_2S contained in it must be removed. An absorber operating at about 250 psig is used to remove the hydrocarbons and a caustic wash is used to remove the H_2S. The removal of the C_3s and heavier is advisable as these hydrocrack under the dealkylation reactor conditions causing additional reactor temperature rise and increase in hydrogen consumption.

Appendix: Sizing a Bitumen Oxidizer

Design Specification

Product required 816 BPSD of 25-pen asphalt

Crude source Pennington – West African offshore (for assay data, see Figs. 21, 22, and 23)

Vacuum unit feed = +650 °F on crude =>75 vol%

Sizing of the oxidizing reactor is required.

Step 1: Predict Yield of Asphalt Patel's equation shall be used for this purpose.

Trial 1 Assume the initial boiling point of asphalt is 1,015 °F which equates to a cut of 95 vol% on crude.

$$\text{Vol\% cut point on crude} = 0.75 \times 0.95 = 71 \text{ vol\%}.$$

Using Fig. 8 and data from the TBP curve (Fig. 21):

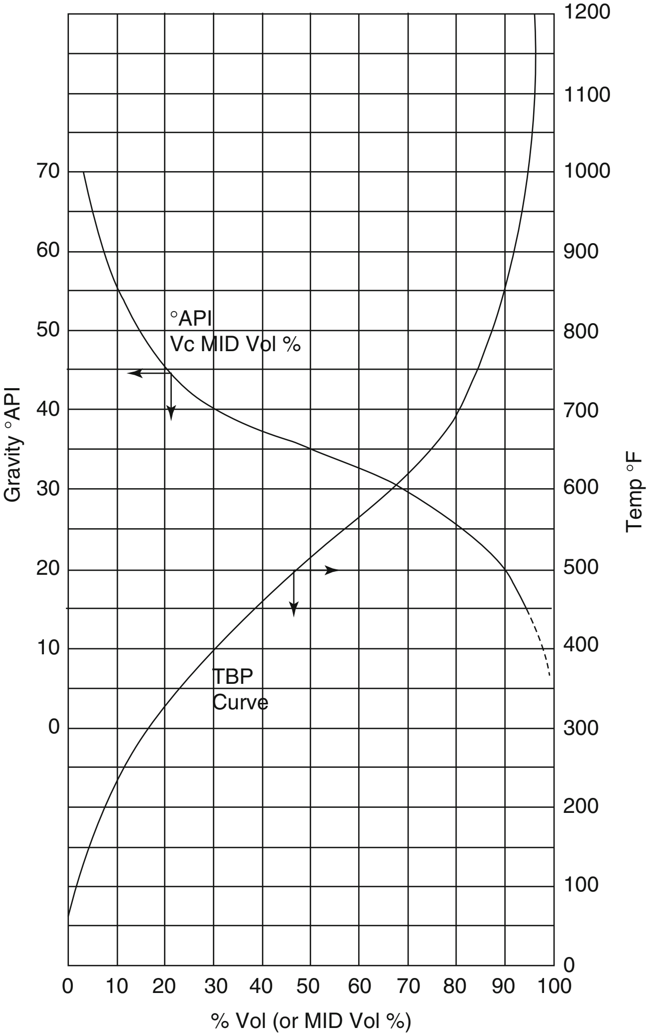


Fig. 21 The TBP and gravity curves for Pennington crude

$$\text{Slope A} = \frac{1{,}015 - 400}{95 - 31} = 9.6$$

$$\text{Slope B} = \frac{1{,}015 - 625}{95 - 71} = 16.25$$

$$\text{Slope C} = \frac{625 - 400}{71 - 31} = 5.6.$$

Conradson carbon content of +750 °F residue = 4.6 wt% (see Fig. 24).

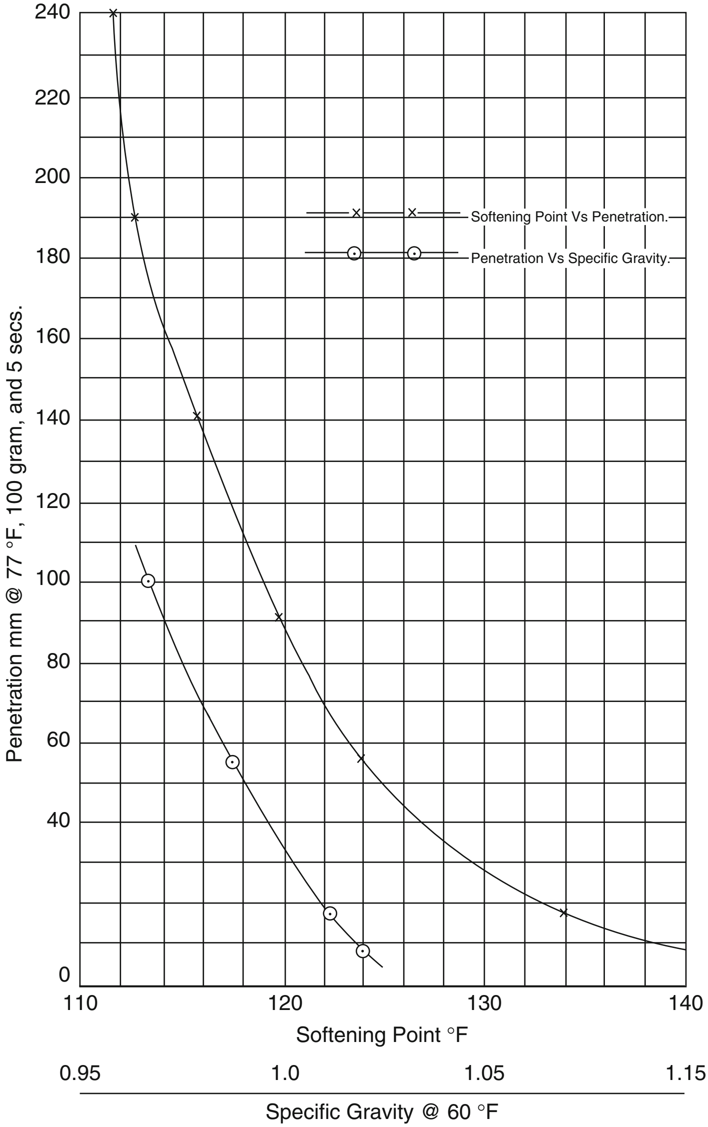


Fig. 22 Plot of softening point versus penetration and penetration versus specific gravity for Pennington crude

$$\text{Watson } K \text{ factor at } 750\ ^\circ\text{F} = 11.2$$

$$\text{Exponent } n = 1.2$$

$$F = \frac{9.6 \times (4.6)^{1.2}}{(16.25/5.6) \times (11.2 - 10.4)} = 25.8.$$

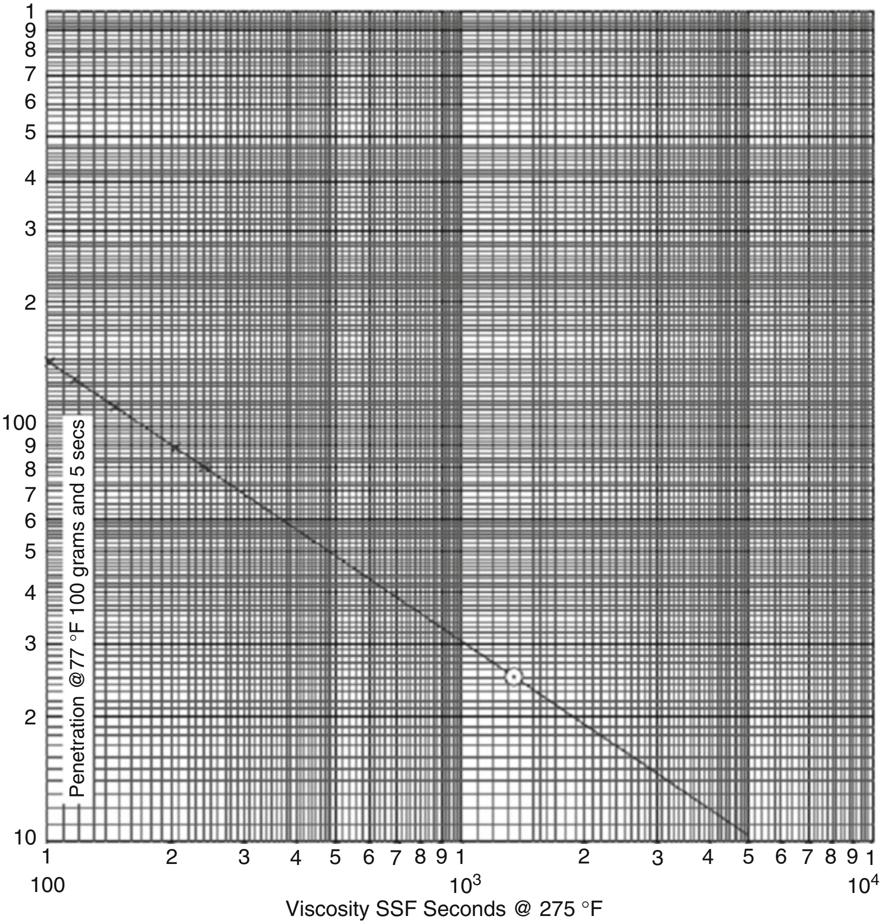


Fig. 23 Plot of viscosity versus penetration for asphalt

From Fig. 9, percent asphalt yield = 4.3 (assumed was 5.0 vol%).

Trial 2 Assume the boiling point of asphalt is 950 °F which equates to a cut of 93.5 vol% on crude or a yield of 6.5 vol%.

Calculated *F* factor is 34.6 correlating to a yield of 7.6 vol%.

Trial 3 Assume the boiling point of asphalt is 850 °F which equates to a cut of 90 vol% on crude or a yield of 10 vol%.

Calculated *F* factor is 42.0 correlating to a yield of 10.0 % which is that assumed and is accepted as the yield of 100-pen asphalt from this crude.

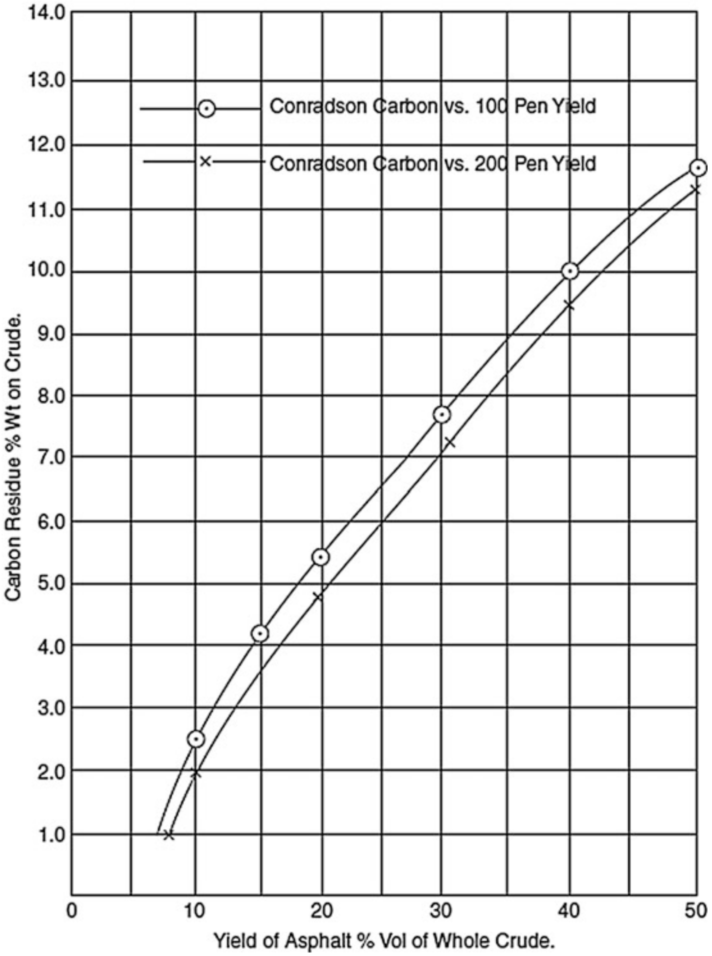


Fig. 24 Asphalt yields versus carbon residue % weight on crude

Step 2: Calculate Throughput of 100 Penetrations and Air to Oxidizer From Fig. 25, the ratio of 100-pen asphalt to a 25-pen asphalt is read off at 0.89 for a characterization factor of 11.2. Then:

For 816 BPSD of 25-pen crude, we require a throughput of $816/0.89 = 917$ BPSD of 100-pen asphalt.

For a continuous process, the recommended air rate is 0.3–1.0 scfm per BPSD. A rate of 0.55 will be used here.

Then air rate will be $0.55 \times 917 = 504.4$ scfm.

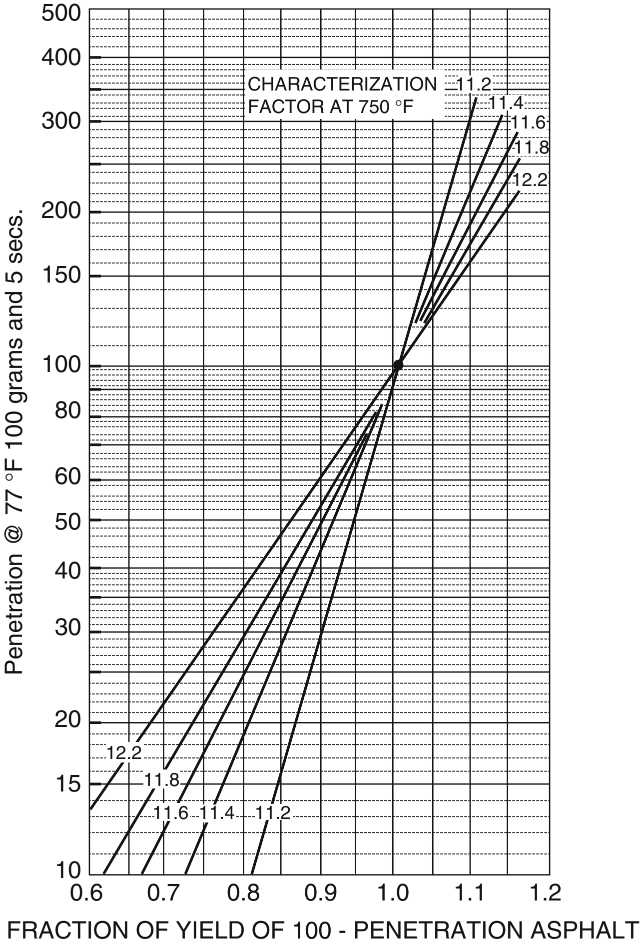


Fig. 25 Fraction of yield of 100 pen asphalts

Step 3: Calculate Residence Time and Capacity of Fresh Feed Required final penetration = 25 mm at 77 °F, 100 g/s.

Equivalent softening point = 131 °F (Fig. 22).

Initial pen = 100 and equivalent softening point is 119 °F.

Change in softening point = 12 °F approximate residence time = $\frac{131-119}{12} = 1$ h.

Capacity of fresh feed: Cuft of feed per hour = $\frac{917 \times 42}{24 \times 7.48} = 214.9$

$$\begin{aligned} \text{Asphalt SG @60 °F} &= 0.966 \\ \text{@500 °F} &= 0.815. \end{aligned}$$

The volume of fresh feed at 500 °F = 254.7 cuft/h. Add 15 % as contingency to 292.9 cuft/h.

Step 4: Reactor Material Balance Material balance over the reactor is as follows:

$$\begin{aligned}\text{Feed of 100 pen in} &= \frac{917\text{BPSD} \times 42}{24}\\ &= 1{,}605\,\text{gal/h}\\ \text{SG@60°F} &= 0.966 = 8.044\,\text{1b/gal}\\ \text{1b/h} &= 12{,}908\end{aligned}$$

$$\begin{aligned}\text{Product 25 pen asphalt out} &= \frac{816 \times 42}{24}\\ &= 1{,}428\,\text{gal/h}\end{aligned}$$

$$\begin{aligned}\text{SG @ 60°F} &= 1.006 = 8.33\,\text{1b/gal}\\ &= 11{,}895\,\text{1b/h} \;(= 0.92\text{ wt\% on feed})\end{aligned}$$

$$\begin{aligned}\text{Air into the oxidizer} = 504.4\,\text{scft/min} &= \frac{504.4 \times 60 \times 29}{378}\\ &= 2{,}322\,\text{1b/h.}\end{aligned}$$

Approximately 90 % of the oxygen in the air reacts with the asphalt:

$$\begin{aligned}\text{lb/h of oxgen reacted} &= 2{,}322 \times 0.232 \times 0.9\\ &= 485\,\text{1b/h.}\end{aligned}$$

Approximately 20 % of oxygen reacted will be in the asphalt product = 97 lb/h:

$$\begin{aligned}\text{Unreacted oxygen leaves unit in the overhead vapor} &= (2{,}322 \times 0.232) - 485\\ &= 54\,\text{lb/h.}\end{aligned}$$

Nitrogen in overhead vapor = 2,322 − 539 = 1,783 lb/h

Hydrocarbon vapor in overhead vapor:

$$\begin{aligned}&= \text{Feed} + \text{air} - (\text{product} + \text{oxygen in product} + \text{nitrogen} + \text{unreacted oxygen})\\ &= 12{,}908 + 2{,}322 - (11{,}895 + 97 + 1{,}783 + 54)\\ &= 1{,}401\,\text{lb/h}\end{aligned}$$

$$\begin{aligned}\text{Total overhead vapor} &= 1{,}401\,\text{lb/h hydrocarbons} + 1{,}783\,\text{lb/h}\,N_2 + 54\,\text{lb/h}\,O_2\\ &= 3{,}238\,\text{lb/h.}\end{aligned}$$

Step 5: Heat Balance Over the Reactor and Amount of Cooling Stream It is intended to maintain a reactor temperature of 500 °F by recycling cold run-down product.

Feed temperature to the oxidizer shall be 550 °F. Heat of reaction in Btu/lb = 1.3 × diff in softening point.

The amount of recycle cooled product as reactor coolant is obtained from the following heat balance where *x*lb/h is the recycle.

Stream	V or L	°API	°F	lb/h	Btu/lb	MMBtu/h
In						
Feed	L	15	550	12,908	254	3.279
Air	V		86	2,322	21	0.049
Recycle	L	10	338	x	148	$238x$
Ht. of reaction	–	–	–	–	–	0.201[a]
Total in				15,230 + x		3.529 + $148x$
Out						
Product	L	10	500	11,895	238	2.831
Dis. O_2	V	–		97	–	Negl.
Recycle	L	10	500	x	238	$238x$
O/head vap.	V	–	300	3,238	124	0.402
Total out						3.233 + $238x$

$$\begin{aligned} x &= \frac{3,529,000 - 3,233,000}{238 - 148} \\ &= 3,289\,\text{1b/h} \end{aligned}$$

The volume of recycle at 500 °F (SG 0.872) = 7.26 lb/gal = 453 gal/h or 60 cuft/h

[a] Heat of reaction as Btu/lb of asphalt feed is calculated as 1.3 × the difference in softening point. In this case, it is 12,908 × (12 × 1.3) = 201,000 Btu/h

Step 6.0: Reactor Sizing The reactor size shall be based on the hot volume of feed + contingency and the hot volume of recycle over the calculated residence time of 1 h. The volume of feed and recycle shall be based on the reactor temperature (500 °F).

The volume of fresh feed and contingency is 292.9 cuft. The recycle is 60 cuft and the total sizing volume is 352.9 cuft.

This amount shall occupy 65 % of the oxidizer's total volume. This allows for the disengaging of vapor leaving the vessel.

The total volume of the oxidizer is $\frac{352.9}{0.65} = 543$ cuft.

The ratio length to diameter shall be 4.5.

$$\text{Thus}\ \frac{4.5\pi D^3}{4} = 543\,\text{cuft}$$

and

$D = 5.36$ f. say 5.5 f. and $L = 4.5 \times 5.5 = 24.8$ f. T-T.

Check height of liquid to NLL $= \frac{352.9}{\text{X sect area}} = 14.8$ ft $= 60$ % of total vessel height which is acceptable.

References

T. Hilbert et al., *Digital Refining* (ExxonMobil and UOP, 2013), Aug 2013, www.digitalrefining.com/article/1000830. Accessed July 2014

R.P. Silvy et al., Oil Gas J. **108**(28), (Petrobras, 2010), Aug 2010. Accessed July 2014

Chemicals from Natural Gas and Coal

Bipin Vora, Gregory Funk, and Andrea Bozzano

Contents

Abstract

Prior to major discovery of crude oil, during the 19th and early part of 20th century chemicals from coal was a well established practice. From 1040s and beyond availability f low cost crude oil and expanding refining capacity industry switched to crude oil based feed stocks. However, by 1990 due to significant increase in crude oil price the industry started looking into conversion of low cost coal and natural gas for the production of petrochemicals. This chapter discusses some of the modern technologies of coal and natural gas conversion to chemicals.

B. Vora (✉)
R&D, UOP LLC, A Honeywell Company, Des Plaines, IL, USA
e-mail: bipin.vora@honeywell.com

G. Funk • A. Bozzano
UOP LLC, A Honeywell Company, Des Plaines, IL, USA
e-mail: gregory.funk@honeywell.com; andrea.bozzano@honeywell.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_14

Keywords
Chemicals from synthesis gas • Methanol intermediate • Methanol to olefins • Light olefins • Ethylene • Propylene • Lurgi MTP process • UOP/Hydro MTO process • CTO • GTO • CTL • Methanol • Olefins • Acetic acid

Introduction

People often think of coal as a fuel of the past. Indeed, coal was one of the first fuels used by man and played an important role in the industrial revolution that began in the late eighteenth century. In more recent times, coal has fallen out of favor due in part to environmental issues associated with its use and in part to the difficulties associated with mining. The relative cost and convenience of crude oil-derived fuels resulted in the displacement of coal as the premier energy source. Nonetheless, coal continues to be a staple in the energy diet of many countries, and the current high prices of crude oil have triggered renewed interest in coal utilization. Table 1 shows coal utilization for the production of electricity for various countries. For some countries like Poland and South Africa, coal accounts for more than 85 % of electric power generation. Even today in the USA, over 45 % of the electric power generated is from coal (International Energy Agency 2011).

Fossil Fuel Resources

Figure 1 shows the geographic distribution of recoverable oil reserves in 1992 and as estimated in 2012 (BP Statistical Review 2013). There has been significant consumption of crude oil between 1992 and 2012; however, the estimated recoverable crude oil reserves in 2012 are actually 60 % greater than that of 1992 estimate. In other words, we have been discovering more oil reserves as well as increasing the estimate of recoverable oil due to technology advances than we are consuming. The share of Middle East reserves declined from 63.6 % to 48.4 %. As shown in Fig. 2, a similar effect is also true for the natural gas reserves. However, in this case the Middle East has slightly increased its share.

Table 1 Percent of total electric power from coal

Country	% of Electricity generated by coal
South Africa	93
Poland	87
China	79
Australia	78
India	68
USA	45
Germany	41

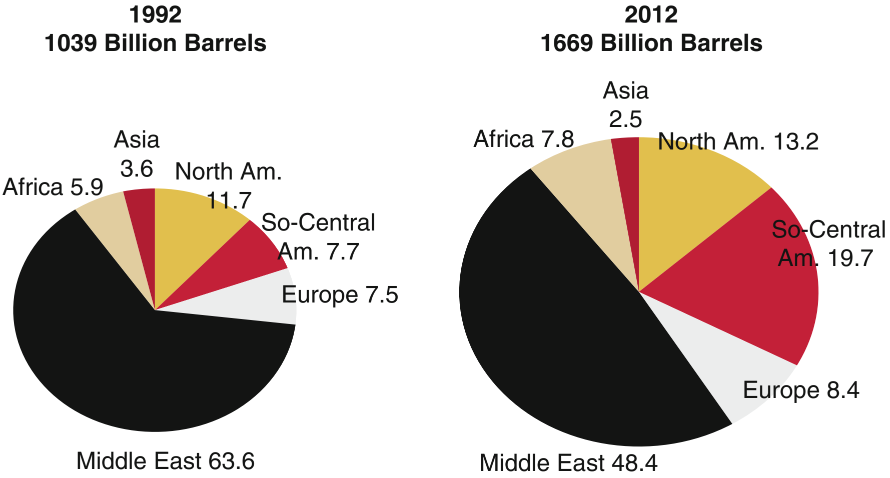


Fig. 1 Distribution of world oil reserves, % (in this nomenclature, one billion denotes 10^9 and one trillion 10^{12})

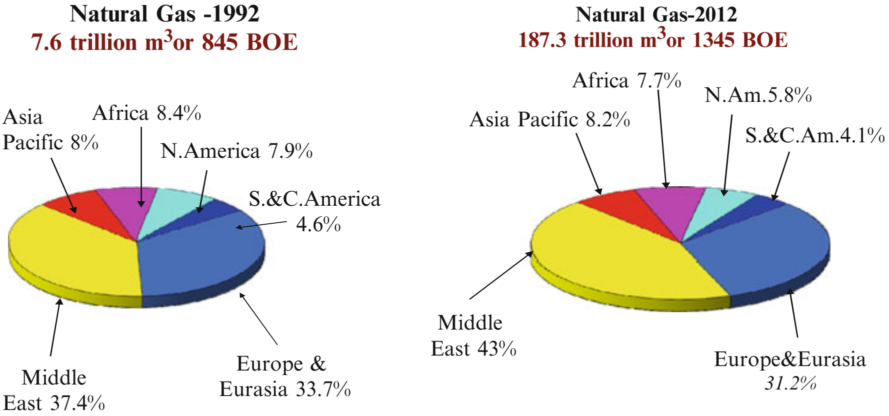


Fig. 2 Estimated natural gas reserves, %

Figure 2 shows the geographic distribution of natural gas reserves (BP Statistical Review 2013). Total gas reserves increased from 117.6 trillion cubic meter in 1992 to 187.3 trillion cubic meter in 2012.

Figure 3 shows the geographic distribution of coal reserves in 2012 (BP Statistical Review 2013). Total coal reserves in 2012 are estimated at 861 billion tons, a net decline of 12 % from 1992 estimate of 981 billion tons. In terms of barrels of oil equivalent (BOE) energy, this is 25 % greater than the estimated combined oil and gas reserves in 2012. A further point is that there is a geographic mismatch between areas of oil and gas reserves and areas of high demand – namely, North America, Japan,

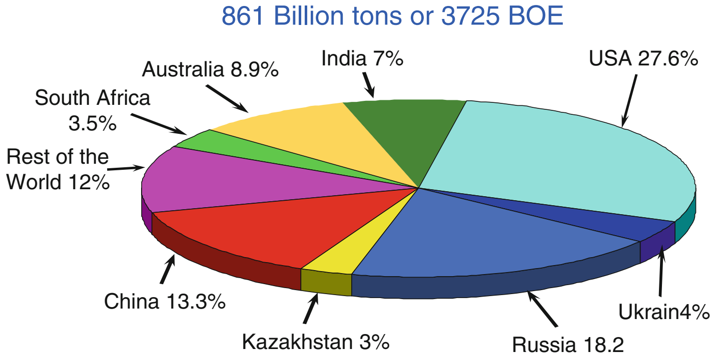


Fig. 3 World coal reserves in 2012, %

Western Europe, and the emerging high demand areas of Asia. On the other hand, coal reserves are advantageously located in these high-energy demand areas. As a result, coal can provide security of raw material for the energy demand to these nations.

In 2013 coal price ranged from 50 to 100 US dollars per metric ton. One ton of coal roughly generates 27 million BTUs (mmBTU) of energy. In terms of energy value, coal at $50 per ton is equivalent to $1.90/mmBTU. This is approximately one-half of the cost of natural gas in the USA during the third quarter of 2013. That is, in North America, the cost of coal in terms of its energy content is one-half of the cost of natural gas. Natural gas can be significantly costlier than coal in countries where natural gas is imported, for example, in India and China, coal is priced at around $100/MT, that is, about $3.80/mmBTU, while natural gas is valued at $12–14/mmBTU.

Though coal has been and continues to be a major source of fossil fuel, its utilization presents significantly greater environmental challenges than do oil or gas. Coal combustion produces higher levels of sulfur dioxide, nitrogen oxides, and particulates. The presence of mercury, arsenic, lead, and other heavy metals in coal is also of concern. These are critical factors that must be considered when looking forward to future uses of coal. The key to utilization of coal reserves will be to use clean coal-burning technology and develop efficient processes for coal to chemicals.

Coal Gasification and Synthesis Gas Production

In conventional coal combustion, complete oxidation of the carbon and hydrogen content of the coal to CO_2 and H_2O is a primary goal. The heat of combustion is used to generate steam and power. On the other hand, coal gasification is a partial combustion, in which the amount of oxygen fed to the reactor is controlled to yield a fuel gas mixture of hydrogen and carbon monoxide $CH_4 + 0.5O_2 = CO + 2H_2$. The gasification product gas produced is called raw synthesis gas and has considerable BTU value. The synthesis gas, after cleanup, can be more efficiently and cleanly burned in a downstream process. Alternatively, the cleaned-up synthesis gas can be used to manufacture a number of different chemicals.

One of the more significant developments in coal utilization is the cogeneration of “clean fuels”—where the heat of reaction and energy content of the waste streams are converted into electricity, with other gasification product being liquid fuels or chemicals from fossil fuels. This is more energy efficient than producing only electricity alone. It also reduces the emissions of greenhouse gases and other pollutants. Thanks to these improvements, coal gasification is receiving greater attention. The integrated gasification combined cycle (IGCC) system is already playing an important role in power generation.

Carapellucci and others (2001) have investigated the performance of an IGCC power plant combining electric power generation with methanol synthesis. Figure 4 shows a schematic flow diagram of such system. In this scheme, synthesis gas from coal gasification is used for both methanol production and power generation. In a stand-alone methanol plant, a large recycle is required to maximize utilization of the synthesis gas. In an integrated operation as shown in the flow diagram, the recycle can be reduced. Instead a purge gas stream can be fully utilized in the power generation section. This simplifies the methanol synthesis and also achieves greater energy efficiency. A similar integration can be made for DME production or for liquid fuel production with a Fischer-Tropsch unit.

There are several well-established technologies for coal gasification (Savage et al. 2004; PERP 2005): the “Texaco” gasifier (now owned by GE), Shell Global gasifier, British Gas/Lurgi gasifier, KRW gasifier, and IGT U-Gas gasifier. The Texaco, Shell, and Lurgi gasifiers account for the majority of gasification units worldwide. Synthesis gas from coal gasifiers requires significant cleanup to remove particulates, carbon dioxide, and sulfur oxides. There are several well-established processes for the synthesis gas cleanup (Lee 1997a), such as the UOP Benfield^{TM} Process and the UOP Selexol^{TM} Process. The UOP Polybed^{TM} PSA and/or Polysep^{TM} membrane processes may also be used for the production of hydrogen or adjusting the CO-H_2 ratio for downstream process applications. After cleanup, the synthesis gas can either be used for power generation or for the production of chemical products such as ammonia, methanol, DME, liquid fuels, and others.

Conversion of coal to liquids (CTL) was widely practiced in smaller capacity units in Germany during World War II. In this process coal is converted to synthesis gas followed by Fischer-Tropsch synthesis to liquid hydrocarbons. Several units

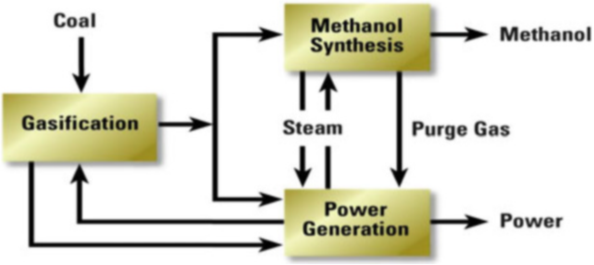


Fig. 4 Integrated gasification combined cycle (IGCC)

were built in South Africa during the 1960s and 1970s, which are currently operating with a capacity of about 150,000 barrels (one barrel is equal to 42 US gallons) per day (Jager 1997). In 1993 Shell began operation of a 12,500 BPD gas-to-liquid (GTL) plant at Bintulu in Malaysia (Shell doubles capacity of GTL plant at Malaysia. Fuels Lubes Wlky).

A similar technology to CTL is the conversion of natural gas-to-liquid fuels ("gas to liquids" or GTL). This also involves the production of fuel from synthesis gas, though in this case, the source of the synthesis gas is partial combustion of natural gas. Typically, the gas comes from "stranded gas" locations, where it cannot be easily utilized or transported by conventional methods. Estimates of known natural gas reserves are increasing as the rate of new discovery of unconventional gas reserves increases. A Sasol-Chevron project of 35,000 barrels per day began operation at the end of 2006 in Qatar (GTL Technology – 21st Century Advances 2004a, b), and Shell began operation of a large GTL plant of 140,000 barrels per day in Qatar in 2011 (GTL Technology – 21st Century Advances 2004b).

The USA in particular, during the past 5 years, has increased natural gas production substantially by increasing shale gas development. This increased production has made natural gas more affordable in the USA benefitting the refining, petrochemical, and midstream industries through low-cost energy. While there is currently only limited use of the technology, as shown in Table 2, a number of projects for natural gas conversion to liquids (GTL), coal conversion to liquids (CTL), and bio-derived raw materials to liquids (BTL) have been announced (ICIS 2012).

Though the fuel market is very large, the margins are low. As an example, Mobil developed methanol-to-gasoline technology (MTG) during the early 1980s and built a 10,000 barrels per day commercial unit in New Zealand (Chang 1994). This plant was in operation for only a few years. Though methanol production has continued, the methanol-to-gasoline portion of the plant has since been shut down due to poor economics. Hence, it is important to search for ways to convert synthesis gas to other, higher-value products.

Table 2 New projects announced for GTL and CTL

Principle	Location	Process	Feed	Capacity, BPD	Status
DKRW	Wyoming, USA	ExxonMobil MTG	Methanol (coal)	10,500	Financing
NuCoal	Saskatchewan, Canada	ChiaHuaneng – XOM	Methanol (coal)	15,000	Feasibility
TransGas Development Systems	West Virginia, USA	ExxonMobil MTG	Methanol (coal)	18,000	Feasibility
CORE BioFuel, Inc.	Texas, USA	CoreMKS	BTL	1,280	Feasibility
SASOL	Louisiana	GTL Primus	Shale gas	94,000	Feasibility
Primus Green Energy	Pennsylvania, USA	–	BTL	230	Development

Synthesis Gas Utilization

As illustrated above, synthesis gas can be produced from either natural gas or from coal. Once the synthesis gas is produced, the downstream processes for synthesis gas to chemicals are common for both initial feedstocks. Therefore, the following discussion on conversion of synthesis gas to chemicals also applies to monetization of remote natural gas.

As seen in Fig. 5, once coal or natural gas is converted to synthesis gas, it opens up a number of options for making different products. Sunggyu Lee provides an excellent review of various processes for methane derivatives via synthesis gas (Lee 1997b). Calkins and Wander provide a good review of chemicals from methanol (Calkins and Wander). The question becomes: producing which product from which feedstock is more economical? For most petrochemical processes, raw materials account for more than 60–70 % of the cost of production. Therefore, a first analysis is to take a look at the differential between the product value and the feed cost. Table 3 shows some of the current values based on natural gas as feed. One can do a similar analysis for coal. This shows the production of olefins, ethylene, and propylene via methanol has the highest differential, making methanol an important intermediate.

Methanol

From the previous discussion, it is clear that synthesis gas can play an important role in the utilization of coal or remote natural gas reserves. Since methanol is a key intermediate in this conversion, it is important to discuss developments in methanol market and technology. The world methanol demand balance for its different uses is

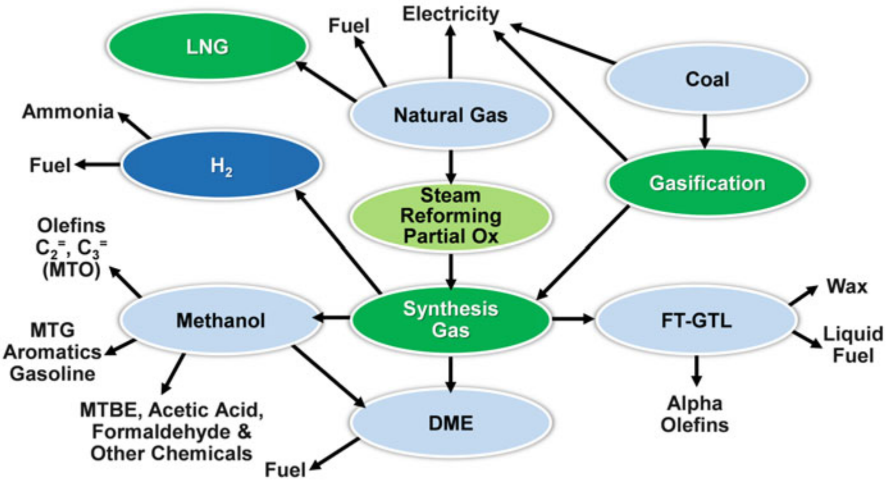


Fig. 5 Natural gas and coal utilization

Table 3 Product-feed price differential, 2013

Product	Product value, $/MT	Approx. ton of NG/Ton product	Differential at 200$/MT = 4/mmBTU	Differential at 400$/MT = $8/mmBTU	Differential at 800$/MT = $16/mmBTU
Gasoline MTG	800	1.46	508	216	−368
Diesel FT	900	1.4	620	340	−220
Ethylene-propylene MTO	1,250	1.46	958	666	82
Propylene MTP	1,300	2	900	500	−300

Assume NG to synthesis gas 80 % C efficiency
Synthesis gas to methanol 95 %
Methanol to gasoline 90 %, synthesis gas to FT liquid 90 %
Methanol to olefins MTO 90 %; methanol to propylene MTP 65 %

Table 4 Methanol demand and end uses

Product, 1,000 metric tons per annum (MTA)	1995	2010
Formaldehyde	7,670	14,880
Acetic acid	1,730	4,800
MTBE	8,030	5,280
Ethylene-propylene	0	1,920
DME, gasoline blending	480	9,600
Other	6,590	12,520
Total	24,500	49,000

shown in Table 4. From 1995 to 2010, methanol production grew at an annual rate of 4.7 %. The recent new application of methanol for the production of ethylene and propylene is expected to become a major and primary use of methanol by 2015 with total methanol production expected to double from 49 million metric tons per annum (MTA) to 98 million MTA.

There are several methanol technology suppliers, of which Lurgi GmbH (Refining Processes, Hydrocarbon Processing 1979), Davy, and Haldor Topsøe (Petrochemical Processes, Hydrocarbon Processing 1993) are some of the main licensors. Until 2000, a typical large methanol plant capacity was 2,500 metric tons per day (MT/D). Some trends in methanol synthesis technology are particularly important for the production of light olefins from gas. First, plant capacity is increasing significantly, as exemplified by several (~5,000 MT/D) mega-scale plants that came in operation during the 2010s (Bonarius 2005). Second, lower feedstock costs in specific geographic areas are having a major impact on methanol production economics. Technology for the production of methanol from synthesis gas is available from several licensors (Methanol Licensors) as seen in Table 5.

Table 5 Major methanol technology licensors

Methanol technology licensor	% Share by no. of plants	% Share by capacity
Davy Process & Johnson Matthey (JM)	24	30
JM/Uhde	5	2
JM/Jacobs	8	7
Lurgi	25	31
Mitsubishi Gas Chemical	12	18
Haldor Topsoe	15	3
JM/Toyo	3	4
Other	8	5

Early development in methanol technology is credited to ICI. ICI first introduced Low Pressure Methanol (LPM) Process in 1966. In 1994, ICI Katalco introduced the Leading Concept Methanol (LCM) Process. Later this became part of Johnson Matthey.

The overall reaction from methane to synthesis gas to methanol can be represented as

$$CH_4 + \tfrac{1}{2} O_2 = CO + 2H_2 \rightarrow CH_3OH$$

Synthesis gas is processed over a fixed bed of catalyst forming methanol and water. Two reactor types are most popular: an adiabatic reactor with multiple quenches of cold stream (ICI system) or a multi-tubular reactor with internal heat exchange (Lurgi system). Both types are operated at a temperature range of 200–280 °C and low pressure of 5–7 MPa using $Cu/ZnO/Al_2O_3$ catalyst. More details are given by Lee (1990) in Methanol Synthesis Technologies, CRC Press (1990). Typical methanol properties and specifications are shown in Table 6.

Methanol Production Economics

Capital investment cost and the feedstock cost vary significantly for different geographic areas. In some parts of the Middle East, the natural gas price in 2013 was 0.75–1.00$/mmBTU, while in the USA it ranged between $3 and $4/mmBTU and over $12/mmBTU in China, Japan, India, and other Asian countries where LNG is imported.

High feed cost units in North America and Western Europe led to significant capacity shut down during the 1980s and 1990s. By 1990, all production in Japan was shut down (Bonarius 2005). Almost all new methanol units were located where natural gas was relatively low in cost, typically in the Middle East and South America. This development led to a dramatic change in the methanol industry. Since 2010 with the development of shale gas, methanol production in North

Table 6 Methanol properties and specifications

Properties	**Value**
Formula	CH_3OH
Molecular weight	32.04
Specific gravity	0.7924 g/cc
Viscosity at 20 °C	0.00592 poise
Vapor pressure at 20 °C	92 mmHg
Freezing point	−97.8 °C
Boiling point	64.7 °C
Methanol specifications	**Grade AA**
Methanol min wt%	99.85
Acetone max wt%	0.002
Aldehyde max wt%	0.001
Ethanol max wt%	0.001
Acidity (CH_3COOH) max wt%	0.003
Appearance	Free of opalescence, suspended matter and sediment
Carbonizable substances	Not darker than color standard no.30 of ASTM D1209 Pt/Co scale
Color	Not darker than color standard no.5 of ASTM D1209 Pt/Co scale
Permanganate fading time, minutes	30
Water max wt%	0.10

Table 7 Methanol production economics

Feedstock	Coal China	Coal USA	Natural gas China	Natural gas USA	Natural gas ME
Feedstock cost	50 $/MT	70 $/MT	12 $/mmBTU	4 $/mmBTU	1 $/mmBTU
Total capital investment, $ Million	1,240	1,500	930	1,160	1,260
Operating cost, $/MT					
Raw material	61.41	99.78	469	160	43
Utilities	73.97	51.53	9	5	5
Fixed cost	38.09	41.93	26	30	33
Cash cost of production	173.47	193.24	504	195	79
Depreciation	60.61	74.40	43	58	63
Return on capital	74.36	89.76	56	70	76
Total cost of production	308.44	357.40	603	323	219

America is reviving again. Table 7 shows cost of methanol production for a unit producing 5,000 MT/D methanol based on 2012 coal prices in China and USA and 2012 natural gas prices in China, Middle East, and USA. These trends are driving a major transformation of the methanol industry (Methanol 2012).

Methanol Derivatives

Acetic Acid

Production of acetic acid employing biological processes has been known for over 10,000 plus years, as long as wine making has been practiced. Vinegar is an aqueous solution of acetic acid. Several aerobic and anaerobic processes have been practiced (Partin and Heise 1993). For the synthetic production of acetic acid, there are three main routs: acetaldehyde oxidation (Fanning 1993), hydrocarbon oxidation (Irick 1993), and methanol carbonylation (Zoeller 1993). Of the three, due to favorable process economics, methanol carbonylation has been the preferred route since 1968.

In 1968 Monsanto disclosed a rhodium iodide catalyst system for methanol carbonylation that operated under milder conditions with high selectivity to acetic acid. The process, known as the Monsanto acetic acid process, has been the basis of all new acetic acid production worldwide (Paulik and Roth 1968). Several publications and patents describe the mechanism of rhodium-catalyzed carbonylation reaction (Roth et al. 1971), as well as, a detailed process description including a schematic plant design (Eby and Singleton 1983). Celanese is also practicing this technology with some proprietary modifications. Later on Monsanto granted rights to British Petroleum (BP). During the late 1990s, BP introduced a rhodium-iridium cocatalyst system and called it the BP Cativa acetic acid process (Jones 2000). Acetic acid is used in several petrochemical derivatives such as vinyl acetate monomer (VAM), purified terephthalic acid, acetate esters, acetic anhydride, and so on.

Formaldehyde

Formaldehyde is an intermediate used in the manufacture of a wide range of products. More than 60 % of it is used in the production of resins, such as urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde. Other applications include 1,4-butanediol and polyacetal resins. In 2004 formaldehyde was classified as a carcinogen to humans by the International Agency for Cancer Research, and as such, it is a highly regulated material. Some of these regulations are still evolving. In 2011 the National Toxicology Program reclassified formaldehyde as carcinogenic to humans (National Toxicology Program 2011). Formaldehyde is highly soluble in water and is sold as a 37 % solution in water, with up to 16 % methanol. For higher concentrations, solution stabilizers are required. Formaldehyde is produced by partial oxidation and dehydrogenation of methanol using either silver catalysts (Reuss et al. 2003) or molybdenum oxide catalysts.

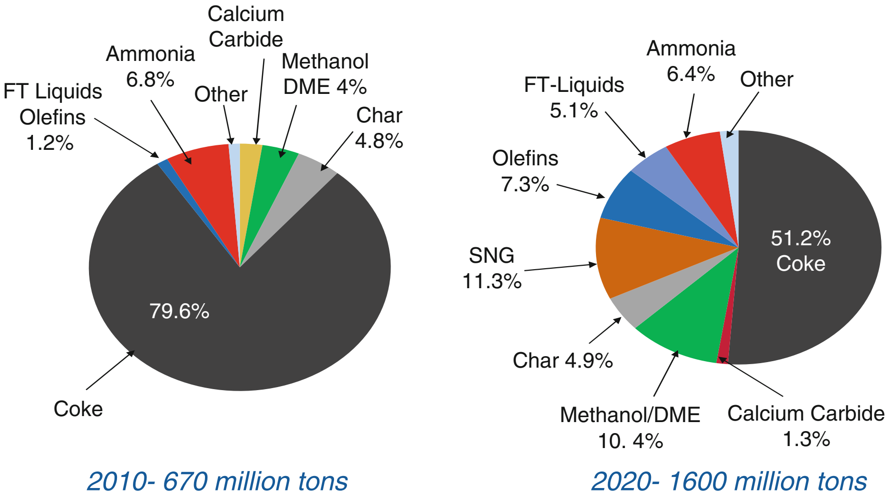
$$\begin{array}{ll} \mathrm{CH_3OH^-} \rightarrow \mathrm{HCHO} + \mathrm{H_2O} & \Delta\mathrm{H} = +2{,}400\ \mathrm{Kcal/Kmol} \\ \mathrm{CH_3OH} + \tfrac{1}{2}\mathrm{O_{2^-}} \rightarrow \mathrm{HCHO} + \mathrm{H_2O} & \Delta\mathrm{H} = -37{,}400\mathrm{Kcal/Kmol} \end{array}$$

There are several technology licensors. Some licensors prefer to operate at 75–85 % methanol conversion with recovery and recycle of unconverted methanol. Others operate near 92–95 % conversion with no methanol recycle. BASF is one of the largest producers of formaldehyde with silver catalysts, but it does not offer the technology for license. The following companies are known to license formaldehyde technology based on silver catalysts: Dyno Industries of Norway, Karl Fischer and Josef Meissner of Germany, Mitsubishi Gas of Japan, ENI (Montedison) of Italy, and DB Western and Monsanto of United States.

Another technology for formaldehyde production is based on the vapor phase oxidation of methanol using metal oxide catalysts: iron/molybdenum oxide with small amount of cobalt, phosphorus, chromium, vanadium, and copper oxides (Klissurski et al. 1991). These technologies are licensed by Axens (France), Dyno Industries (Norway), Haldor Topsøe (Denmark), Nippon Kasei (Japan), Lummus-CBI (USA), and Joseph Meissner and Karl Fischer (Germany) (Formaldehyde 1996).

Olefins

Conversion of methanol to olefins could potentially play a large role in increasing methanol demand. Figure 6 shows China's planning of the use of coal for chemicals (Yajun 2012). In 2010, of the total 670 million tons (MT) of coal consumed, 12 % was used for the production of FT liquids, olefins, ammonia, and methanol/DME. By 2020, coal consumption is expected to increase to 1,600 million tons, and about 28 % of it will go the products mentioned above. The bulk of the increase is in the utilization of coal for the production of FT liquids (5.1 %), for the production of olefins (7.3 %), and for DME 5.1 %. In addition, 11.3 % will go to the production of SNG. During the same period, the share of conventional electric power and industrial use will decline from 79.6 % to 51.2 %. Coal is emerging as a feedstock for new large-scale methanol plants in China, and some of these plants are linked to the production of ethylene and propylene (Gregor 2012; Heng 2012).



Source: Presented by Dr. YajunTian, National Institute of Clean-and-low-carbon Energy, Beijing, China; at Woodrow Wilson International Center for Scholars, July 2012

Fig. 6 China coal utilization planning

Before we discuss ethylene and propylene production from methanol, we must understand the current technologies and the market. Ethylene and propylene are two of the largest volume chemicals produced for the petrochemical industry. Over 200 million metric tons of light olefins were produced in 2010 with an equivalent value of about US$100 billion. Light olefin demand is primarily driven by polyolefin production, but other olefin derivatives such as ethylene oxide, ethylene dichloride, propylene oxide, acrylonitrile, and others consume about 40 % of the light olefins produced today. The majority of the light olefins used for petrochemical applications are produced by the steam cracking of ethane, naphtha, or other gas liquids as shown in the Table 8.

The main factor in olefin production economics is the cost of feedstock, so locations for new capacity are influenced by the availability of cost-advantaged feedstocks. This is evident in the large capacity buildup of ethane-based ethylene production in the Middle East since 1990. Prices for ethane in the Middle East are especially low because there are large amounts produced in association with crude oil production and countries provide incentives for ethane utilization. Availability of ethane also has increased with the discovery and production of shale gas in North America. It is seen from the data in Table 9 that use of naphtha as a feedstock for ethylene production as a percent of total production is declining with some gains in use of LPG, ethane, and the new entry of methanol as feed for ethylene production in China.

During the 1960s, ethylene was also produced by dehydrating ethanol, but with advances in steam cracking and the availability of naphtha and light hydrocarbons, this route is economically no longer favored. Economic analyses done by consulting firms have shown that Middle East ethane crackers and the remote gas MTO

Table 8 2012 light olefin production sources

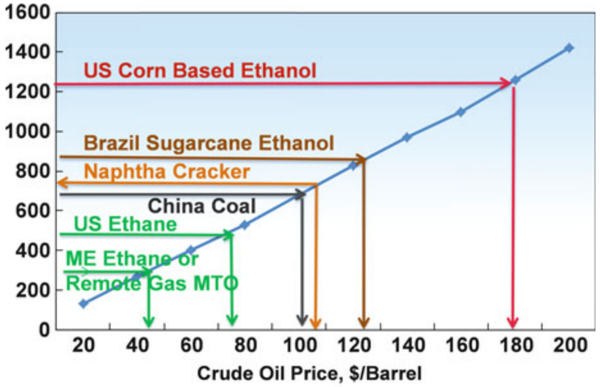
Production sources	Ethylene	Propylene
Ethane cracking	35 %	–
Propane cracking	9 %	
Butane cracking	4 %	
Naphtha cracking	47 %	58 %
Fuel oil cracking	3 %	
Refineries (recovered from FCC units)	–	32 %
Propane dehydrogenation (PDH)	–	5 %
Others	2 %	5 %

Table 9 Ethylene production sources; mmMTA (% of total)

Feed source	2000	2010	2015 Est.
Naphtha	52 (58)	65 (53)	73 (47)
Ethane	28 (31)	40 (33)	47 (30)
LPG	10 (11)	17 (14)	26 (17)
Methanol	0	0 (0)	9 (6)
Total	90 (100)	122 (100)	155 (100)

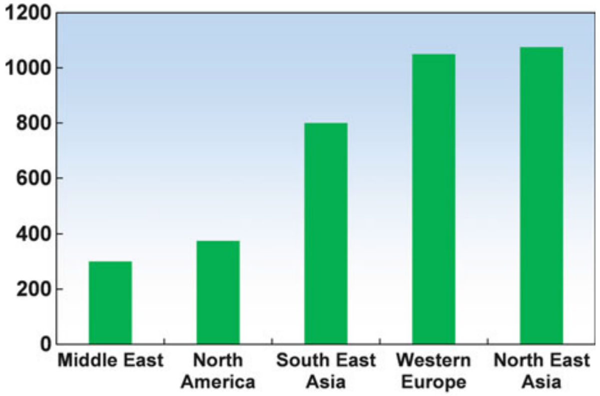
have the lowest cash cost of ethylene production, followed by North American ethane crackers, based on ethane recovered from shale gas. Figure 7 shows the cash cost of ethylene production according to Chemical Market Resources, Inc (Chemical Market Resource Inc. 2013). The cash cost of production is similar for China's coal and naphtha cracker-based ethylene production. It is also seen that the production of ethylene from sugarcane or corn-derived ethanol in Brazil and the USA is not economical. A similar analysis done by IHS-CMAI (HIS Chemicals 2013) for the cash cost of production of existing capacity on a geographic basis is shown in Fig. 8. It is seen that ethylene produced from lower-cost ethane gives the Middle East a significant advantage in cash costs, followed by North America due to shale gas discoveries that have lowered the ethane and LPG prices.

When it comes to propylene, in addition to naphtha crackers where propylene is produced in significant quantities along with ethylene, the refinery FCC units also play an important role, supplying nearly 30 % of the demand in 2012. Because of increasing use of ethane in place of naphtha for the production of ethylene, the



Source: Chemical Market Resources, Inc July 22nd,2013 Volume 7 Issue 15

Fig. 7 Cost of ethylene



Source: IHS Chemicals -2013 World Light Olefins Analysis

Fig. 8 Cash cost of ethylene, $/MT production, $/MT combined production of propylene from naphtha crackers and FCC units falls short of meeting propylene demand. Therefore, since 1990, alternate sources for propylene, such as propane dehydrogenation and metathesis, have emerged to meet the propylene supply gap (Gregor and Vermeiren 2003).

Methanol to Olefins: Processes and Catalysts

Methanol-to-hydrocarbon conversion reactions were first discovered in the early 1970s using ZSM-5 (MFI) catalysts (Chang and Silvestri 1977; Chang 1994). Mobil commercialized a methanol-to-gasoline process in New Zealand in the 1980s and also developed methanol to olefins employing a ZSM-5 catalyst. With support of DOE funding, a 100-barrel per day demonstration unit was operated in Germany (Conversion of Methanol to Gasoline-Extended Project: Methanol to Olefins Demonstration Plant Milestone Report 1986).

In the1980s, scientists at Union Carbide Corporation discovered SAPO-34, a silicon-aluminum-phosphorous-based molecular sieve, which is an excellent catalyst for the conversion of methanol to ethylene and propylene (Kaiser 1985a, b). The structure of SAPO-34 and the small sizes of pore openings are keys to the high selectivity to produce light olefins using a SAPO-34 catalyst. The small pore size (about 4 Å) of SAPO-34 restricts the diffusion of heavy and branched hydrocarbons, which leads to high selectivity to the desired olefins. On the other hand, ZSM-5 molecular sieves produce much lower light olefin yields, primarily due to larger pore openings (about 5.5 Å) in the MFI structure (Fig. 9). A further advantage of SAPO-34 is that the majority of the C_4–C_6 fraction is olefinic. This C_4–C_6 fraction can be converted to light olefins and thus increase the production of C_2 plus C_3 olefins to near 90 %. This reduces the net purge of C_4–C_6 fraction to about 5 % of the carbon yield.

A number of technologies have been developed based on the use of ZSM-5 or SAPO-34 as catalyst. These are the UOP/HYDRO MTO™ ("Methanol to Olefins") Process, which employs a catalyst based on SAPO-34 material (Vora et al. 1997, 1998; Chen et al. 2004) and the Lurgi MTP™ ("Methanol to Propylene") Process

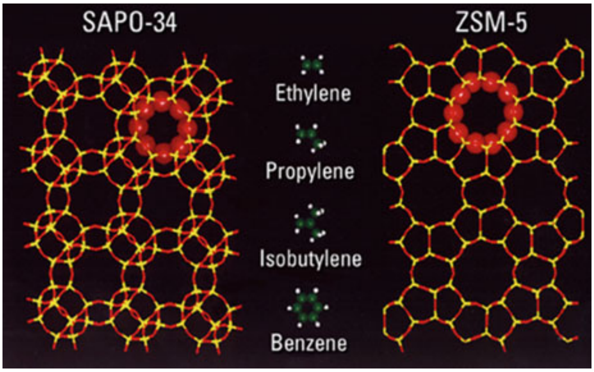


Fig. 9 Framework of SAPO-34 and ZSM-5 molecular sieves

based on a ZSM-5 type catalyst (Gronemann 2005). Similar technologies have also been developed by Dalian and Sinopec in China (Ying et al. 2013). In China one commercial unit of each of these technologies came in commercial operation during 2011, and several more units are in design and construction. Both Chinese processes use the same bound SAPO-34 in a fluidized bed reactor with continuous catalyst circulation and regeneration. In addition, there are two methanol-to-propylene units licensed by Lurgi in operation in China. The MTO Process mainly produces ethylene and propylene and some C_4 olefins, while the MTP process mainly produces propylene with gasoline range C_5-plus hydrocarbon by-product. Honeywell's UOP has announced the licensing of four units in China. The first unit at Wison, Nanjing, successfully came on-stream during the later part of 2013, and a second unit is schedule to begin production during the later part of 2014 (Funk and Vora 2014).

Because ZSM-5 catalysts allow larger molecular weight gasoline range materials to come out of the pores, there is less formation of coke on the catalyst relative to SAPO-34 which only lets n-butene and lower molecular weight hydrocarbons. Thus, for the ZSM-5-based catalyst system, it is feasible to design a fixed-bed reactor system with cyclic regeneration, such as in the Lurgi MTP design. On the other hand, SAPO-34-based catalyst systems employ a circulating fluidized bed reactor regenerator similar to that used in the fluid catalytic cracking process (FCC) in petroleum refining.

Lurgi MTP Process

The Lurgi MTP process uses a fixed-bed catalyst manufactured commercially by Süd-Chemie AG (Lurgi – Generic MTP 2003; Wurzel 2006). It provides high propylene selectivity, low coking tendency, low propane yield, and limited by-product formation. An MTP plant with a feed of 5,000 MT/day methanol produces 1,410 MT/day propylene, 540 MT/day gasoline, and 109 MT/day LPG. Additionally, up to 60 MT/day of ethylene can optionally be recovered from the purge gas, otherwise used as fuel.

Methanol, both fresh and recycle (as recovered from aqueous streams), is the feed to the MTP unit. The methanol is vaporized, superheated, and fed to a DME reactor. The DME reactor is a single-stage adiabatic reactor where most of the methanol is converted to dimethyl ether (DME) on an alumina catalyst. The reaction is exothermic and achieves almost thermodynamic equilibrium.

The product of the DME reactor is sent to three MTP reactors in parallel: two of the reactors are in operation, while a third one is in regeneration or on standby. For the purposes of reaction control, each MTP reactor features six zeolite-based catalyst beds over which the methanol/DME mixture is converted to a mixture of olefins, typically from ethylene to octenes, but such that the carbon distribution peaks at propylene, at an operating temperature of about 450 °C and an operating pressure of 0.15 MPa (about 20 psia). Side products from the reaction include naphthenes, paraffins, aromatics, and light ends. The oxygen chemically bound in the methanol results in process water.

The intermediate reaction product from each catalyst bed is cooled and mixed with additional DME/methanol feed before entering the next bed. The composition of the feed to each bed is adjusted so that the adiabatic temperature rise is about the same across each bed. In order to minimize carbonization and blockage of the active catalyst sites, process steam is added to the feed of the first bed; the steam also serves as a heat sink for the exothermic reaction and helps to control the temperature rise over the catalyst.

The regeneration of the MTP reactors is performed in situ by the controlled combustion of coke with an air/nitrogen mixture at temperatures similar to the normal reactor operating temperature.

The MTP reactor effluent is cooled in a heat recovery system and, finally, through a quench section in which the hydrocarbons are separated from the bulk of the water. The water is condensed and sent to the methanol and DME recovery column, from which they are recycled to the DME reactor. The water with traces of oxygenates is routed to battery limits.

The hydrocarbon vapor from the quench section is compressed to about 2.5 MPa (365 psia) by a multistage centrifugal compressor with intercoolers and partial condensers. The liquid and vapor hydrocarbons are sent to the purification section. The hydrocarbon streams are first dried by using molecular sieves before the hydrocarbon liquid is fed to a debutanizer column, and the vapor is processed through a DME recovery system. The C_4+ bottom product is fed to a dehexanizer where aromatics and C_7+ are separated from the C_6- stream. The majority of the C6− fraction is sent back to the MTP reactors, while the C_7+ fraction is the gasoline by-product.

The compressed hydrocarbon vapors, including light olefins and DME, and the overhead C_4+/DME from the debutanizer are fed to a DME removal system in which C_3- hydrocarbons are separated from C_4+ hydrocarbons and oxygenates. The methanol and DME stream are routed to the methanol recovery column for recycle to the DME reactor. The C4 hydrocarbon fraction is recycled to the MTP reactor for further propylene production, except for small purge that is added to the LPG by-product stream.

The C_3- fraction is fed to the deethanizer in which a C_2- stream is recovered as top product; one part of this stream is recycled to the MTP reactor, while the rest can optionally be sent to a two-column ethylene purification unit or to fuel gas. The C_3 bottom product from the deethanizer contains about 97 % propylene and 3 % propane, but no methylacetylene or propadiene; it is routed through guard bed of activated alumina and fed to the C3 splitter for the recovery of polymer-grade propylene (Fig. 10).

UOP/HYDRO MTO Process

The UOP/HYDRO MTO Process can use “crude” methanol, “fuel-grade” methanol, Grade AA methanol, or even DME as feed. The choice of feedstock generally depends on project-specific situations. Figure 11 illustrates a simple flow diagram for the UOP/HYDRO MTO Process. The MTO process utilizes a circulating fluidized

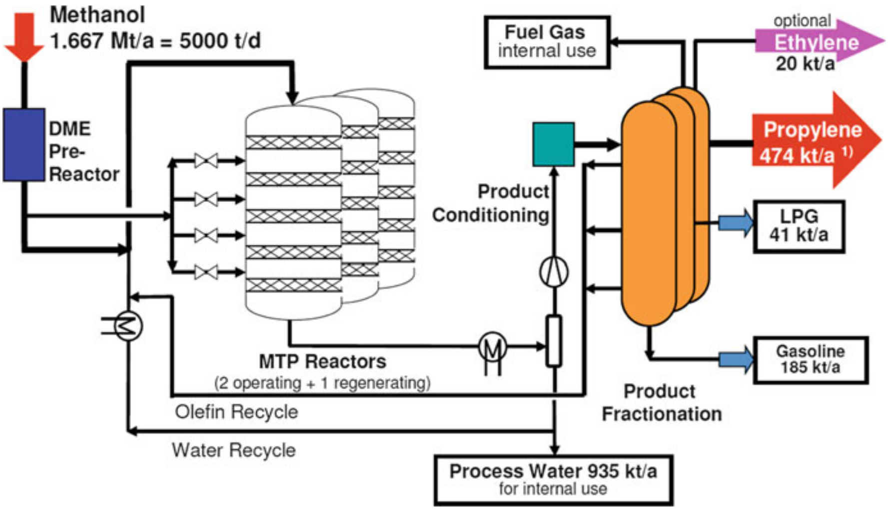


Fig. 10 Lurgi MTP process

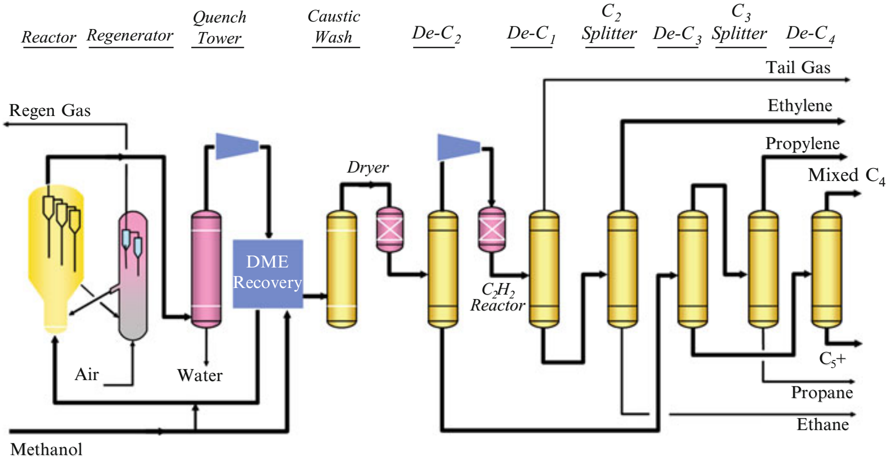


Fig. 11 UOP/HYDRO MTO process flow scheme

bed reactor that offers a number of advantages over both fixed-bed reactors and other types of fluidized bed reactors. The circulating fluidized bed reactor provides better mass transfer than bubbling bed fluidized bed reactors as well as better temperature control than riser and fixed-bed reactors, especially given the highly exothermic nature of the methanol-to-olefins reactions. This type of reactor has been widely used in the fluid catalytic cracking (FCC) process units in petroleum refineries.

Constant catalyst activity and product composition can be maintained via continuous regeneration of a portion of used catalyst by coke burning with air. UOP's MTO catalyst has demonstrated the required selectivity, long-term stability, and attrition resistance necessary for attractive economics with low operating costs.

The overall selectivity of the UOP/HYDRO MTO process is about 75–80 % to ethylene and propylene on a carbon basis, about 15 % C_4 plus hydrocarbons, and the balance is C_1–C_3 paraffins plus coke on catalyst. The C_4 plus material is mostly linear butenes and some pentenes. Propylene to ethylene ratios in the product can be adjusted within the range of 0.80–1.33 to reflect the relative market demand and values for ethylene and propylene. The reactor temperature is the key variable for controlling propylene to ethylene ratios, with higher temperatures leading to a higher ethylene yield. The temperature requirements have to be balanced with higher coke formation at higher temperatures.

Reactor pressure is normally dictated by mechanical considerations. Lower methanol partial pressure leads to higher selectivity to light olefins, especially ethylene. Therefore, a slight yield advantage occurs when using a crude methanol feed compared to high purity methanol. The reactor effluent is cooled and quenched to separate water from the product gas stream. The reactor provides very high conversion so there is no need for a large recycle stream. A small amount of unconverted oxygenates are recovered in the oxygenate recovery section, after which the effluent is further processed in the fractionation and purification section. Conventional treating methods have been shown to be effective for removing by-products to the specification levels required for producing polymer-grade ethylene and propylene products.

Total ethylene plus propylene yield can be further enhanced by incorporating a cracking process to convert C_4 plus material to propylene and ethylene. Overall carbon selectivity for the integrated flow scheme approaches 90 % ethylene plus propylene (Fig. 12).

Integration of CTL/GTL with CTO/GTO

GTL and CTL offer large market opportunities for natural gas and coal utilization but are challenged by high capital costs and relatively low transportation-fuel product values. Since synthesis gas production is a common step in the manufacture of GTL and methanol, there are possibilities for integrated complexes. Figure 13 illustrates such a complex, using coal or natural gas as feedstocks and producing both olefins and liquid fuels. Both coal or natural gas liquid fuels (CTL, GTL) and coal or natural gas to polymers (CTP, GTP) facilities incorporate sizeable front-end synthesis gas units for the processing of natural gas—over 60 % of the capital cost is related to the production of synthesis gas. These units are the major contributors to

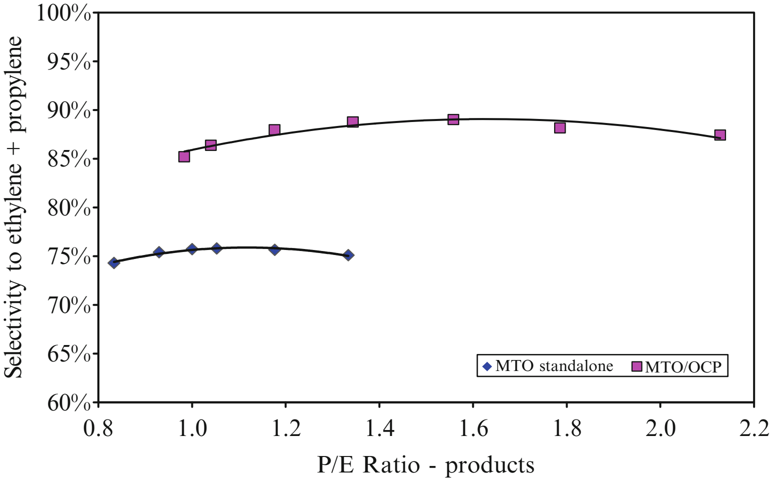


Fig. 12 Olefin selectivity vs. operating severity of the UOP MTO process with and without olefin cracking process (OCP) integration

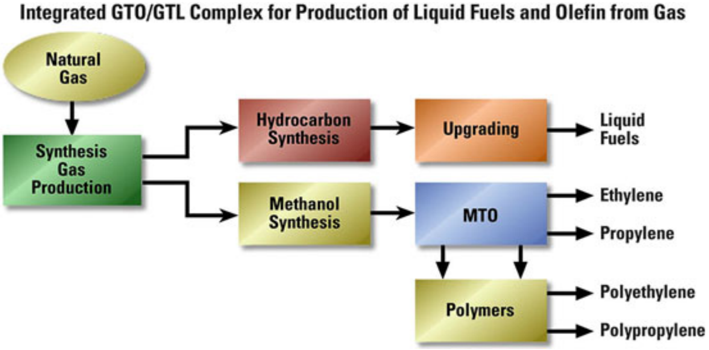


Fig. 13 Conversion steps for coal or natural gas to liquids and polyolefins

the relatively high investments required for these complexes. It follows that the integration of these facilities could offer substantial synergistic savings.

A rough rule of thumb is that the quantity of synthesis gas required to produce 25,000 barrels per day (BPD) liquid hydrocarbons could also be used to produce in excess of one million MTA light olefins. A typical liquid fuel plant is likely to have the capacity of 100,000 BPD or more. Thus, the addition of one million MTA light olefins represents roughly 25 % additional synthesis gas production capacity. The incremental production will require substantially less capital cost than a stand-alone smaller unit. The integration of methanol and liquid fuel facilities combined with the conversion of methanol to olefins can provide cost-saving synergies together with the production of high value-added olefins and polymer products.

Conclusions

Though there are no direct routes for the conversion of coal or methane to liquid hydrocarbons or petrochemical products, these raw materials can be converted to liquid fuels or high value-added petrochemicals via synthesis gas. The vast resources of coal in areas of high demand, namely, the USA, China, and India, could provide long-term raw material security.

References

J. Bonarius, Mega methanol, CMAI, Methanol – too much, too little or just right. Presented at CMAI World Methanol Conference, Miami, 12–14 Dec 2005

BP Statistical Review (2013)

W.H. Calkins, Chemicals from methanol. Catal. Rev. Sci. Eng. **26**(3 and 4), 347–358 (1984)

R. Carapellucci et al., Performance of IGCC power plant integrated with methanol synthesis process. J. Power Energy **215**, 347–356 (2001)

C.D. Chang, Chapter 4-Methanol to gasoline and olefins, in *Methanol Production and Use*, ed. by C. Wu-Hsun, K. Harold (Marcel Dekker, New York, 1994), pp. 133–170

C.D. Chang, A.J. Silvestri, J. Catal. **47**, 249 (1977)

Chemical Market Resource Inc., vol 7, No. 7 (2013). 19 Dec 2013

J.Q. Chen, B.V. Vora, P.R. Pujadó, A. Gronvold, T. Fuglerud, S. Kvisle, Most recent development in ethylene and propylene production from natural gas using the UOP/HYDRO MTO process. Stud. Surf. Sci. Catal. **107**, 1–6 (2004)

Conversion of methanol to gasoline-extended project: Methanol to olefins demonstration plant milestone report; US Department of Energy, DOE?ET?14914-H; DE86 015960 (1986)

R.T. Eby, T.C. Singleton, Appl. Ind. Catal. **1**, 275 (1983)

T. Fanning, *Ethylene and Acetylene Based Processes for Acetic Acid, Acetic Acid and Its Derivatives* (Marcel Dekker, NewYork, 1993). Chapter 2

Formaldehyde, PERP Report No. 94/95-2 Chem Systems (1996)

G. Funk, B.V Vora, Coal and natural gas to Olefins. Presented at 11th Petrotech-India Conference, New Delhi, 12–14 Dec 2014

J.H. Gregor, Maximize profitability and Olefin production via UOP's advanced MTO technology. Presented at HIS World Methanol Conference, Madrid, 27–29 Nov 2012

J. Gregor, W. Vermeiren, Meeting changing needs of Olefins market,in *Proceedings of 5th EMEA Petrochemicals Technology Conference*, *Paris, 25–26 Jan 2003* (2003)

V. Gronemann, 3 in 1 – Lurgi Syngas to Propylen. Presented at 2005 World Methanol Conference, Miami, 12–14 Dec 2005

G.F. Jose Luis, G. Arie and V.P. Ricahrd, GTL Technology – 21st century advances (A study published by The Catalyst Group Resources, Spring House, 2004a), p. 59

G.F. Jose Luis, G. Arie and V.P. Ricahrd, GTL Technology – 21st century advances, section 3.2 commercial and demonstration GTL processes, (A study published by The Catalyst Group Resources, Spring House, 2004b), pp. 49–77

H. Heng, Focus China- Annual methanol demand to spike on MTO, MTP projects, ICIS.com, Article 9604963, 30 Oct 2012

HIS Chemicals, *World Light Olefins Analysis* (2013)

ICIS (June 2012)

International Energy Agency, *Statistical Data* (2011)

G. Irick, *Acetic Acid Manufacture via Hydrocarbon Oxidation, Acetic Acid, Acetic Acid and Its Derivatives* (Marcel Dekker, New York, 1993). Chapter 3

B. Jager, Developments in fischer-tropsch technology, in ed. by M. de Pontes, R. L. Espinoza, C. P. Nicolaides, J. H. Scholz, M. S. Scurrel. Natural Gas Conversion IV. Studies in Surface Science and Catalysis, vol. 107 (Elsevier, Amsterdam, 1997), pp. 219–224

J.H. Jones, Platin. Met. Rev. **44**(3), 94–105 (2000)

S.W. Kaiser, Arab J. Sci. Eng. **10**, 361 (1985a)

S.W Kaiser, US Patent 4,499,327, (1985b)

D. Klissurski et al., Multicomponent oxide catalyst for oxidation of methanol to formaldehyde. Appl. Catal. **77**, 55–66 (1991)

S. Lee, *Methanol Synthesis Technologies* (CRC Press, Boca Raton, 1990)

S. Lee, Chapter 3, Methane derivatives via synthesis gas, in *Methane and Its Derivatives* (Marcel Dekker, New York, 1997a)

S. Lee, Chapter on Synthesis Gas, in *Methane and Its Derivatives* (Marcel Dekker, New York, 1997b)

Lurgi – Generic MTP Information (anonymous), July 2003

Methanol Licensors, *Chem System PERP Report*

Methanol, *Chem System PERP* 2012-5 Table 1.1

National Toxicology Program, report on carcinogens, 12th edn. (2011)

L.R. Partin, W.H. Heise, *Bioderived Acetic Acid, Acetic Acid and Derivatives* (Marcel Dekker, New York, 1993). Chapter 1

F.E Paulik, J.F Roth, J. Chem. Soc. Chem. Commun., 1578 (1968)

PERP Report 03/04S11, Nexant-ChemSystems (2005)

Petrochemical Processes, Hydrocarbon Processing (1993), pp. 70–139

Refining Processes, *Hydrocarbon Processing* (1979), 71–1301

G. Reuss, W. Disteldorf, A.O. Gamer, A. Hilt, Formaldehyde. In: Ullmann's Encyclopedia of Industrial Chemistry, (2003) 6th rev. edn, Vol. 15, Wiley-VCH Weinheim, Germany

J.F. Roth et al., Chem. Technol. **1**, 600–605 (1971)

P.R. Savage et al., Back to coal, in *Thinking Energy, An Imprint of the Thinking* (Energy, Falmouth, 2004), pp. 101–120

Shell doubles capacity of GTL plant at Malaysia. Fuels Lubes Wlky. **4**(43) (23 Oct 2012)

B.V. Vora, T.L. Marker, P.T. Barger, H.R. Nilsen, S. Kvisle, T. Fuglerud, economic route for natural gas conversion to ethylene and propylene, in ed. by M. de Pontes, R.L. Espinoza, C.P. Nicolaides, J.H. Scholz, M.S. Scurrel, Natural Gas Conversion IV. Studies in Surface Science and Catalysis, vol. 107 (Elsevier, Amsterdam, 1997), pp. 87–98

B.V Vora, Eng C, Arnold E, Integration of the UOP/HYDRO MTO Process into Ethylene Plants; 10th Ethylene Producers' Conference, American Institute of Chemical Engineers, 8–12 Mar 1998

T. Wurzel, Lurgi megamethanol technology, in *Synthesis Gas Chemistry*, DGMK conference, 4–6 Oct 2006

T. Yajun, National Institute of Clean-and –Low Carbon Energy, Beijing. Presented at Woodrow Wilson International Centre for Scholars, July 2012

L. Ying, M. Ye, Y. Cheng, X. Li, A kinetic study of methanol to olefins process in fluidized bed reactor, in *The 14th International Conference on Fluidization- From Fundamentals to Products*. NH Conference Centre Leeuwenhorst Noordwijkerhout, The Netherlands (2013)

J.R. Zoeller, *Acetic Acid manufacture via Methanol Carbonylation, Acetic Acid, Acetic Acid and Its Derivatives* (Marcel Dekker, New York, 1993). Chapter 4

Unconventional Crudes and Feedstocks in Petroleum Processing

Steven A. Treese

Contents

Steven A. Treese has retired from Phillips 66.

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_15

Abstract

In addition to the numerous conventional crude oils marketed, there are several types of “unconventional” crudes or feedstocks that a refinery may process. These are unconventional in that they are produced by methods other than typical exploration and production techniques. This chapter discusses the sources, properties, and processing characteristics of several unconventional stocks, including shale oil, shale crude, bitumens, extra heavy oils, synthetic crudes, gas- or carbon-to-liquids stocks, renewable feedstocks, recycled lube oil, transmix, and tank farm stocks.

Keywords

Refinery • Shale • Bitumen • Syncrude • GTL • Gas-to-liquids • Renewable

Introduction

In addition to the numerous conventional crude oils marketed, there are several types of “unconventional” crudes or feedstocks that a refinery may process. These are unconventional in that they are produced by methods other than typical exploration and production techniques. For example, renewable feedstocks originate from biological processes that produce alcohols, vegetable oils, fats, and other materials that can act like petroleum products.

The specific stocks that will be discussed in more detail in this section are:

- Traditional shale oil
- Shale crude and gas
- Bitumens
- Synthetic crudes (abbreviated as syncrudes)
- Gas-to-liquid (GTL) stocks

- Renewables
- Other unconventional feeds

Each of these materials will be discussed in more detail below, including the properties and processing challenges of each.

Traditional Shale Oil

Traditionally, the term “shale oil” described a specific type of product produced by thermal degradation of an organic-mineral rock matrix called kerogen. Shale oil is also known as kerogen oil or oil-shale oil. In fact, oil shale is not a shale at all but is a marlstone, a calcium carbonate-rich mud with variable amounts of clay and silt. It acquired the term oil shale because it looks like a shale.

Raw shale oil itself is an unsaturated, full-range hydrocarbon stock that is normally high in nitrogen and arsenic but low in sulfur.

There have been several processes tested or employed for shale-oil production, both in the ground (in situ) and above the ground (surface or ex situ). Both types of operations employ a pyrolysis process generally termed “retorting” where the oil-shale rock is heated to high temperatures (over 700 °F) to decompose the organic-mineral rock matrix to yield oil, gases, residual carbon/coke, and mineral residue.

Distinction from Shale Crude

Shale oil, historically, is a different material from the more recent shale crudes and gases that are produced from tight shale formations using fracturing techniques. Unfortunately, it has become common to call the more recent production fluids “shale oil.” This has led to confusion about the processing characteristics for these oils. The challenges of processing traditional shale oil are different from those when processing the shale crudes.

For purposes of this book, the term “shale oil” will refer to traditional shale oil. We will use the term “shale crude” to refer to tight shale production fluids.

Production Locations

There are deposits of oil shale from which shale oil can be produced in many locations around the world. Refer to Fig. 1. The largest concentration of deposits (74 %) is in the USA. The total recoverable shale oil, with current production techniques, is about 2.8 trillion barrels.

Shale-oil production has notably been practiced on a commercial scale in Brazil, China, Estonia, Scotland, and the USA. However, none of these areas is really currently (2013) producing significant quantities of shale oil.

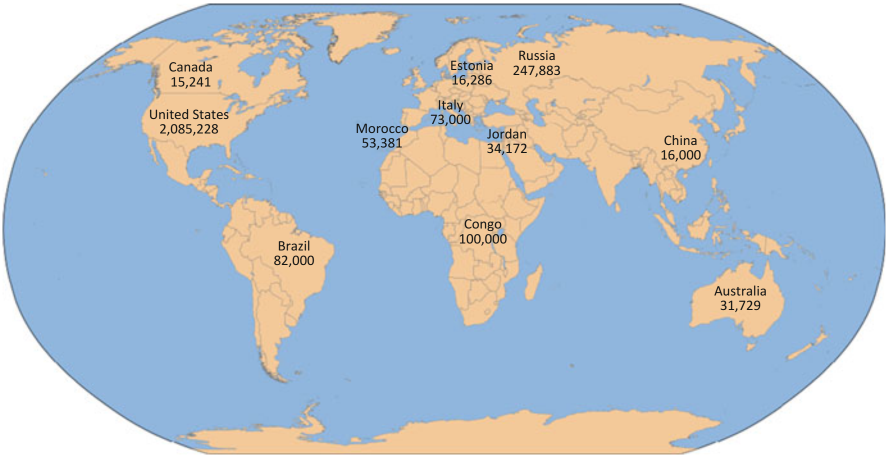


Fig. 1 Distribution of primary world oil-shale resources, estimated million barrels of oil (Data: US Department of the Interior, 2006)

History and Production Rates

The history of shale oil goes back to the earliest uses of mineral oils. The earliest recorded use of shale oil was in Switzerland and Austria in the fourteenth century. It has been used as a medicine, as well as fuel – in spite of raw shale oil being carcinogenic.

In the nineteenth century and on into the twentieth century, several plants were built to extract shale oil throughout the world. The advent of large-scale crude oil production at very low cost has forced shutdown of almost all these plants. Production in Estonia, Russia, and China has continued into the twenty-first century, although the total production is less than five million barrels per year worldwide.

When the price of crude oil rises, there is always renewed interest in shale-oil production techniques, but no major projects have been started since the shutdown of the Unocal facility in Colorado in 1991.

Production Methods

The refining properties of shale oil depend on the production method, so it is useful to understand the processes that have been developed.

Traditional shale oil is produced by a retorting process. In the process, the kerogen rock, which contains the oil precursors in an organic-mineral matrix, is heated to temperatures in the 650–1,000 °F range. The kerogen decomposes to yield liquid and vapor hydrocarbon products, with by-product water, carbon dioxide, H_2S, and other contaminants. Some processes gasify the remaining coke off the mineral residue at temperatures up to 1,700–1,800 °F; this makes hydrogen but also results in large amounts of CO_2 and water vapor being produced. Several processes employ direct combustion of some of the oil shale to heat the balance of the rock, resulting in a mixture of products somewhere between straight retorting and gasification.

The oils produced by all these processes tend to be highly unsaturated due to the thermal cracking nature of the processes. Some still contain residuum boiling-range materials, while others are "bottomless," depending on the retorting process used. For direct combustion processes, the oil will also contain significant amounts of oxygen compounds.

Gases produced from retorting vary in heating value. Lower temperature retorting processes tend to produce a high-heating-value gas (over 1,000 Btu/scf). Higher temperature processes (like gasification and direct combustion) tend to decompose more of the carbonate rock components, generating large amounts of carbon dioxide that dilute the combustible gases with, essentially, inerts, producing low Btu gas (less than 200 Btu/scf).

Oil-shale production efficiency is evaluated against the amount of oil that can be produced by "Fischer assay." In the assay, 100 g of oil shale is heated in a closed retort at 22 °F per minute to 930 °F and then held for 40 min. This is essentially a simple batch retort. During the assay, the evolved vapors are condensed and liquids (oil and water) collected. A material balance is developed to account for all the materials. The most important number derived from the Fischer assay is the oil yield, expressed as gallons per ton (GPT) referenced to the original raw shale-oil charge. Most retorting processes target oil shale that will yield 20–60 gal of oil per ton of rock. Below this level, too much heat goes into just heating rock. Above this level, the rock tends to fall apart into powder, creating handling and permeability problems. Recovery of 100 % of Fischer assay oil is achievable by several processes.

In Situ Retorting

A great deal of effort has gone into developing a process to retort oil shale in place, or "in situ." Several approaches to in situ or modified in situ retorting are summarized in Table 1.

Two primary approaches have been used:

- Direct heating of the oil shale in place by various methods for an extended period followed by creation of porosity in the rock and production of the resulting fluids using more conventional oil-field methods (e.g., Shell ICP).
- Mining of a room inside the rock formation, breaking up the overlying oil shale so it falls into the room, and then retorting the "rubble" by direct heating or combustion of part of the rubble. This is also called modified in situ (e.g., Occidental MIS).

In situ production on a commercial scale has proven to be difficult, for several reasons:

- In the direct heating approaches, an enormous amount of energy is used to heat the oil shale and a lot of it is ineffectively lost to the surrounding rock. Then you

Table 1 In situ shale-oil production processes

Heating method	Processes	2013 status
Internal combustion	Geokinetics horizontal, Lawrence Livermore National Lab RISE, Occidental Petroleum modified in situ, Rio Blanco	No commercial applications
Thermal conduction through rock	Shell ICP, American Shale Oil CCR, Independent Energy Partners GFC	Shell testing technology. No commercial production
Externally heated hot gas	Chevron CRUSH, Omnishale, Mountain West Energy IGE	Conceptual only. No commercial production
Reactive fluids	Shell ICP (some forms)	No commercial production
Induced heating	Radio waves, microwaves, electric current	Conceptual only. No commercial production

Primary sources: Wikipedia articles on oil-shale production; Jensen et al. (1971); Princeton University (1980); Stauffer & Yanik (1978)

have to recover what is produced, but a lot is left in the ground by conventional production methods. The net yield is low and the process tends to be inefficient overall. Research is continuing into this type of production to address these issues.

- During the 1970s and 1980s, several full-scale, modified in situ (rubble)-type retorts were operated in Colorado by Occidental and others. Recovery tended to be less than desired and the heating approach (normally direct firing) was hard to control. This type of retort also required mining of a large amount of the rock to create the retort room – this rock had to be retorted ex situ or spoiled.
- Most of these processes recover less than 85 % of Fisher assay from the rock handled.

Ex Situ Retorting

Most commercial experiences in shale-oil production have come from ex situ or surface retorting. In these processes, the oil shale is mined, crushed, brought to the surface, and placed in a retorting device for heating. The retorted shale or ash must then be dumped and sent to disposal. Several different retort styles have been employed. Most of these processes are able to recover 100 % (or more) of Fisher assay oil. Some of the ex situ processes are summarized in Table 2.

The two primary approaches to rock handling in surface retorting are:

- Batch retorting (e.g., Pumpherston)
- Continuous retorting (e.g., PetroSIX and Union B)

There are further differences in the approaches to heating the oil shale between batch and continuous retorts as shown in the table.

The oldest processes, and those that have been used the most, are the simple batch retorts. This approach is still used in small-scale commercial production today.

Table 2 Ex situ shale-oil production processes

Heating method	Processes	2013 status
Internal combustion	US Bureau of Mines gas combustion, NTU, Kiviter, Fushun, Union A, Paraho Direct, Superior Direct	Several demonstrations. Production from Kiviter and Fushun processes in Estonia, Russia, and China
Hot solids – direct contact (inerts or retorted shale)	Alberta Taciuk, Galoter, Enefit, Lurgi-Ruhrgas, TOSCO II, Chevron STB, Lawrence Livermore HRS, Shell Spher, KENTORT II	Limited commercial production from Galoter and Enefit. Others pilot or demo scale only
External heat through vessel wall	Pumpherston, Oil-Tech, EcoShale In-Capsule, Combustion Resources	Commercial production from Pumpherston process late nineteenth to early twentieth century in Scotland, Spain, and Australia. Others conceptual, pilot, or demo only
Externally generated hot gas	PetroSIX, Union B, Paraho Indirect, Superior Indirect, Syntec	Several pilots and demos. Union B commercial production 1983 to 1991. PetroSIX limited production in Brazil
Reactive fluids	IGT Hytort, donor solvent, Chattanooga fluidized bed reactor	No commercial production. Pilot plants only

Primary sources: Wikipedia articles on oil-shale production; Princeton University (1980); Stauffer & Yanik (1978); Pan et al. (2012)

Several approaches to continuous retorting have been developed since the 1940s. PetroSIX, Kiviter, Fushun, and Paraho retorts are in use today.

All of the surface production methods are challenged by the amount of rock that must be handled (both mining and disposal), the number of solid-handling operations required, the environmental impacts of surface operations, and the availability of water in the oil-shale areas.

Properties from Various Processes

As noted above, the properties of shale oil vary significantly with the production process. Table 3 summarizes some of the more significant process results. The impacts of some of these contaminants on refining are discussed in the next section.

Refining Characteristics

Most of the refining challenges presented by shale oil are known to a refiner; but, the extent to which they will influence shale-oil refining is much greater than with other refinery feeds.

Shale oil has very low aromatic content. It is good for making distillates but not so good for gasoline.

Table 3 Sampling of shale-oil properties

Retort location	Ex situ (surface)									In situ	
Process	Fischer assay	NTU	Gas combustion	TOSCO	Union A	Union B	Union syncrude	Paraho Direct	Galoter/ Enefit	Occidental MIS	USBM
Shale source	USA	USA	USA	USA	USA	USA	USA	USA	Estonia	USA	USA
API gravity	22.3	19.4–25.2	10–20	21.2	18.6	22.7	39–41	19.3	7.4	24.0–25.0	28.4
Specific gravity	0.92	0.90–0.94	0.93–1.0	0.93	0.94	0.81	0.8	0.94	1.02	0.90–0.91	0.89
Sulfur, w%	0.61	0.8–0.9	0.7	0.7–0.9	0.9	0.8	<0.001	0.6–0.7	0.6	0.7	0.6–0.7
Nitrogen, w%	1.96	1.8–2.2	2.1	1.9	2.0	1.7	<0.01	2.0–2.2	0.1	1.5	1.4–1.6
Oxygen, w%		~1.1	1.7	0.8	0.9	0.9		1.4	3.0	1.1	1.2
Carbon, w%	84.59	84.6	83.9	85.1	84.0	84.8		84.9	88.3	84.9	84.6
Hydrogen, w%	11.53	11.4–11.8	11.4	11.6	12.0	11.6		11.5	8.1	11.8	12.1
Distillation, °F	ASTM	ASTM	ASTM	ASTM	ASTM	ASTM	ASTM	ASTM	Sim Dist	ASTM	ASTM
5 %			380–440	200	390	370	130			400–410	<100
10 %	326	493	440–500	280–360	465	425	200	520–530	528	440–460	380–620
50 %	655	670	740–810	700–780	775	700	530	800–810	702	680–700	420–730
90 %			1,030–1,070	>1,000	>1,000	910	750	980	915	910–920	NA–870
95 %			>1,100			960	860	>1,050		1,000–1,050	NA–914
Pour point, °F	80	70–90	85	80	80	60	−30	85		40–65	40
Contaminants, wppm											
Arsenic						25–50	~0	20			
Iron			108	>100	55	10–20		71			
Nickel			6.4	6	6	<2		2.5			
Vanadium			6	3	1.5	<2		0.4			

Primary source: An Assessment of Oil Shale Technologies, Princeton University, 1980

The most significant shale-oil contaminants are listed in Table 4 along with their refining impacts. Approaches to dealing with the contaminants are explored more below. These impacts apply to pure shale oil. If the oil is blended with other stocks, the impacts are proportionally reduced or may become irrelevant.

As with other crudes, a relatively low concentration of shale oil can be coprocessed with other conventional crudes without too much concern. Where shale oil must be specifically considered is when it is a high-concentration (or the only) crude being processed. Dilution helps manage the impurities.

Shale-oil upgrading units (or refineries) can be built to saturate and stabilize the oil, if the scale of operation is sufficient. The resulting syncrude can be a premium stock with very high quality. Figure 2 illustrates possible options in shale oil “pre-refining” ahead of a conventional refinery. The options for pretreatment can range from no preprocessing to complete hydrotreating and dewaxing. Note that a full shale-oil upgrader has to deal with all the other undesirable properties of the oil discussed below.

Unsaturates

Unsaturated compounds (olefins and diolefins) in the shale oil will promote rapid fouling of refinery equipment and catalyst beds. The very high concentrations of unsaturates in the shale oil can be mitigated by hydrotreating the oil to reduce or eliminate the double bonds and stabilize the oil.

Any facility running shale oil can expect to see an increased tendency for gum formation and fouling in the heat exchangers and furnaces. This is due to polymerization of the unsaturated compounds. The polymerization reactions are initiated and/or promoted by the nitrogen and oxygen compounds commonly found in shale oil.

As the oil is hydrotreated, the cold flow properties of the oil (e.g., pour point) degrade. The oil becomes more waxy and difficult to move at ambient temperatures. A shale oil that is only hydrotreated will have a pour point over 120 °F. To improve product cold flow properties to an acceptable level, hydrotreated shale oil must normally be catalytically dewaxed.

Fines

Many of the processes for producing shale oil leave rock fines in the oil. Most notably, the TOSCO II (hot ball) and other processes which used direct heat contact between the oil shale and a hot solid produce an oil with several percent ash. These mineral fines require removal. The primary removal processes employed have been:

- Delayed coking – Used for very high fine levels. Because the oil has already been coked once, the coke yield is low and the resulting coke is almost all fines – meaning very low value.
- Electrostatic separation – Similar to a desalter or an electrostatic precipitator. In this approach, the high shale-oil conductivity is a challenge. Special electrode configurations and chemicals are required.

Table 4 Shale-oil refining challenges

Refining challenges	Unsaturates (olefins/diolefins)	Mineral fines and ash	Arsenic	Iron	Nickel, vanadium, other metals	Nitrogen	Oxygen	Cold properties	Toxicity
Typical range	Bromine numbers from 25 to 60 depending on process	Several hundred ppm to several percent in hot solid processes	20–50 ppm	10 – >100 ppm	<2–20 ppm	Up to 2.2 w%	0.8–3.0 w%	40–90 °F pour point raw shale oil, over 100 °F in heavily hydrotreated oil	Raw shale oil is toxic and carcinogenic
Refining impact	Gum formation and fouling in preheat exchangers, heaters, and reactors	Rapid fouling of equipment with accumulated solids. Made worse by gum formation from unsaturates	Severe catalyst poison in all types of catalytic units	Fouling of equipment with accumulated solids, deposits of iron sulfide	Catalyst poisons and potential foulants in catalytic units	Temporary poison for cracking and other catalysts	Equipment corrosion from organic acids, promotes gum formation from unsaturates	Handling issues with raw shale oil, may limit the percentage of shale-oil products in finished products	Handling issues with raw shale oil
Impact management approaches	Selective hydrogenation, full hydrotreating to saturate olefins. Creates cold property problems	Coking, electrostatic precipitation, filtration	Arsenic trap ahead of catalyst beds	Can be managed like mineral fines and ash by coking or filtration, mechanical removal, dissolved Fe will form FeS deposits	Metal traps ahead of catalyst beds	Severe hydrotreating	Removed by hydrotreating; TAN managed by metallurgy	Blending off the shale-oil products, coprocessing, heated pipes and tanks, hydro-dewaxing shale oil	Handling similar to other thermally produced oils, hydrotreating reduces toxicity and eliminates carcinogenic properties

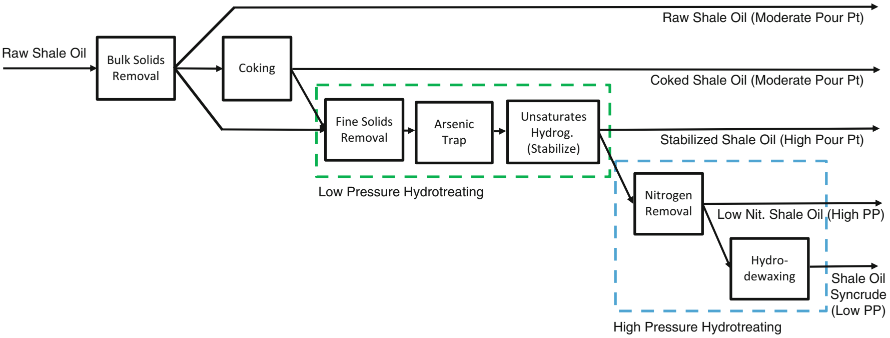


Fig. 2 Shale-oil upgrading schemes

- Filtration – Practical only for low concentrations. A "sand filter"-type approach has been effective for fines removal, but frequent bed changeout may be required.

Note that the gum-forming nature of the unsaturated compounds, combined with the fines, makes fouling in shale-oil processing worse than either of these factors would alone.

Arsenic

Raw shale oil typically contains 30–50 ppm arsenic. This arsenic tends to be in the distillate and heavy naphtha boiling ranges but is also spread throughout other cuts. Arsenic is a severe poison for almost all catalytic refining processes.

The arsenic levels in shale oil can be managed by dilution if the shale oil is a small enough portion of the refinery crude diet.

Arsenic traps (normally nickel sulfide-type materials) have been used in process units such as hydrotreaters. The spent arsenic traps are hazardous. They normally require special handling and decontamination procedures for catalyst handlers.

Disposition of the spent arsenic trap needs to be planned well in advance. Nickel smelters that process arsenious nickel ores have been able to recycle some of the spent materials in the past. Metal reclaimers can also process low levels of arsenic, but often the spent arsenic sorbent has ended up, unfortunately, in hazardous waste landfill.

Iron

Raw shale oil produced by most processes has a high iron content compared to normal crude oils. Some of this is due to wear and tear in the solid-handling equipment and corrosion, but the shale rock also contains iron pyrites that break down on heating. Where the oil is hydrotreated or where H_2S is present, additional iron sulfide solids will be generated.

Coking and fine solid removal should eliminate most of the iron. Normally, no catalyst impacts would be expected.

Nickel, Vanadium, and Other Metals

Slightly elevated levels of nickel, vanadium, and other metals may be found in shale oil. The levels observed are not significantly worse than those in conventional crudes.

Metals are managed using conventional metal traps or by coking of the raw shale oil.

Nitrogen

Unlike conventional crudes, where sulfur is the most common contaminant, shale oil may contain up to 2.2 w% nitrogen. Refer to Table 3 for some typical ranges in raw shale oil. The nitrogen will vary, depending on the retorting process and the kerogen formation characteristics.

Where the shale oil is coprocessed with other crudes, the nitrogen level will be mitigated. It may not require any special processing.

For higher concentrations, the nitrogen can be removed by severe, conventional hydrotreating. The required process conditions are similar to hydrocracker pretreating (e.g., 1.0 LHSV, 1,800 psia hydrogen partial pressure) and hydrogen consumption will be high. The processing severity will necessarily eliminate almost all the unsaturated compounds and other contaminants in the oil. Severe hydrotreating conditions will also make the oil cold flow properties worse, possibly requiring a subsequent dewaxing step. High ammonia partial pressures from hydrotreating shale oil will result in high ammonium salt (NH_4HS and NH_4Cl) deposition temperatures in the hydrotreater effluent. High wash water rates and possible recycle gas water scrubbing will be required to avoid buildup of ammonia in the hydrotreater recycle gas.

At high production rates, the ammonia produced by hydrotreating may be worth recovering. This has been practiced on a limited scale using the Phosam process (ammonium phosphate).

Oxygen

Shale oil will contain more oxygenated compounds (carboxylic acids, aldehydes, ketones) than conventional crude oils. Shale oil from retorts heated by direct combustion, where the unsaturated oil contacts carbon dioxide, would tend to have higher acid numbers than oil from indirect retorts. This may not be a problem if the oil is coprocessed with other crudes. Equipment metallurgy may need to be reviewed to avoid issues with high acid numbers.

If the shale oil is hydrotreated to remove nitrogen, the oxygen compounds will also be effectively removed. Otherwise, the oxygen compounds are no worse than for other crudes.

Cold Properties

Raw shale oil has a pour point that is in the 40–90 °F range. It needs to be handled as any other high pour point crude – using heated tanks and pipes within most refineries to prevent freeze-up. The other cold properties of shale oil are correspondingly worse.

Once it has been hydrotreated, the resulting oil is even more paraffinic, with pour points that can be above 120 °F. The distillate fractions will need to be blended with other stocks to meet cold flow property requirements or the stocks can be hydro-dewaxed. Full-range shale oil has been hydro-dewaxed with good results. See the column in Table 3 for Union B shale-oil-derived syncrude.

Because it is processed so severely in hydrotreating and dewaxing, the product distillates will have very low conductivity. This can be a problem in fuel handling, especially for jet aircraft. Expected conductivity additive levels can be expected to be higher than for normal oils.

Toxicity

Raw shale oil has been categorized as a carcinogen and is toxic. The severity of these factors is no worse than other thermally derived stocks but needs to be borne in mind when running shale oil. Employees in the Scottish shale-oil industry suffered frequently from cancer due to poor industrial hygiene practices when they did not know or understand the risks.

The toxicity of shale-oil-derived syncrude, following hydrotreating and dewaxing, is no worse than conventional refinery products. Processing the oil eliminates most of the toxic issues.

Care must still be taken when handling the spent catalysts and sorbents that result from processing shale oil.

Concluding Shale-Oil Comments

Significant quantities of shale oil are not expected to be available in the USA in the foreseeable future. Small quantities will continue to be produced in a few other countries using existing processes and improvements.

Shale-oil production is severely challenged by both economic and environmental issues, as well as technical difficulties. While it is possible to make a liquid fuel from shale oil, there has to be sufficient incentive to take the leap. Old-timers in the shale-oil business in the USA say “it is a promising technology, and it always will be.” Improvements in production concepts and demand for liquid fuels may eventually prove them wrong.

Shale Crude and Gas (Tight Oil)

There has been a surge in production of crude and gas from shale deposits in the early twenty-first century. Widespread improvements in directional drilling and application of hydraulic fracturing (“fracking”) have led to a resurgence of production, especially in the USA. This has not been without resistance for environmental reasons and concern over the potential for groundwater contamination.

We will focus primarily on the shale crudes in the following discussion. The coproduced shale gases look and process essentially like any other petroleum gases. They do not present any special problems.

The crude produced from shale presents some unique challenges in refining. Specific issues have been observed with phosphorus, calcium, silicon, incompatibilities, and other factors that are discussed below. These are different from traditional shale-oil refining issues.

Shale crude is much more widely available than any traditional shale oil, which lends more importance to understanding the shale-crude-processing issues.

Definitions

For purposes of this book, we will use the term "shale crude" and "shale gas" to distinguish fluids produced by fracking of tight shale deposits from those produced by oil-shale retorting ("shale oil"). In the case of shale crudes and gases, the term shale is actually more correctly applicable, since traditional shale oil was really produced from marlstone, not shale.

Shale crude has also been referred to as "tight oil" or "tight shale oil" in literature.

Production Locations

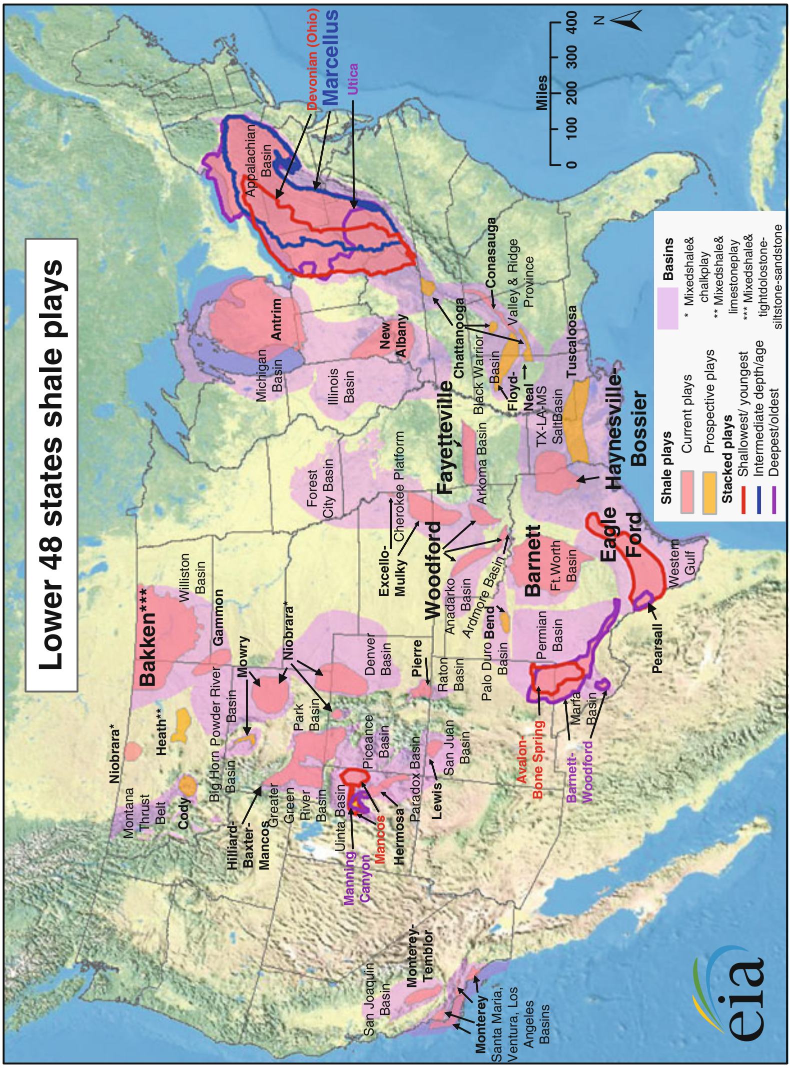
Extensive deposits of shale that can produce crude are distributed worldwide. See Fig. 3 for known shale locations in the USA, and Fig. 4 shows potential shale plays elsewhere in the world. Estimated recoverable reserves from tight shale in the USA alone are 3.6 billion barrels. The distribution of these resources is in Table 5.

The properties of the shale crude vary significantly (and geographically) within the shale formations. Crudes marketed as "shale crudes" are really blends from several different fields masquerading as a single crude. They can have widely varying properties and refining characteristics. Figure 5 shows the general trend for API gravity and oil/gas ratio in the Eagle Ford field as an example of these variations. The crude gravity is lowest (highest density) near the north and west portions of Eagle Ford, and the crude API gravity increases (lower density) toward the south and eastern portions of the play.

Production Rates

The production of shale crude has grown rapidly since 2000, with improved production techniques. Figure 6 shows the growth in shale-crude production in the USA and the projected future impacts. This growth has allowed the USA to greatly reduce the need to import crudes and has driven crude prices down.

Unfortunately, the locations where shale crudes can be produced are not necessarily near available crude pipelines. Extensive use of rail transport has developed as a short-term approach for getting the shale crudes to market.



Source: Energy Information Administration based on data from various published studies.
Updated: May 9, 2011

Fig. 3 Shale plays in the USA

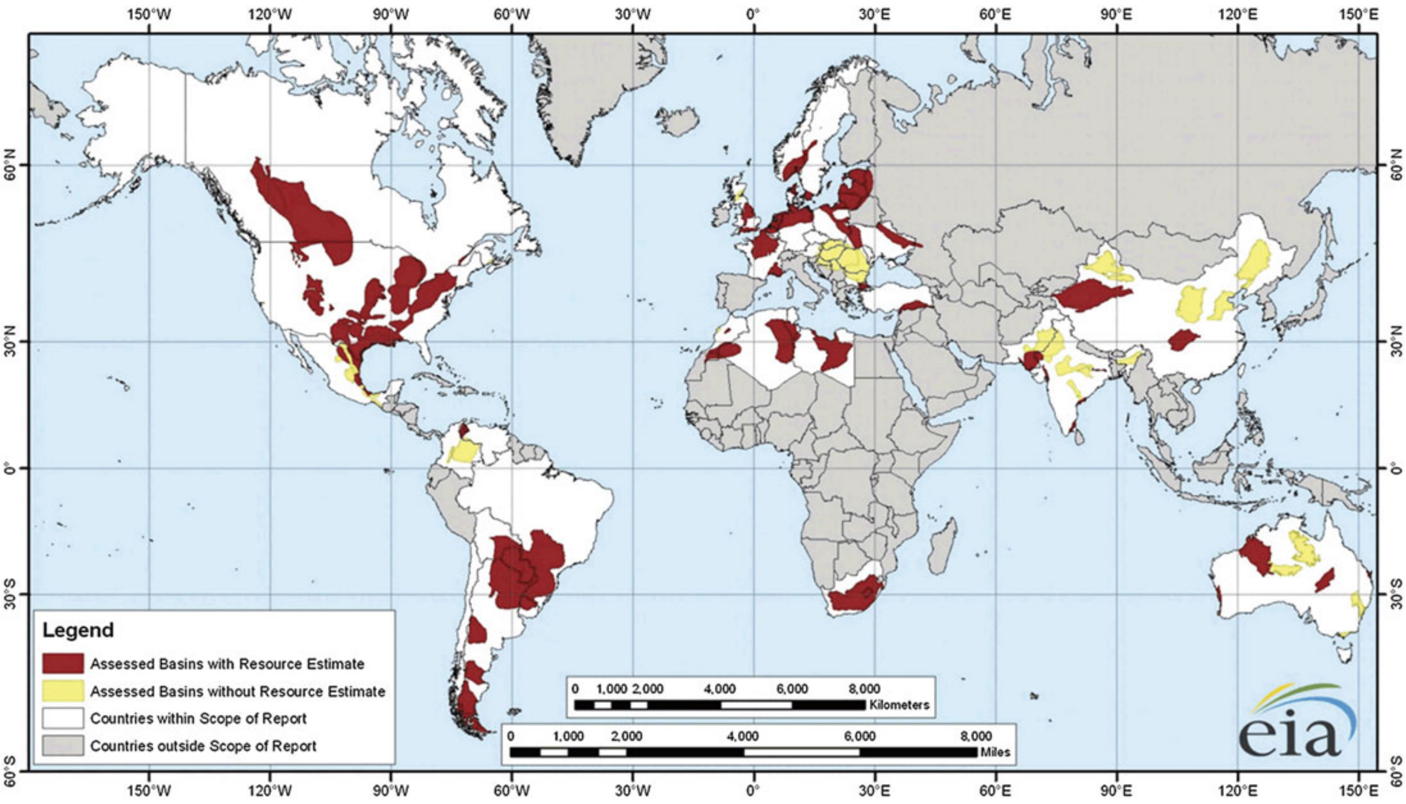


Fig. 4 Shale plays elsewhere in the world (Source: US Energy Information Administration)

Table 5 Estimated shale-crude reserves in the USA

Basin	Play	State(s)	2011 (million barrels)	
			Production	Reserves
Williston Basin	Bakken	ND, SD, MT	123	1,988
Western Gulf	Eagle Ford	TX	71	1,251
Fort Worth	Barnett	TX	8	118
Denver-Julesburg	Niobrara	CO, KS, NE, WY	2	8
Subtotal			204	3,375
Other tight oil plays			24	253
All US tight oil plays			228	3,628

Includes condensates

Source: US Energy Information Administration, Form EIA-23, "Annual Survey of Domestic Oil and Gas Reserves," 2012

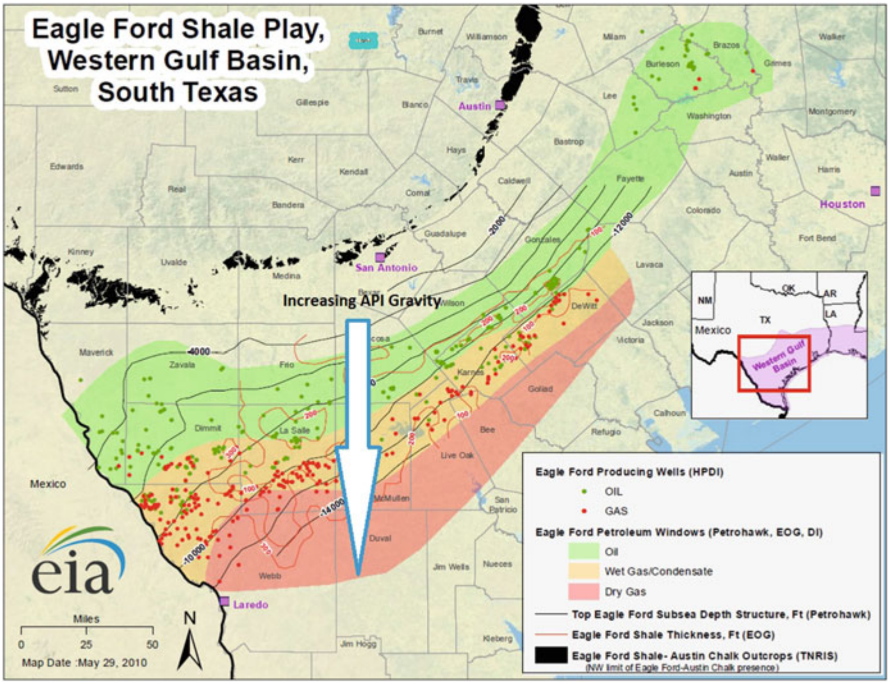


Fig. 5 API gravity trend in Eagle Ford shale-crude production

Methods of Production

Shale crude and gas are produced from "tight" shale deposits. In these deposits, there is free oil and gas present; but there is no rock porosity available to allow the oil and gas to flow to a production well.

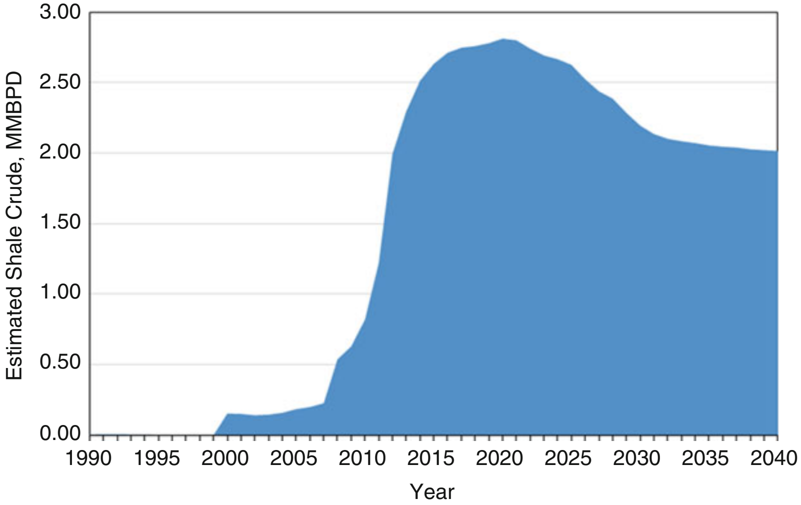
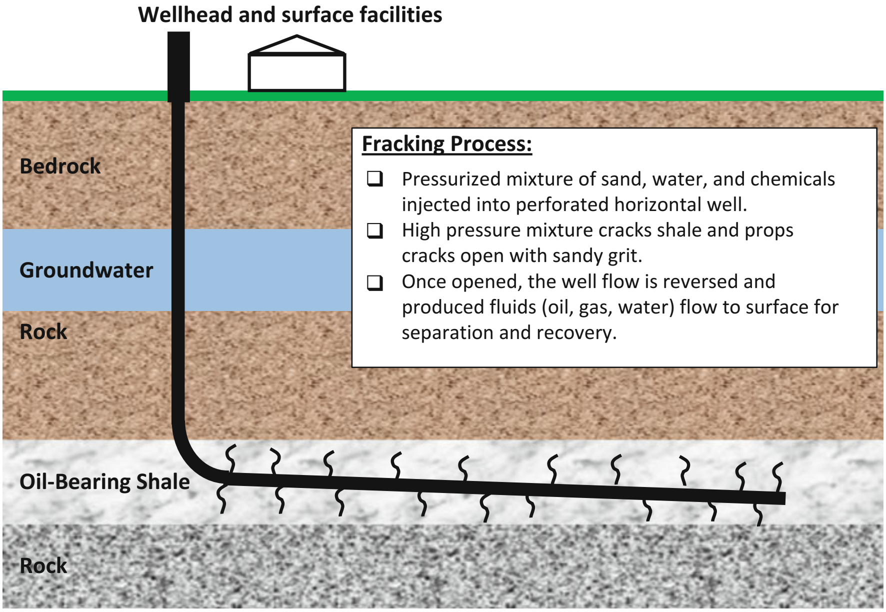


Fig. 6 US estimated shale-crude production trend (Source: US Energy Information Agency, 2013)



Fracking Process:

- ☐ Pressurized mixture of sand, water, and chemicals injected into perforated horizontal well.
- ☐ High pressure mixture cracks shale and props cracks open with sandy grit.
- ☐ Once opened, the well flow is reversed and produced fluids (oil, gas, water) flow to surface for separation and recovery.

Fig. 7 Hydraulic fracturing to produce oil and gas from shale

Hydraulic fracturing of the shale rock is required to create the porosity to allow the oil and gas to be removed from the formations. Figure 7 illustrates one of the common production methods as well as the implications and environmental concerns with the technique.

A horizontal well is drilled into the shale formation. The rock is hydraulically fractured by pumping proprietary mixtures of chemicals and “proppants” (like sand) into the formation at very high pressure. This high-pressure material cracks or fractures the shale formation, creating porosity. The well flow is then reversed, initially pulling the fracking chemicals out, leaving the propants in place, followed by the freed oil, gas, and coproduced water. The shale crude will contain residual fracking chemicals in addition to production chemicals. These affect the refinery impacts of the crude.

The production life of a tight shale well has been shorter than conventional wells. It has been necessary to keep drilling and fracturing to maintain production. This means that there is much more influence of the fracking and production chemicals than a refinery might experience in most conventional crudes.

Properties of Shale Crudes

Table 6 provides a sampling of properties from some of the more commonly available shale crudes. The crudes themselves generally compete with light or medium sweet crudes.

The shale crudes have been largely brought to refineries by rail. Use of this method has expanded greatly in the past few years. This has not been without issues. The crude as shipped has a very high vapor pressure because it is spiked with lighter hydrocarbons. The rail tragedy in Lac-Mégantic, Quebec, Canada, in July 2013 serves as a grim reminder of the need to diligence in transporting these high vapor pressure materials.

As noted above, the properties vary considerably from one field to another, so production from one area of Eagle Ford may not look anything like production from another area of Eagle Ford, for example. Because of field blending, there are really no truly typical shale-crude assays, so we end up settling for some averages. One cargo to the next will vary.

Refining Considerations and Practices

Shale crudes tend to be fairly light and sweet from a refining standpoint. Reported problems processing shale crudes (and similarly produced materials) have included:

- Increased fouling rates in crude unit preheat, furnaces, and towers
- Increase crude corrosion rates
- Incompatibility with other crudes
- Loss of compatibility with other crudes during processing
- Increased catalytic unit fouling

Many of these issues can be traced to the production techniques for shale crudes. Table 7 summarizes the potential fracking and production chemical impacts on a refinery by the chemical used. Table 8 provides a summary of expected impacts of shale crude in a refinery by unit. Additional discussion follows.

Phosphorous

Phosphorous chemicals are used extensively in both fracking and production of shale crudes. The chemicals are normally phosphate esters or phosphonates with the general formulas illustrated in Fig. 8.

Table 6 Range of published shale-crude qualities for Bakken and Eagle Ford

	Bakken	Eagle Ford
Crude	Typical ranges[a, c]	Typical ranges[b, c]
Whole crude		
API gravity	41–42.1	47.0–58.8
Sp. gr., 60 °F	0.82–0.83	0.74–0.79
RVP, psi	High	6.5–9.7
Sulfur, w%	0.13–0.20	0.05–0.11
Pour point, F	−25 (spiked)	6–15 (spiked)
Con. carb., w%		0.07–0.24
Viscosity, SSU		
@60 °F		31–41
@80 °F		30–37
@100 °F		29–35
H_2S, wppm		<1 (scav.)
Metals, wppm		
Ni		0.1–0.21
V		0.03–0.5
TAN, mg KOH/g		0.02–0.03
Salt, lb/Mbbl		0–1
Organic chloride, wppm		<1
Distillation, °F		
IBP	<50	<50
10 %	144–162	156
50 %	452–480	445
90 %	940–955	920
95 %	1,050–1,060	1,030
EP	~1,250–1,280	~1,300
Cut properties		
375–500 °F kerosene		
Sulfur, w%	0.02	0.02
500–620 °F diesel		
Sulfur, w%	0.09	0.07
620–1,050 °F gas oil		
Sulfur, w%	0.24	0.19

(*continued*)

Table 6 (continued)

	Bakken	Eagle Ford
Crude	Typical ranges[a, c]	Typical ranges[b, c]
1,050 F – plus resid		
API gravity	14	
Sulfur, w%	0.68–0.75	0.60
Con. carbon, w%	11.3	
Metals, wppm		
Ni	7	2–4
V	2	0.5–0.6

Data sources:

[a] "Draft Supplemental EIS for Keystone XL Pipeline" (Original source was Crudemonitor 2012a, 5 year avg.)

[b] "Effects of Possible Changes in Crude Oil Slate on the U.S. Refining Sector's CO2 Emission," MathPro Inc., International Council on Clean Transportation, 3/29/2013

[c] www.caplinepipeline.com, "Crude Oil Quality Assay Reports."

In refineries, the impacts of phosphorus have been observed in several units. Under refinery conditions, the phosphorous compounds will decompose and react. Among problems most commonly reported attributed to these compounds are:

- Crude unit preheat exchanger, furnace, and tower fouling – Sometimes rapid and extensive. Tray fouling tends to be in the upper portions of the tower. Attempts to control this with chemicals have met with variable success. Dilution with other crudes may help mitigate the issues.
- Crude tower corrosion from phosphates and phosphoric acid – Tower metallurgy may be increased. Chemical control has had limited success.
- Distillate hydrotreater fouling or poisoning – Phosphorous chemicals tend to end up in the distillate boiling range. Catalyst fouling and/or deactivation has been observed in diesel hydrotreaters, depending on the chemical types. The catalyst foulant has been in the form of a very fine powder that deposits in the top of the lead reactor. Cleaning exchangers and skimming catalyst beds to manage pressure drop have been successful. Chemical treatments have not seen great success. If the phosphonate survives upstream processing, it can poison hydroprocessing catalysts.

Silicon

Silicon contamination of shale crudes has not been much worse than with other crudes. The silicon may arise from production and shipping chemicals (emulsion breaking and antifoams), as well as materials from the shale formation itself. The antifoams are probably more significant.

Silicon traps in hydroprocessing units are required in most cases. This is nothing new.

Table 7 Impacts of production chemicals on shale-crude processing

Applications	Typical chemicals	Refinery impacts
Fracking additives		
Surfactants	Acids (citric, lactic, etc.)	Crude unit corrosion, desalting
Cross-linkers	Boric acid, Al, Zr, KCl, NH_4Cl. $CaCl_2$	Corrosion, deposits, catalyst poisoning
Scale control	Phosphate esters and phosphonates	Crude and catalyst fouling, crude corrosion
Biocides	Glutaraldehyde and others	May impact wastewater treating
Corrosion control	Formic acid, Kl, Sb, imidazolines, quaternary amines, etc.	Catalyst poisoning, crude overhead corrosion
Pipe cleaning	HCl, HF, HBr, DDBSA	Corrosion in crude and catalyst units
Paraffin control	Polyalphaolefin polymers	Crude impacts, chloride corrosion from chlorinated versions
H_2S scavenger	Triazines	Overhead corrosion, catalyst problems
Production additives		
H_2S scavenger	Triazines	Overhead corrosion, catalyst problems
Corrosion control and biocides	Quaternary amine and chloride salts	Crude corrosion, catalyst poisoning
Emulsion breaking	Water-treating polymers, metal salts ($ZnCl_2$, $AlCl_2$, poly aluminum chloride), oxyalkylate resins, silicone	Some will affect refinery units, especially chlorides
Paraffin control	Solvents, polyalphaolefins	Corrosion from chlorinated varieties or dumped solvents
Scale and corrosion control	Phosphate esters and phosphonates, acrylic acids	Crude and catalyst fouling, crude corrosion
Biocides	Glutaraldehyde and others	May impact wastewater treating

Primary source: *Shale and Tight Oil . . . The New Frontier*, S.A Lordo & B. Mason, Nalco, 3rd Opportunity Crude Conference, 2012

Metals

A number of metals have been observed in shale crudes that affect refinery processing. Specific elements observed in shale crudes include:

- Calcium
- Magnesium
- Aluminum
- Zirconium
- Potassium
- Antimony
- Zinc

Table 8 Impacts of shale crude on refinery operations

Unit	Shale-crude impacts
Tankage/bulk handling	Incompatibility, waxy deposits
Desalting	Wax-stabilized emulsions, fouling, salt carry-over, high filterable solids
Crude distillation	Preheat fouling, upper tray fouling, light end lift limits, undersized crude heater, more overhead corrosion
Vacuum distillation	Lower gas oil yields, waxy deposits, oversized vacuum heater
Fluid catalytic cracking	Good cracking and selectivity, lower octane, less slurry make, lower regenerator sulfur
Olefin processing	No significant differences
Hydroprocessing (general)	Lower severity and rates, increased fouling in preheat, instability, chlorides
Distillate hydrotreating	Poor cold flow properties, possible dewaxing needed, possible cut point changes, chloride issues, preheat fouling
Gas oil hydrotreating	Easier treatment to low sulfur levels (Tier 3?), feed, and/or product incompatibility
Naphtha reforming	Lower octane due to paraffins, higher gas production
Coking	Less vacuum resid (unloaded), high API, low carbon feed
Wastewater treating	Solid carry-under at desalter, alkaline metals, biocides
Sulfur recovery	Lower sulfur, lower ammonia – possibly unloaded

Primary source: *Shale or Tight Oil Processing*, Scott Sayles, KBC Advanced Technologies, AFPM Q&A Sessions, 2 October 2012

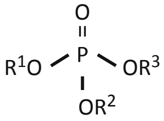


Fig. 8 Organic phosphate ester. R^1, R^2, and R^3 are organic chains, hydrogen, or metals

The presence of calcium and magnesium in the crudes can come from the chemicals used in the fracking processes (e.g., $CaCl_2$), as well as being produced from acidic treatments of the formation. Some will be removed by desalting, but calcium and magnesium salts (e.g., chlorides) can make it through the desalter. These compounds will decompose in furnaces or reactors. If chloride salts decompose in furnaces, they will cause HCl corrosion of the related towers and equipment where water condenses with the corrosion product eventually showing as iron sulfide. Ca or Mg that reaches catalyst beds will cause fouling.

Aluminum, potassium, and zirconium compounds in the shale crudes originate in fracking additives, emulsion-breaking chemicals, or corrosion control chemicals. These tend to cause exchanger and other deposits. Chloride forms of the metals will decompose on heating to release HCl, resulting in corrosion wherever water condenses. The corrosion product eventually shows as iron sulfide deposits.

Antimony can be introduced in corrosion control chemicals used in some fields. While effective for field corrosion control, it can result in rapid catalyst deactivation by poisoning.

Zinc emulsion-breaking chemicals, as zinc, will cause some fouling. If the zinc is in the chloride form, it will release HCl on heating to cause corrosion. The corrosion product (causing fouling) will appear as iron sulfide eventually.

Crude and Product Compatibility

Shale crudes tend to be somewhat paraffinic, as reflected by their higher API gravities (lower specific gravities). Problems have been observed when mixing these crudes with other, more aromatic crudes. The shale crudes tend to cause other crudes to be less stable and to precipitate asphaltenes or other heavy aromatic structures. Instability is possible in storage tanks along with wax depositions on the walls of unheated tanks.

The instability observed has occurred over specific ranges of mixtures, with an onset as some low percentage of shale crude and the instability disappearing at a high percentage. Testing of specific crudes for compatibility will help identify potential problems when processing shale crudes.

It has also been observed that heavy shale-crude stocks that are severely co-hydroprocessed with other crude stocks may reach a point of instability somewhere within a catalyst bed, resulting in high pressure drops in unusual locations. This is likely similar to asphaltene issues that are sometimes observed in resid hydrotreating. Chemical treatment is usually ineffective in this case.

Shale crudes contain very high boiling-range paraffinic hydrocarbons. In some cases, these are believed to have caused equipment fouling. The deposits can sometimes be removed with heat.

Other Factors

Difficulty desalting shale crudes has been noted due to the surfactants present and paraffinic nature of crude. The waxes can cause stable emulsions that are hard to break. Salts can carry over with the crude, causing downstream issues. At the same time, increased solid carry-under may be noted. Changes in desalter operating conditions may be needed. Coprocessing with other crudes may mitigate the impacts and may also create the incompatibility issues noted above.

A number of fracking and production chemicals are acids and/or otherwise contain chloride or some other halide. These materials cause corrosion when they reach the refinery. The corrosion products will almost always be found as iron sulfide deposits. Do not be fooled by thinking this is sulfide corrosion. Options for controlling this corrosion include metallurgy upgrades and chemicals. Unless controlled, more frequent cleaning of equipment is needed than you might see with other crudes.

It is a common practice to use triazine for H_2S scavenging. Quaternary amines are also used for corrosion control and as biocides. In a crude unit, these compounds transport corrosives up the crude tower and into the overhead until the water condensation temperature is reached. Then severe corrosion results. These corrosion products often leave the crude unit through the naphtha streams, causing fouling in the naphtha processing units. Good control of crude overhead corrosion has been achieved using chemicals. This is a problem common to any unit running crude with H_2S scavenger or with the same corrosion control additives, so it is not unique to shale crudes, except that the additives are used more extensively.

Glutaraldehyde is used in shale-crude fracking and production as a biocide for water treatment. Other biocides may also be present. The biocides will be present at some level in the shale crude. These materials do not present any additional oil processing issues aside from those noted above; but they can cause problems in refinery wastewater processing. Because they are biocides, any activated sludge or trickle-bed units that process the refinery wastewaters from shale crudes may see die-off of “bugs.”

Because the shale crudes tend to be lighter, there will be impacts from differences in distillation in the refinery. The crude unit will need to lift more light ends; hence, hydraulic limits may be reached in the upper portions of the tower and the heater may be undersized to drive the light ends overhead. Note that most of the shale crudes are heavily spiked, up to their RVP limits, which mean more light ends to contend with than a conventional crude.

By the same token, the lighter shale crude would provide less feed to the vacuum unit, resulting in lower yields and an oversized heater. The gas oil products from the vacuum unit will be waxy. With less vacuum resid and more waxy feed, a coker may be unloaded.

An FCC running shale-crude-derived gas oil will see some benefits: good selectivity and yields and lower slurry production. The product octane will be reduced by higher paraffin content.

Hydroprocessing units will be influenced by the potential fouling materials in the feed as discussed above as well as the paraffinic nature of the feed. The lower sulfur and nitrogen contents in the crudes should unload the units some. Distillates will have worse cold properties but very good cetane and smoke. Dewaxing, cut point changes, and additives may be used to control the cold properties within limits. Incompatibility may develop among feeds and products in gas oil units as noted above. Hydrocrackers would produce lower-octane naphthas, but selectivity to distillates should be good – with appropriate adjustments for cold flow properties.

Naphtha reformers will produce lower-octane product without adjustments; however, higher gas makes should be possible.

In addition to the possible impacts of biocides in the shale crude on wastewater treating, there would be impacts from increased solid carry-under in the desalter and alkaline and other metals in the crude. These have to be managed using available methods.

Concluding Remarks on Shale Crudes

While most of the impacts discussed above are not significantly different from those observed in processing more conventional crudes with the same additives and similar compositions, chemical impacts appear to be more noticeable with shale crudes. This is believed to be caused by the shorter production life of wells produced from tight shale by hydraulic fracturing. There is more frequent use of chemicals and in greater quantities such that they influence the refining characteristics more than in conventional crudes. The paraffinic nature of the oil is also a factor to consider, but this is not much different from other light, paraffinic oils.

The refining impacts of shale crudes are still being recognized and understood. The foregoing comments only present a synopsis of problems known or attributed to shale crudes to date (2013).

Bitumens and Extra Heavy Oils

Much of the world's remaining crude is in the form of "bitumen" or "extra heavy oil." This is essentially residuum or tar remaining in the ground after all the other hydrocarbons have disappeared. This material is attractive from a pricing standpoint because not everyone can refine it, but refining it is very difficult. At one time, these materials were called "disadvantaged" crudes; but, with improvements in production and refining technology, they are often now referred to as "advantaged" crude because of relatively low pricing. Many refineries are now capable of running these heavy materials and taking advantage of the low prices.

There is environmental and political controversy over these materials. The environmental issues arise from land damage caused by the extraction methods, the need to run pipelines to carry the oil, and the high carbon concentrations in the materials that can contribute to CO_2 emissions (global warning concerns). The political issues arise, especially in Venezuela, because of strained relations between and among governments and companies.

The next section of this handbook will discuss the sources, properties, and processing characteristics of various bitumens available on the market today; but first let us be clear about what stocks we are discussing.

Definitions

The term "bitumen" is applied to a sticky, black, highly viscous, liquid or semisolid form of petroleum (essentially tar) usually found in natural deposits. In the past, it has also been referred to as asphalt or asphaltum. Here we will use the term bitumen for the naturally occurring material, which is our concern in this section. We will use asphalt to refer to the material used for paving, roofing, and other products made from both resids and bitumens.

Formally, the World Energy Council (WEC) defines natural bitumen by viscosity ($>$10,000 cP under reservoir conditions) and API gravity ($<$10° API) (from Wikipedia article).

Comments about bitumen also apply to resources called "extra heavy oil" (EHO). Extra heavy oil pretty much fits the same description applied to bitumen. Generally, the materials from Canada are called bitumens and those from Venezuela are called

Fig. 9 Oil sand appearance (Source: Suncor Energy Inc., www.ems.psu.edu article, oil sands)

extra heavy oils. For practical purposes, there is not much difference in refinery processing issues. We will use the terms somewhat interchangeably in the discussion.

Bitumens and EHOs are different from shale oil in that the hydrocarbon is not chemically part of the rock matrix but coats sand and sandstone. The rock matrix does not have to be retorted to release the bitumen, although some oil-shale retorting processes have also been used to obtain bitumen and extra heavy oil. Figure 9 shows oil sand as it appears naturally, coated with bitumen.

The heavy oils are distinguished from conventional crudes in that they cannot be produced using conventional oil-field methods. They must be removed from the ground by heating, solvation, and other nonconventional methods.

These oils are too heavy and tarry to transport very far in any practical way. They are usually diluted with a solvent or pre-refined before being sent to a normal refinery. The most commonly available forms of bitumen or extra heavy oil received by a refinery are:

- Dilbit – A naphtha solvent, another lighter crude, or condensate may be used to cut the heavy oil. The solvent may be recovered and recycled.
- Synbit – Where some of the bitumen is upgraded to a synthetic crude oil near the production site and the resulting syncrude used as diluent for additional bitumen. The syncrude is not normally recycled. In this material, the diluent may also include other, lighter crudes or condensates.
- Dilsynbit (or **syndilbit**) – Where the "crude" is a mixture of bitumen/extra heavy crude and all the other possible diluents (condensate, light crude, naphthas, syncrudes, etc.).

Production Locations

Bitumens and EHOs are found in many areas of the world. The most commonly thought of bitumens are from Canada. Similar materials are available elsewhere, however – such as Venezuela.

Table 9 Bitumen or extra heavy oil deposits worldwide

Global region	Estimated billion barrels of recoverable bitumen/EHO
South America	1,127
Middle East	971
North America	651
Russia	182
East Asia, China	168
Africa	83
Europe	75
Southeast Asia, Oceania, Australia	68
Transcaucasia (SW Asia)	52
South Asia, India	18
Worldwide total	3,395

Source: US Geological Survey, 2003

The known distribution of bitumen/EHO deposits is indicated in Table 9. The most significant production locations are Canada and Venezuela. About 85 % of the world's recoverable bitumen reserves are in the Alberta province of Canada, and about 90 % of the recoverable extra heavy oil reserves are in Venezuela in the Orinoco Belt, so we will focus primarily on those areas. In these deposits, there are an estimated 3.4–3.6 billion barrels of oil (USGS, Fact Sheet 70-03, August, 2003).

Methods of Production

There are several production approaches used for bitumens and extra heavy oils. The approaches are somewhat different for the two materials.

Bitumens are produced from "oil sands" (also called "tar sands"). These materials consist of clay and sand that are coated with water and oil. Where the deposits are near the surface, they can be mined for processing. Deeper deposits require other approaches. The specific methods that have been applied commercially are:

- *Mining extraction* – This is a long-proven approach where the overburden is low (less than 150–250 ft.). The oil sands are mined using huge machines. The resulting rock is sent to a processing plant where the bitumen is normally washed off the rock using hot water or solvent. This approach recovers a high percentage of the bitumen with limited greenhouse gas emissions. Application is limited to locations where overburden is sufficiently low (about 10 % of the Canadian resource), by the need to move enormous amounts of rock and by the environmental damage from the strip-mining operation. This has been a common, simple method of extraction in the Athabasca tar sands. Tests to recover the oil using surface oil-shale retorting approaches have also been conducted, but those are much more expensive than "washing off" the oil and suffer from the oil sand turning into, well, sand once the oil is removed.

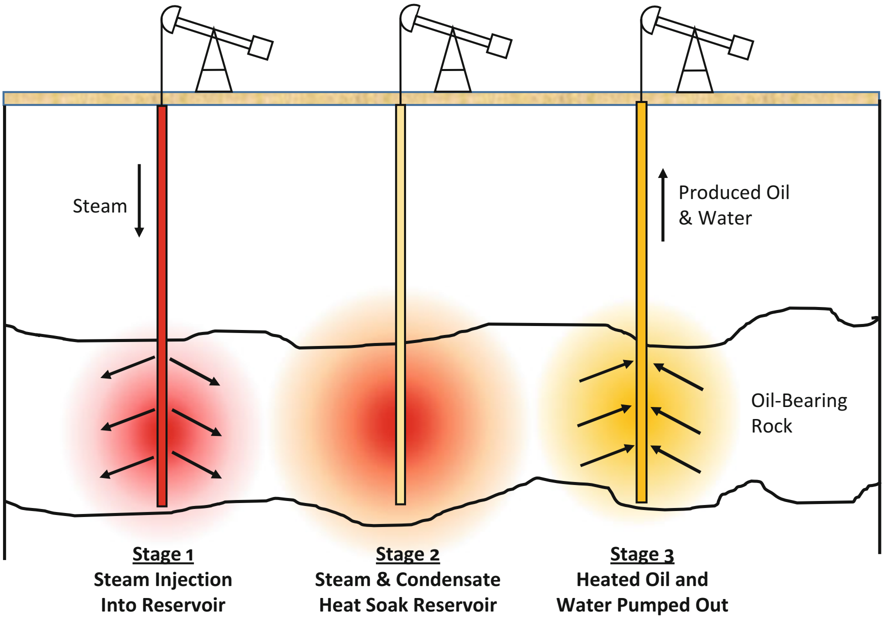


Fig. 10 "Huff and puff" extra heavy oil production

- *Huff and puff* – This method has been used in Canada and Venezuela. It can be used for deeper deposits of bitumen and EHO. Superheated steam is injected into a well. The heat is allowed to soak into the reservoir around the well. Finally, the flow is reversed to extract the melted bitumen and EHO. See Fig. 10. The cost is relatively low, but recoveries are generally poor (<15–20 %) for this method. A lot of energy is used heating the reservoir, with accompanying high CO_2 emissions.
- *Steam-assisted gravity drainage* (*SAGD*) – This newer method has been proven in several tests in Canadian production and elsewhere and is being commercially implemented. It takes advantage of improved directional drilling techniques. In this approach, a steam injection well is drilled through the oil sand formation horizontally. Somewhat below the injection well, a parallel production well is drilled, also horizontally. Superheated steam is injected into the formation from the steam well and the steam front melts the bitumen or EHO and drives it toward the production well, where it is pulled out. Refer to Fig. 11. The method recovers up to 60 % of the oil and is fairly quick. It suffers from a large energy need and significant CO_2 emissions.
- *Other methods* – A few other approaches have been explored but are not proven in oil sands: in situ combustion and solvent injection. Both offer the possibilities of high recoveries, low energy consumptions, and relatively low environmental consequences; but these approaches have either had only limited success or are "not ready for prime time."

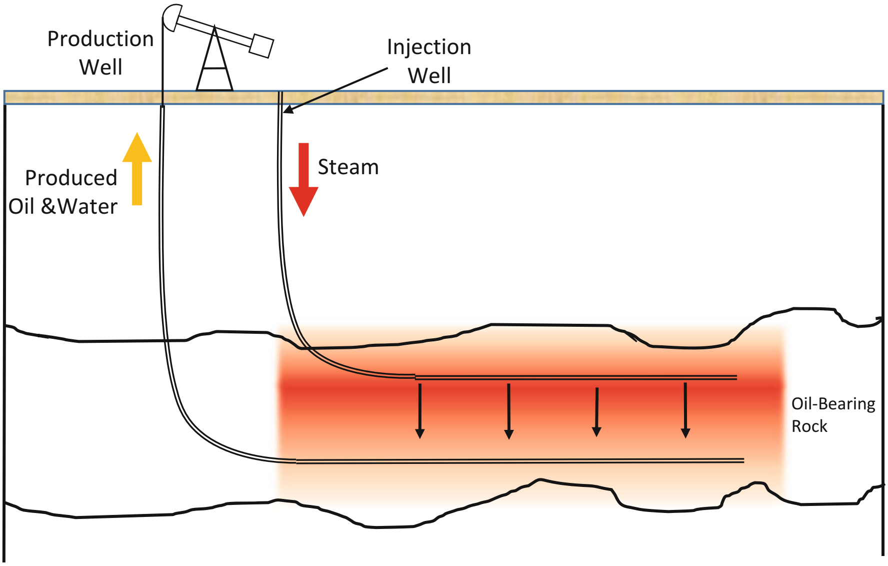


Fig. 11 Steam-assisted gravity drain (SAGD) bitumen and EHO production

Extra heavy oils can be produced using the methods above for bitumens, but they also offer one additional option:

- *Cold production* (*AKA Cold Heavy Oil Production with Sand or CHOPS*) – This has been used in Venezuela and Canada where the production reservoir is warmer than most of the oil sand areas in Canada and, hence, the extra heavy oil is a little more fluid. In this process, sand is deliberately coproduced with the oil. It is a proven approach, using normally available oil-field technologies and equipment and requires limited investment. Environmental impact is low. On the downside, recoveries are poor (<5–10 %); it is unsuitable for bitumens or reservoirs with active aquifers. The produced fluids need to be separated and the sand disposed of.

Once you have the bitumen or EHO, you need to make it into a more marketable product. These oils are too heavy to transport without some processing and they contain high concentrations of contaminants. The three primary levels of upgrading found today are:

- Low-level upgrading – This means essentially cutting the bitumen/EHO with diluent. This approach is used in several locations. The diluent may be light conventional crude, condensates, LPG, and other stocks. Examples of this level of upgrading are Canadian dilbits and some of the Venezuelan grades.
- Medium-level upgrading – In this approach, some of the oil is coked and/or lightly hydroprocessed to make it lighter and remove the worst actors ahead of a

conventional refinery. The resulting syncrude is blended with other heavy oil or bitumen, giving rise to stocks like Canadian synbit and other Venezuelan grades.

- High-level upgrading – Much more heavy upgrading can be applied to the bitumen or EHO to create a much lighter, bottomless stock that looks a little like a conventional light crude and would command a premium price. These materials, marked by deeper hydroprocessing, are available as syncrudes.

The production method and degree of upgrading affect the final bitumen or EHO product received at a refinery. The next section provides some typical properties for more commonly available bitumen and EHO products.

Properties of Bitumen-Derived Feeds

Figure 12 compares the typical straight-run cuts from Canadian bitumen, synbit, and dilbit to Arabian heavy crude – another heavy sour crude.

Note that the bitumen looks pretty much like an atmospheric resid. The dilbit is naphtha plus atmospheric resid. The synbit has some middle distillates plus atmospheric resid and little naphtha. Compared to conventional heavy, sour crudes, the bitumen/EHO-derived material yields will fill a refinery's units differently. Some units could be short of feed, while others will be limiting crude rates. The entire refinery crude slate would be impacted to keep the units full.

Table 10 illustrates the range of crude properties on the market today for a few stocks derived from bitumen and extra heavy oil.

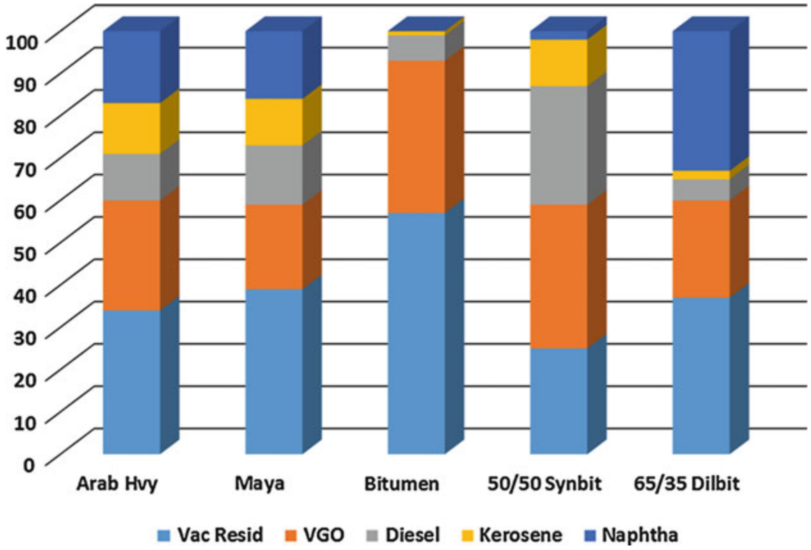


Fig. 12 Boiling-range distribution comparison – conventional heavy sour crudes versus Canadian bitumen-derived stocks (Date source: Turini et al. (2011))

Table 10 A sampling of available refinery crudes derived from bitumen or extra heavy oil

Crude source	Canada				Venezuela						
Name	Western Canadian Select (WCS)	Albian heavy synthetic (AHS)	Statoil Cheecham synbit (SCS)	Christina dilbit blend	Orinoco whole crude	SCO	DILORIN	Extra heavy whole crudes	Upgraded low	Upgraded medium	Upgraded high
Type of material	Dilsynbit + conventional (bitumen + conventional + condensate + syncrude)	Dilsynbit (bitumen + condensate + syncrude)	Synbit (bitumen + syncrude)	Dilbit (bitumen + condensate)	Extra heavy oil	Upgraded oil	Diluted (naphtha) extra heavy oil to upgrader (like a dilbit)	Extra heavy whole crudes	Upgraded oil	Upgraded oil	Upgraded oil
V% diluent in blend	Varies	Varies	30	50	0	0	30	0	0	0	0
	1 year Avg 2013	1 year Avg 2013	1 year Avg 2013	1 year Avg 2013							
Gravity, °API	20.8	19.1	20.3	21.4	8.5	32.2	20.8	7.8–9.8	16	22	28+
Density, ka/m3	928.3	938.7	931.2	924.9	1,010	864	929				
Sulfur, w%	3.51	2.43	3.08	3.88	3.8	0.1	2.7	3.5–4.0	3.5	2.6–3.0	<0.5
Nitrogen, w %	NA	NA	NA	NA	0.6	0.03	0.4				
MCR, w%	9.84	13.13	8.33	10.41				18 (ConCarb)	15 (ConCarb)	5 (ConCarb)	5 (ConCarb)
Sediment, wppm	296	784	71	97				2.7	1	1–2	0.1
TAN, mg KOH/a	0.93	0.48	1.57	1.57							
Salt, ptb	30.9	10.5	3.3	7.1							

Metals, wppm											
Nickel, wppm	61	45	59	70	89	0	62	~120	120	<20	<20
Vanadium, wppm	144	87	153	186	414	0	290	300–500	500	<100	<100
Olefins. w%	ND	NA	ND	NA							
RVP, psi	NA	NA	NA	NA							
Sim Dist, °F, w%, hist. std. dev.											
IBP	93+/−3	94+/−8	97+/−6	93+/−1							
5 %	140+/−34	142+/−37	177+/−40	101+/−2							
10 %	272+/−61	233+/−50	235+/−27	163+/−8							
30 %	642+/−2S	707+/−32	593+/−27	612+/−37							
50 %	873+/−28	892+/−27	852+/−28	863+/−30							
70 %	1147+/−39	1071+/−35	1150+/−47	1154+/−33							
90 %	1319+/−10	1290+/−29	1270+/−56	1292+/−26							
95 %	–	–	1,314	–							
Max	–	–	–	–							
Sources	(1) Canadian Crude Quality Monitoring Program, CrudeMonitor.ca, November 2013; (2) Cenovus (2013)				"Unconventional crude upgrading challenges," Scott Sayles, KBC Advanced technologies, www.digitalrefining.com, 4th Qtr 2007			"Upgraded crude properties," Latin Petroleum magazine, www.latinpetroleum.com, Faja315 print supplement			

ND Not detected by analysis method, *NA* Not available, – Beyond test range

Refining Considerations

Looking at the range of bitumen/EHO crude properties, several factors stand out as potential refining issues. Others are not so obvious.

Table 11 summarizes some of the refining impacts that have been observed by unit when processing the extra heavy oil stocks. While many of these are not new, the impacts may be much more pronounced with these materials.

Important factors impacting processing of these crudes include:

- Dumbbell distillation
- High aromatics
- Low API gravity of the bitumen/EHO portion
- High sulfur
- High nitrogen
- High metal contents (Ni, V, Fe)
- High alkaline metals (Na, Ca)
- High contents of other contaminants (As, Ti, Si)
- High asphaltenes
- High total acid number (TAN)
- High chlorides
- High viscosity
- High coking/cracking propensity when heated

Not all factors and impacts apply to all crudes. The degree to which a specific refinery is impacted will depend on the normal crude diet the refinery is accustomed to and the percentage of the bitumen or EHO-derived feedstock included in the crude slate.

We will explore each of these impacts and a few possible remedies briefly in the following discussions.

Dumbbell Distillation

Dumbbell distillation means that there is an abundance of light material and heavy material in the crude with little distillate in the middle boiling ranges. Issues with distillation in processing bitumen and EHO stocks primarily occur with dilbits. The dilbits contain essentially atmospheric resid cut with naphtha and other light ends for transportation. While the combination looks like a crude on simple inspection, it is really just a blend of two separate boiling ranges. In other grades of these heavy oils, high vapor pressure in shipping is the primary issue.

The impacts from the dumbbell distillation are seen in several areas:

- The light ends in the “crudes” may lend high vapor pressure to the stock, whether dilbit, synbit, or dilsynbit. This must be considered in transportation, receiving, and storage.
- The light ends will vaporize early in the crude preheat train, potentially generating high pressure drop. At the same time, the high viscosity of the heavy oil

Table 11 Summary impacts of bitumen/EHO feedstocks on refinery operations

Unit	Impactfactors													Bitumen and extra heavy oil impacts
	Dumbbelldistillation	Aromatics	APIgravity	Sulfur	Nitrogen	Metals(Ni, V, Fe)	Alkalinemetals(Na, Ca)	Others(As, Ti, Si)	Asphaltenes	Acidnumber(TAN)	Chlorides	Viscosity	Coking/crackingpropensity	
Tankage/bulk handling	X		X						X			X		Corrosion increase, crude incompatibilities, harder to pump
Desalting			X						X	X		X		Corrosion increase, poor separation, thick rag layer (hard to detect), undersized, crude incompatibilities (fouling)
Crude distillation	X			X					X	X		X	X	Corrosion increase, too much or too little naphtha (early or inadequate vaporization), crude incompatibilities (fouling), faster heater coking, more cracked gas make, heater capacity, preheat fouling, high kerosene sulfur

(*continued*)

Table 11 (continued)

Unit	Impactfactors													Bitumen and extra heavy oil impacts
	Dumbbelldistillation	Aromatics	APIgravity	Sulfur	Nitrogen	Metals(Ni, V, Fe)	Alkalinemetals(Na, Ca)	Others(As, Ti, Si)	Asphaltenes	Acidnumber(TAN)	Chlorides	Viscosity	Coking/crackingpropensity	
Vacuum distillation				X						X			X	Corrosion increase, high cracked gas make, high use of capacity, faster heater coking, heater capacity limits, more stripping steam required, high metals limit cut points
Coking	X			X		X	X		X	X			X	Higher capacity required (or more VR sales), faster heater coking, corrosion increase, coke metals vs. specs
Fluid catalytic cracking		X		X		X	X	X		X				Lower yields, high sulfur products or more severe pretreatment, metal poisoning potential, corrosion increase
Olefin processing														Limited impacts observed

Hydroprocessing (general)	X			X	X	X	X	X	X	X	X			Corrosion increase (TAN, S, Cl), changes in capacity requirements, high hydrogen demand, more severe operating conditions, decreased cycle length, catalyst poisoning by metals Si and As, increased percentage of coker products, higher fouling rates (exchangers and heaters), potential feed incompatibilities, increased wash water requirements, higher amine loadings, potential increased FCC product post-treating
Naphtha reforming		X												May be unloaded if diluent recycled or overloaded if not recycled, increased N+2A
OSBL piping				X						X				Corrosion increase (TAN, sulfur)
Wastewater treating			X						X			X		Desalter water carry-under, high BOD/COD, solids/emulsions from desalter
Amine system				X										Increase corrosion (sulfur), potential overloading (consider alternate amines)
Sour water stripping				X	X									High ammonium salt loading, more wash water required (need to optimize wash water, possible recycle)
Sulfur recovery				X	X									Greatly increased sulfur and nitrogen loading, air demand

Primary sources: (1) Turini et al. (2011); (2) Sayles, S. (KBC Advanced Technologies, 2007) *Unconventional crude upgrading challenges*, http://www.digitalrefining.com/data/articles/file/172598306.pdf reduces heat transfer, exacerbates fouling of the preheat trains as their solvent action is lost, and may increase asphaltene instability.

- A high amount of light ends may overload the upper portions of the crude tower and the high heavy oil concentration may overload the bottom of the tower. Changes to operating conditions will be needed. Some have unloaded the crude tower with pre-flash to eliminate the lighter materials.
- Low distillate contents will unload the distillate treating units and reduce production. In some materials there are also low gas oil contents, unloading those units along with the FCC. Consideration to filling these units may be required.
- If naphtha diluent is not to be recycled to the field, then the natural gasoline will impose additional load on the naphtha reformer. It will lower reformer product octane without operating condition changes.
- The high content of bitumen/EHO will put additional load on the coker and is likely to require lowering of the vacuum tower cut point. This also means that a higher proportion of the feeds to hydroprocessing and other units will be derived from the coker.

High Aromatics

The bitumen/EHO stocks generally have higher, heavy aromatic content, as you would expect from a resid. This will result in lower FCC yields, unless the FCC feed is heavily hydrotreated beforehand.

In the naphtha reformers, the impact could go either way, depending on the type of oil. As noted above, a dilbit may provide a low N+2A feed and result in lower product octane and lower yield, but this would be partially offset by a higher coker naphtha portion of the feed. If the heavy oil stock has syncrude blended into it, the impact on naphtha processing may be minor.

More aromatic stocks fed to the distillate units will lower distillate quality.

Low API Gravity of the Bitumen/EHO Portion

The very low API gravity of the bitumen portion of the stock increases difficulties in pumping the stock and is also reflected in crude incompatibility issues.

The desalter is more likely to develop a thicker “rag” layer and experience poor oil water separation. Desalter oil carry-under increases and must be managed in wastewater treatment (high solids, high BOD/COD).

High Sulfur

The very high sulfur levels in the heavy oil stocks have corrosion implications throughout the refinery, including hot OSBL piping between units. Metallurgy upgrades have been required in many cases. Watch out for sulfur content “creep” effects (e.g., naphtha hydrotreater convection coil metallurgy).

In many refineries, jet fuel is produced from straight-run stocks without much processing. With the heavy oil crudes, this is not normally possible, since the native kerosene has too much sulfur. Hydroprocessing of the kerosene portion can be expected.

Of course, higher sulfur feed will require more hydroprocessing to eliminate sulfur from all the products. There will be more sulfur for the amine systems, sour water strippers, and sulfur plants to handle.

To meet ultralow-sulfur product specifications, the operating severity of the hydrotreaters will be much greater. Additional wash water may be required.

If the heavy oil stock contains syncrude, the sulfur will appear to be lower, but the sulfur remaining is very refractory. The low sulfur in syncrude is more of an illusion. Hydroprocessing severity will be nearly as severe as if there had been no desulfurization for each cut; and there will be more naphtha, distillates, and gas oil impacted.

All the treating severity increases will be reflected in greatly increased chemical hydrogen consumption. The additional hydrogen must be supplied from incremental hydrogen plant production (internal or over the fence) or higher reformer severity.

The much higher sulfur present in the heavy oil “crudes” will increase demand on the sulfur plant. Claus plants may be debottlenecked with oxygen enrichment or changes in sparing philosophy may be needed (no spares).

High Nitrogen

High nitrogen content in the heavy oil stocks will affect hydroprocessing, sour water stripping, and the sulfur plant. If the higher nitrogen reaches the FCC, there will be impact there, also.

In hydroprocessing (including hydrocracking), the nitrogen imposes additional load on the process, requiring more severe conditions to remove the nitrogen. The higher nitrogen content also increases the deposition temperatures for ammonium salts in the effluent trains. More wash water is then required to prevent the salt deposits. Again, higher hydroprocessing severity will require more hydrogen.

A higher wash water rate will mean more sour water needs to be stripped and the resulting ammonia processed in the sulfur plant. Higher oxygen demand in the Claus units can be expected.

High Metal Contents (Ni, V, Fe)

The high metal content in most bitumen/EHO-derived stocks has impact on the vacuum tower, coker, fluid catalytic cracker (FCC), and hydroprocessing units.

In the coker, the resulting coke will have a high metal content, lowering its quality. Because the vacuum tower and the coker may be more loaded by these oils, there is a likelihood of increased entrainment into the heavy gas oil cuts with a resulting increase in metals in the gas oils.

The metals are catalyst poisons and the iron, converted to iron sulfide, will be a persistent foulant. The hydrotreaters will need to deal with the higher metals, normally by increasing the amount of metal traps used. The iron will need to be managed by filtration or deeper graded beds in the reactors. Preheat train fouling can be expected to increase. If the refinery has a fluid or ebullated bed hydrocracker, more catalyst changeout would be required.

The Ni and V are also poisons in the FCC. Increased catalyst changeout is normally used to control the FCC catalyst activity.

Most of these remedies are not unusual in the affected units, so no big surprises should come from processing high-metal, heavy oil stocks.

High Alkaline Metals (Na, Ca)

Alkaline metals drive fouling primarily. They may also form surfactants in the desalter by reaction with organic acids, making separation of the oil and water difficult.

Alkaline metals notably promote fouling of fired heaters in the crude, vacuum, and coker units. In the hydroprocessing units, they can foul the catalyst beds and bring in chlorides.

These metals have to be eliminated as much as possible in the desalters. Chemicals and operating condition changes may be needed.

High Contents of Other Contaminants (As, Ti, Si)

There are slightly elevated levels of a few other metals or near metals in bitumen/EHO-derived crudes. These metals include arsenic, titanium, and silicon. Some come from the oil itself. Others, like the silicon (used as antifoam), may originate in the oil recovery process or shipping.

These elements primarily affect the catalytic units. An FCC can manage them by increasing catalyst changeout rate. A hydroprocessing unit can manage the materials using various traps in the graded bed. Specific traps would be required for Si and arsenic. Note that the arsenic level in these crudes is about two orders of magnitude lower than shale oil.

High Asphaltenes

Asphaltenes in heavy oil stocks impact all of the refinery where the resid and heavy gas oils are present. In tankage and bulk handling of the crude, mixing of the heavy crudes with other, less-aromatic stocks may result in instability and precipitation of the asphaltenes.

In the desalter, they will help form and stabilize the emulsion or “rag” layer in the desalter vessel, potentially increase preheat fouling, and increase solid/oil carry-under.

In the crude, vacuum, and coker units, they will increase preheat fouling. The impact would be increased if the crude blend is unstable due to incompatibility.

In heavy gas oil hydrotreaters, the asphaltenes would promote preheat fouling and may become incompatible during processing. Similar effects are observed when processing resids.

The water separation problems caused in the desalters are passed on to the wastewater treating system, where separation and high BOD/COD problems may appear.

High Total Acid Number (TAN)

Many of the heavy oil crudes contain relatively high concentrations of organic or naphthenic acids, observed as high total acid number (TAN). The high TAN will increase corrosion rates wherever the oil must be heated above ~500 °F.

This includes crude, vacuum unit, coker, FCC, and hydroprocessing units, in addition to OSBL piping.

In most units, metallurgy upgrades can mitigate the impacts. In hydroprocessing units, the addition of hydrogen into the oil as it is preheated appears to reduce naphthenic acid corrosion.

Once processed, the TAN impacts are not significant.

It has been noted that Venezuelan stocks may have relatively low TAN when shipped but high TAN when received. This is the result of exposure to oxygen and CO_2 in the inert-blanketed holds during shipping. The blanket gas is engine exhaust. The exhaust gas will react when exposed to the partially coked oil.

High Chlorides

Chlorides in heavy oil crudes are elevated over more conventional crudes. The chlorides are not necessarily removed in desalting but will hydrolyze later upon heating or will be converted to HCl by hydrotreating. They most commonly cause problems in hydrotreater effluents, where they form NH_4Cl salt deposits. Wash water practices manage the chlorides.

High Viscosity

By definition, the bitumen and extra heavy oils are very viscous. The high viscosity reduces heat transfer coefficients. Preheat of these crudes can be difficult. Dilbit would especially present issues once the diluent has been vaporized. Exchanger baffling and other changes may be required to process large portions of heavy oil stocks in the desalters and crude units.

The high viscosity makes handling the crudes difficult. It will affect pump power requirements. It also impacts desalter separation efficiency, resulting in increased carry-under of oil to the water phase and taxing wastewater treatment.

High Coking/Cracking Propensity

It has been noted that the bitumen/EHO-derived crudes have a higher tendency to coke in crude, vacuum, and coker heaters. This results in more rapid heater fouling. Attempts to control this with chemicals have had some success. Otherwise, the heaters need to be closely monitored for fouling and decoked on an appropriate schedule.

The crudes also tend to thermally crack more easily than other crudes, likely related to the coking tendency. This produces higher amounts of light ends that can overload the upper trays in distillation towers. This impact is in addition to the extra light ends that may come from diluent in dilbit.

Concluding Remarks

The availability of bitumen and extra heavy oil “crudes,” mostly from Canada and Venezuela, can be expected to continue to expand. These materials can offer a price advantage to a refiner that can manage the impacts of these atypical crudes.

A refinery built for heavy, sour crudes can probably process the oils without too much trouble. Refineries designed around light sweet, medium sweet, or medium sour crude slates may also be able to include some of the heavy oil crudes with appropriate processing accommodations.

Synthetic Crudes and Syncrudes

There are several materials derived from unconventional crude sources that are used as crude oils. These synthetic crudes, or syncrudes, have been preprocessed and/or blended to look like a conventional crude oil. In a few cases they will process like a conventional crude oil. For the most part, however, the syncrudes generally have some fatal flaws that complicate processing and depress the price. For a refiner that can deal with the issues, the syncrudes can be very economically attractive.

Syncrudes are covered in other discussions of unconventional crudes in this book and are not detailed further here, except to acknowledge the different types of materials:

- Shale-oil-derived syncrudes – See section on shale oil.
- Bitumen-derived syncrudes – See section on bitumens and extra heavy oil. These are mostly from Canada.
- Extra heavy oil-derived syncrudes – See section on bitumens and extra heavy oil. These are mostly from Venezuela.

“x”-to-Liquid (xTL) Feedstocks

There are several processes that create potential refinery feedstocks, in addition to final products of their own, using Fischer-Tropsch (FT) synthesis or via methanol synthesis (syngas to gasoline plus – STG+). Both approaches start with a synthesis gas containing a specific ratio of hydrogen to carbon monoxide. The synthesis gas is converted to long-chain or other liquid hydrocarbons by reaction over a catalyst. The resulting products are processed further to finished products.

The FT process was developed in Germany in 1925, where it was initially commercialized in 1936. During World War II, about 9 % of German military fuel and 25 % of the German automotive fuel supply was made by the FT process applied to coal. More recently, the process has been used in a few large-scale projects – the largest being Sasol in South Africa to make fuels from coal (since 1952) and natural gas. Other commercial plants have included facilities by Shell (Qatar, Malaysia), PetroSA (South Africa), Ras Laffan (Qatar), ExxonMobil, and Chevron (USA). Feedstocks and products have varied.

Methanol synthesis was developed in Germany, also, in 1923. Methanol itself and its derivatives have value, so the basic methanol synthesis has been widely used. Use of methanol to produce various fuels has been less common. Several approaches for fuels have been developed, but have not seen large-scale commercialization.

The initial feedstock for either synthesis can be natural gas, coal, biomass, or any other material containing carbon. Products produced have included fuels, lubes, methanol, and other solvents.

These routes to fuels are expensive and complex. On a commercial scale, aside from methanol production, they have been limited primarily to generating high-value products (like lubes and specific solvents) or where there was no alternative for fuels at some point in time (like Sasol and Germany). Extensive work has gone into using the processes to monetize stranded natural gas resources by converting the gas to liquids at the field before shipment, but these efforts are economically challenged at present (2013).

Development of these technologies continues as a way to take advantage of materials that would otherwise be wasted or used for less valuable purposes. More detailed discussions of these technologies can be found under the topic entitled "Chemicals from natural gas and coal in hydrocarbon processing."

Definitions

Because the process depends on organic carbon as the primary feedstock, a number of flavors of the process have been developed:

- Gas to liquid (GTL) – This is the process form you most often hear about. The feedstock considered is normally natural gas. The FT process has also been proposed for reclaiming various hydrocarbon gases made in a refinery. Essentially anything that could be fed to a normal SMR hydrogen plant could be used in FT or methanol synthesis.
- Carbon to liquid (CTL) – In this embodiment, the feedstock could be any organic carbon-containing material – solid or liquid. Research has included conversion of coal, biomass, resids, and so on. This is a more complex process to implement, normally involving partial oxidation or gasification of feedstocks before synthesis.

Production Rates

Aside from methanol and related products, the total amount of xTL liquids produced is limited and most of the production is allocated to specific purposes. We won't spend a lot of time reviewing production rates, except to note that the worldwide production of xTL materials for purposes other than methanol is less than about 500 MBPD.

Production Processes

The overall synthesis process blocks are illustrated in Fig. 13.

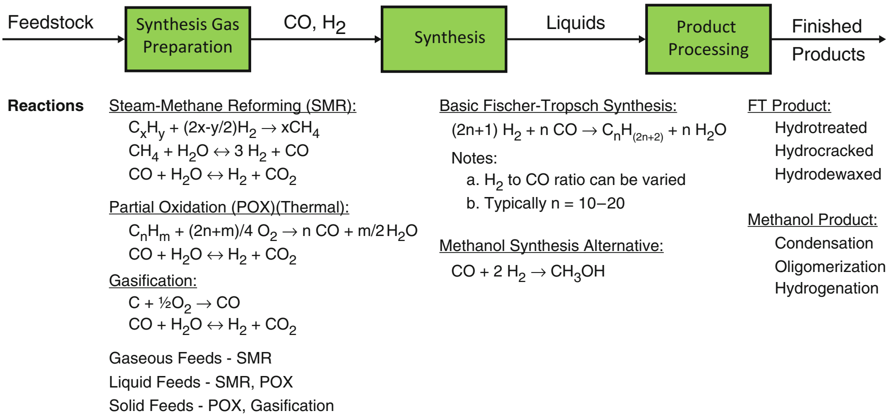


Fig. 13 Generalized block flow diagram for xTL processes

There are three primary process blocks in xTL processes, but each contains multiple process steps:

- Synthesis gas preparation – Here the synthesis gas (CO and H_2) is made by ripping apart the feed containing carbon using steam-methane reforming, partial oxidation, or gasification. The synthesis gas composition is controlled to produce the specific ratio of H_2 to CO that is needed for the synthesis step. For methanol, the ratio is 2:1. For Fischer-Tropsch the ratio is slightly higher.
- Synthesis (FT or methanol) – The synthesis gas is reacted over a catalyst to form the desired products. In the FT process, the catalyst is selected to form long hydrocarbon chains that will usually contain some oxygen and double bonds. The carbon atom distribution depends on the catalyst employed. Generally, the hydrocarbon chains will be C_5–C_{25}. The production is entirely paraffinic. In the STG+ methanol approach, the product is, of course, methanol.
- Synthesis product processing – The paraffinic FT product normally must be cracked or dewaxed. It contains only C, H, and O – no sulfur and little, if any, nitrogen. Normal processing would include hydrotreating to remove the oxygen and ensure saturation, followed by hydrocracking or hydrodewaxing to reduce the length and isomerize the paraffin strands. Processing methanol into liquid fuels is more complex. The methanol may be converted to dimethyl ether, the ether polymerized to a wide variety of hydrocarbons, and the final product is hydrotreated to stabilize it. Methanol can also be polymerized to an unsaturated hydrocarbon directly, oligomerized, and then hydrotreated to stabilize the products.

We will not go into further detail on the various approaches that have been used here, except to note that the process that produces the xTL stock will affect the refining properties. Refining the stock will generally fall into the final block above.

Properties of xTL Feedstocks

Comments in this section apply primarily to Fischer-Tropsch products if they are brought to a refinery. A few notable factors you will observe are:

- Very low contaminant levels, especially sulfur (<5 wppm). When these stocks are hydrotreated, it is actually necessary to inject a small amount of a sulfur compound into the hydrotreater to maintain activity of the sulfided catalyst.
- If the materials have not been dewaxed, the cold flow properties for distillates will be very poor.
- Distillate combustion (~85 cetane, extremely high smoke point) and the lube oil characteristics (~140–144 VI) for FT stocks are very good; but gasoline properties are very poor (~30 octane).
- Lubricity and conductivity of the distillates is poor. Additives will be required.

Refining Considerations

Refining a full-range xTL feedstock requires that the specific shortcomings of the stock be addressed in processing. As with other stocks, if the xTL feed is present as a very low percentage (say <2 %) of the refinery crude slate, the material impact will probably be negligible. If the xTL feed is much greater, it may need to be processed separately. We will focus on FT products here, as these are the larger volumes.

A few things to consider in refining FT oils are:

- The oils are very paraffinic. It will be necessary to reduce the wax content of the oils by hydrocracking or isomerization. Operating conditions to accomplish this would be fairly mild (owing to essentially no nitrogen present) and hydrogen consumption would be low. It will be necessary to use an acidic catalyst.
- The oils also contain olefins and oxygenates. These need to be removed by hydrotreating before hydrocracking the oil. Again, the required operating conditions are mild and hydrogen consumption is low. Normally, you would use a sulfide catalyst, so this is where you need to inject some sulfur-containing chemical to maintain catalyst activity. The required sulfur level is very low, however. Your catalyst supplier can advise on the required concentration.
- FT naphtha makes terrible gasoline. It is better used for cracking feedstock.
- FT gas oils are excellent lube stocks. As with the distillates, isodewaxing would be required to meet lube stock requirements. This will slightly reduce the VI of the stock, but it will still be a super-premium product.
- A full-range FT oil, if mixed with conventional crudes, may cause instability and precipitation of asphaltenes or waxes from the blend. Some testing of blends before attempting to process these stocks would be wise.

- Similarly, products from FT oils will impact product blend properties when they are used. In distillates, they may greatly improve the combustion properties but may have adverse effects on cold properties and conductivity. Performing hand blends before finalizing a blend recipe is probably a good idea.

Concluding Remarks on xTL Feedstocks

The availability of synthetic oils from GTL or CTL processes is limited. The economics of the processes drive the products toward high-value, niche markets (like premium lube stocks). Some have considered the GTL approach to monetize stranded natural gas reserves. Refer to the topic entitled “Chemicals from natural gas and coal in hydrocarbon processing” for more detailed discussion of xTL feedstocks for petrochemicals.

The primary challenges in making these products are in the synthesis stages. Once the hydrocarbon strands are made, they present fewer challenges in refining. They are somewhat easy to process, if properly handled, and offer some potential product quality improvements. They need to be handled as paraffinic stocks.

It is expected that availability will continue to be limited for general fuel use, but expanding use for specialty hydrocarbons (like lubes) can be anticipated.

Renewable Feedstocks

Since 2000 there has been a growing influence of renewable feedstocks in the fuel business. This is in support of reducing greenhouse gas (GHG) emission to combat global warming. In the USA, the renewable contents for fuels are dictated by the Renewable Fuels Standards resulting from the Energy Policy Act (EPAct) of 2005. Elsewhere in the world, similar, and often stronger, legislative drivers have been implemented.

In 2007, the US Energy Independence and Security Act (EISA) expanded the RFS program to include:

- Diesel, in addition to gasoline
- Much higher and faster volume increases in the renewable components
- New categories of renewable fuel with separate volume requirements for each category
- Created a requirement that EPA applies life cycle greenhouse gas performance threshold standards to ensure each category of renewable fuel emits less GHGs than the petroleum fuel it replaces

We cannot get away from mentioning one aspect of the US RFS, and that is the RIN system. Quoting Wikipedia: “A Renewable Identification Number (or RIN) is a serial number assigned to a batch of biofuel for the purpose of tracking its production, use, and trading as required by the United States Environmental Protection Agency's Renewable Fuel Standard implemented according to the Energy Policy Act of 2005." The RIN is 38 digits long. An "obligated company" (the requirement excludes small refiners) must demonstrate it has blended (or supported the production of) the required amount of renewables into its products using the RINs. If a company fails to meet the requirement, it must buy RINs on the market. A company can generate RINs by processing renewable feeds. The amount of RINs generated by a specific processing scheme varies. The system is geared toward incentivizing the use of renewables. Of course, the RINs are just numbers. Many refiners that had to buy RINs to meet their RFS obligation have found that the RINs were fraudulently created (i.e., no actual renewable fuel was produced). This has been a problem with this free-market attempt to expand renewables.

Ethanol has been the primary renewable fuel that has been commercialized on large scale for meeting the RFS mandate. It is the only renewable fuel available in significant quantities at present.

Ethanol has primarily only been used as a blend component in gasoline at the final blend point, so it does not generally impact the refinery processes, aside from adjustments that must be made in process operations to offset the high RVP of ethanol. The high octane of ethanol helps boost gasoline octane, but mileage is reduced with ethanol.

The current limit on ethanol in gasoline in the USA is normally 10 v% of the finished gasoline for all vehicles. Some vehicles are designed for up to 85 % ethanol, but this market is limited and localized. The 10 % limit is based on vehicle design, especially sealing materials, which can tolerate only so much ethanol.

In the US market, the 10 % ethanol limit presents a problem for refiners. This is because higher mileage is also being required for new vehicles and the automotive industry has been meeting the objectives. As a result gasoline consumption has remained relatively flat or decreased. But the required quantity of renewable use has increased, causing the gasoline supply to approach the limit of 10 % for almost all gasoline. This is called the "10 % blend wall." The Environmental Protection Agency (EPA) has been forced to temporarily back off on the rate of increase in the renewable volumes required by the RFS in recognition of this limit. Raising the limit to 15 % has been proposed, but there are technical issues with this that have not been resolved to date.

In diesel, a few direct blendstocks have been developed for fuel use, notably fatty acid methyl esters (FAME). The processes for making the fatty acid esters will be touched on briefly in the discussion following; but the esters are produced in dedicated facilities separate from the refinery. The esters are then just blended with refinery petroleum products, which have minimal impact on the refining processes. These materials are available in limited, but growing, quantities thus far.

Where refining impact has been seen is in processing various oils that can be derived from renewable sources into diesel blendstocks. These vegetable oils and animal fats cannot be directly blended to products but must be processed in the refinery.

The oils that have been investigated and/or used in production of renewable diesel include:

- Soybean oil
- Palm oil
- Coconut oil
- Rapeseed oil
- Safflower oil
- Corn oil
- Beef tallow
- Hog fats
- Chicken fat
- Algal oil

All these materials present issues when being refined. These will be discussed briefly below. The good news is that the products have very high cetane numbers, which help improve diesel cetane overall. Progress is continuing on bringing more renewables into the diesel blend pool.

To date, there has been limited work on developing renewable jet fuels; so we will not discuss renewable jet here.

The following discussion will focus on refining renewable vegetable oils and animal fats to diesel. We will not address green gasoline via catalytic cracking or ethanol production by fermentation. We will also not discuss biologic products from pyrolysis as these are not available in quantity at this time. The issues and solutions can be applied to almost all of renewable oils, with only a few differences.

More detailed discussion of this topic can be found in the topic entitled: “Renewable stocks in petroleum processing.”

Definitions

There are a few definitions that should be clarified in discussing the renewable oil processing for fuels. The route taken to create the fuel determines the specific category used for a given fuel. The categories are important because they are each treated differently in the regulations.

Figure 14 illustrates how some of the specific terms relevant to renewable oils fit together in the renewable fuel landscape.

Specific terms to note are:

- Biodiesel – Applies to long-chain methyl, ethyl, and propyl esters, like FAME. These are made by transesterification of lipids.
- Biofuel, renewable fuel – Any fuel derived from recently fixed carbon (usually plant or animal sources. This is in contrast to petroleum or other oils where carbon was fixed in the distant past.

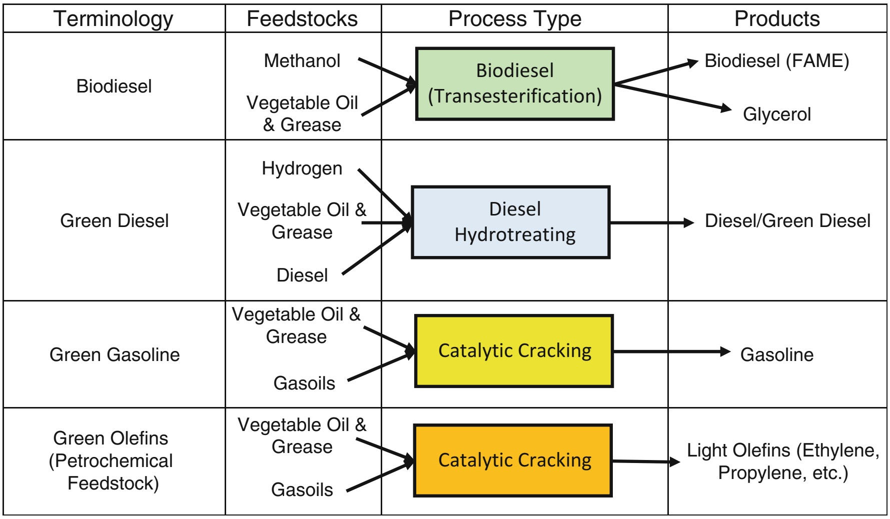


Fig. 14 Routes from renewable oils to fuel products (Original data: Christolini 2006)

- Biocrude, biooil, pyrolysis oil – Renewable oil made by destructive distillation of biomass – such as wood or corn stover pyrolysis.
- Bioethanol – Ethanol made from a renewable source, usually corn or sugar cane.
- Green diesel – Diesel produced by hydrotreating and cracking of renewable oil, coprocessed with petroleum oil.
- Green gasoline – Gasoline made by catalytic cracking (in an FCC) of renewable oils along with conventional petroleum feedstock.
- Green olefins – Made by catalytic cracking (in an FCC) of renewable oils along with conventional petroleum feedstock.

Renewable Oil Properties

The properties of some of the renewable oils that have been used to produce distillates are shown in Table 12. In general, the following observations apply:

- The vegetable oils have lower pour points than the animal oils because they are less saturated. This is indicated by the iodine value, which measures the double bonds in the hydrocarbon chains.
- The sulfur and nitrogen contents of the oils are generally very low.
- Aside from rapeseed oil, the TAN for these materials is low as received.
- There can be significant amounts of ash, insolubles, phosphorous, and other potential foulants and poisons present in the oils.
- Moisture contents are not listed, but there is some moisture present in all the stocks.
- If processing a renewable stock, be sure to get a specific analysis from the supplier.

Table 12 Potential renewable diesel feedstocks – vegetable oils, animal fats, and algae

Oil source	Soybean		Sunflower			Corn	Cottonseed	
	Crude	Degum/ deod	Crude	Degum/ deod	Dewaxed		Crude	Once refined
Spec. grav.	0.914–0.923	0.902–0.918	0.909–0.923	0.908–0.92	0.907–0.92	0.910–0.915	0.912–0.925	0.913
°API gravity	21.8–23.3	22.6–25.4	21.8–24.2	22.3–24.3	22.3–24.5	23.1–24	21.5–23.7	23.5
Sulfur, wppm	0.01	0.01	0.01			0.01	0.01	
Nitrogen, wppm	0.009	0.004	0.004	0.001–0.004	0.002		0.035	0.002
Oxygen, wppm	10.5–10.7		10.5	10.4	10.5		11	10.6
Cetane no.	35.4–38.1		36.7–41.8			37.5	34–60	
Pour point, °F	−10	10	−9 to −12	−9	−9	−40	−3 to −15	−4
D189 carbon residue, w%	0.24–0.27		0.23–0.28			0.22–0.24	0.24–0.25	
Iodine value, g/100 g oil	110–130		132	133	132	119–140	90–140	109
Contaminants								
Particulates, wppm	100	15	187	1.6	2		385	16
Insolubles, w%								
Peroxide no., ppm Oxygen	11–45	4–55	262	72.5	304	18.4	2.5–65	149
Phosphorus, w%	0.027–0.97	0.015–0.14	0.007	ND	ND		0.062	ND
Ash, w%	0.01–0.08	0.002–0.04	0.03	<0.01	<0.01	0.01	0.23	0.01
TAN, mgKOH/g	0.2		0.1–0.15			0.11	0.07–0.24	

Data sources: (1) Boundy (2011); (2) Darpro Solutions (2012); (3) European Biofuels Technology Platform (Unknown Date); (4) Garner et al. (2010); (5) Gregg (Unknown Date); (6) Knothe (2011); (7) National Reneres' Assoication (2008); (8) Turin et al. (2011)

[a] Depends on grade. Refined and bleached/deodorized grades have lower content

[b] Properties are for grade 1 beef tallow (has been processed to remove high solid content found in grade 6)

[c] Properties vary widely depending on production method and species of algae

	Rapeseed	*Jatropha*	Palm	Peanut	Canola	Beef tallow[b]	Lard	Algal[c]
Bleached and deod								
0.902	0.910–0.921	0.92	0.910–0.918	0.902–0.918	0.92	~0.88 (140 °F)	0.917–0.938	0.857–0.920
25.4	22.1–24.0	22.3	22.6–24.0	22.6–25.4	22.3	25.7	19.4–22.8	22.3–33.6
	0.01		0.044	0.01				
0.006				0.001–0.003		<10		<10
10.7	10.5–10.8			10.2–10.3				10.2
	37.5–48	40–45	42–52	34.6–41.8	33.5			
−4	−32		6	−7 to 2		~103	86–118	
	0.3			0.22–0.24				
109	94–120		35–61	80–119[a]		35–48	45–75	
17				3–28[a]				
				0.02		~0.02	<0.05	
137	30.2			21–240[a]			4	
ND				0.015		<0.001		(<1 ppm)
<0.01	0.006–0.054	0.01	<0.01	0.005–0.02[a]	0.004			
	1.1–2.0		0	0.2		0.2–0.7	3.4	<0.05

Reactions

In this discussion, we will focus on two primary processes for renewable fuel feedstocks:

- Transesterification of renewable oils
- Hydrotreating and cracking of renewable oils to make diesel.

We will not discuss catalytic cracking of the renewable oils for gasoline or olefins, since the catalytic cracking route does not get regulatory credit as a way to produce a renewable or green product in the USA.

Transesterification

Several processes have been commercialized which make esters in the diesel boiling range from renewable oils. The general process chemistry employed is illustrated in Fig. 15. The resulting product (usually FAME or FAEE) blends nicely with conventional petroleum diesel. The facilities that make these esters are generally separate from the refinery.

Table 13 compares typical FAME properties with a petroleum-derived ULSD and green diesel product from hydroprocessing.

Typical net yields from FAME production are in Table 14.

Hydrotreating

Coprocessing of renewable oils in refineries has mostly been by hydrotreating the oil along with petroleum diesel. These materials can be processed in a stand-alone unit as well. The process conditions required in a dedicated unit are mild, but stand-alone processing presents other challenges.

The general reactions for the renewable oil during hydrotreating are illustrated in Fig. 16 using a typical tallow feedstock. In coprocessing, these are just a small part of all the reactions occurring. The product slate and reaction route for the renewable

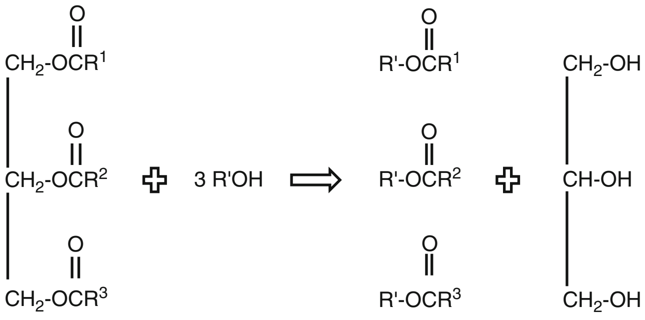


Fig. 15 Biodiesel from transesterification of renewable oils

Table 13 Typical renewable stock blend properties

Diesel stock source	Biodiesel (FAME)	Green diesel	Petroleum diesel
Specific gravity	0.88	0.78	0.83–0.85
API gravity	29.3	49.9	35–39
Sulfur, wppm	<1	<1	<10
Distillation, F, 10 % / 90 %	644/671	509/608	360/630
Cloud point, F	23–59	14–23	~23
Cetane	50–65	70–90	40–55
Oxygen, w%	11	0	0
Lower heating value, MJ/kg	38	44	43
GHG emissions, gCO_2/MJ	Rapeseed: 46; veg./animal oil: 10; palm oil: 54		
Storage stability	Marginal (microbio)	Good	Good

Data source: Kalines et al. (2008)

Table 14 Typical FAME process material balance

Basis = 100 % renewable oil volume		
	w%	v%
Process inputs		
Vegetable oil	100	100
Methanol	10	11
Chemicals	4	–
Total input	114	111
Product output		
FAME	96	100
Glycerol	10	7
Losses/by-products	8	–
Total products	114	107

Data source: Kalines et al. (2008)

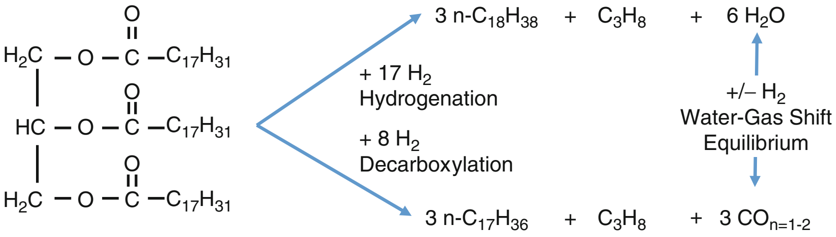


Fig. 16 Green diesel from hydrotreating of renewable oils

Table 15 Typical renewable oil hydroprocessing material balance

Basis =100 % renewable oil volume		
	w%	v%
Process inputs		
Vegetable oil	100	100
Hydrogen	1.5–3.8	–
Total input	102.7 avg	100
Product output		
Green diesel	75–85	88–99
Propane	5	9
Butanes	0–2	0–3
Naphtha	<1–7	1–10
Water/gases	~12.7	–
Total dry liq. prod.	102.7 avg	109.5 avg

Data source: Kalines et al. (2008)

oil depend on the catalyst used. You would need to work with a catalyst supplier to select the right catalyst for your specific unit. The potential pitfalls are discussed under refining issues below.

The direct hydrotreated products from renewable oils have poor cold flow properties and may require dewaxing. Alternately, if the material is coprocessed, the percentage of the renewable feed in the blend can be limited.

Table 13 previously included typical green diesel product properties from hydroprocessing with a petroleum-derived ULSD and FAME.

Typical yields from green diesel production are in Table 15.

Renewable Diesel Stock Properties

Table 13 compares key properties for the most common renewable diesel stocks with typical petroleum ultralow-sulfur diesel (ULSD). You can see that the alternative stocks are not perfect fits, but they would work well as blendstocks. From the source, it is not clear whether the green diesel was dewaxed, but it appears likely from the cloud point.

Refining Issues

Raw Material Supply

Most of the oils are available in limited quantities, locally. Significant cost may be incurred getting the oils to a refinery. The total quantity of all these oils and fats is almost negligible compared to the total fuel consumption. It is hoped by EPA that algal oil will become a large source, but attempts to produce large amounts of algal oil are still in pilot phases.

Economics

The oils produced at present are basically balanced with their markets. The price of the oils, in many cases, are higher than the value of the diesel that can be made from them. What production has been seen has been largely supported by government subsidy or special dispensation. Experience has shown that diverting part of these oil supplies to fuel production greatly increases the oil price – i.e., the markets are not very elastic.

Plugging

The oils contain calcium, magnesium, phosphorus, insolubles, and gums that will foul exchangers and catalyst beds. This has been the most common major problem, even in coprocessing. The highly unsaturated oils form polymers when heated due to exposure to oxygen during transportation and storage. To manage plugging, the oils require fine filtration (<5 μm) on receipt and before feeding to a reactor from tankage. The raw renewable oils should be stored in nitrogen-blanketed tanks.

Catalyst Poisoning

Some of the trace impurities in the oils are catalyst poisons. Phosphorous would be the most probable issue, but some metals may contribute to poisoning. This is not as bad an impact as for some feedstocks.

Hydrogen Consumption

The oils are unsaturated and contain a large amount of oxygen, meaning that hydroprocessing requires a lot of hydrogen. As seen in Fig. 16, hydroprocessing requires very large amounts of hydrogen. If the reaction followed the hydrogenation route, the consumption would be 2,256 scf/b for the illustration. Via the decarboxylation route, the consumption would be 1,062 scf/b. From a practical standpoint, the actual reaction is somewhere between these two. A typical value for tallow and other animal fats would be about 1,500 scf/b. For vegetable oils, which are more unsaturated, the hydrogen consumption would be closer to 2,500 scf/b as a rule of thumb.

Cold Flow Properties

The oils make long-chain hydrocarbons with terrible cold flow properties. You can coprocess some low percentage of renewable oil with petroleum diesel without severe impacts. Dewaxing is required when processing higher percentages. If you want to hydrotreat the renewable oil in a stand-alone unit, dewaxing would likely be required.

Corrosion

Because they contain high oxygen concentrations, hydroprocessing can generate high CO_2 levels in treat gas that present a new corrosion and deposit source in the reactor effluent. You can see the potential if reactions proceed along the decarboxylation route. If the oil is processed in a stand-alone unit, you can expect high corrosion potential from carboxylic acid in the effluent. In coprocessing, carboxylic acid may also cause trouble, even with ammonia present from the other feedstocks because the CO_2 solution will strip off the protective sulfide coating in the effluent equipment. These issues appear even when the materials are processed in low concentrations.

Ammonium Bicarbonate Deposition

In hydroprocessing, we are used to using wash water to manage ammonium salts of sulfur and chloride. When processing renewable oils, there is the additional chance for ammonium bicarbonate salts to deposit. This may require adjustments to the wash water rate. The salts would tend to deposit at conditions similar to those that cause ammonium bisulfide deposition. Keep in mind the carbonate may tend to compromise the protective sulfide layer on the effluent equipment, as mentioned under corrosion.

Concluding Remarks on Renewables

From a refining standpoint, renewables would be an occasional feedstock for diesel hydrotreating units. They can be coprocessed in most diesel units at some level of concentration. The renewable oils need to be appropriately cleaned up ahead of time to eliminate solids, metals, gums, and other contaminants. They can be expected to increase water make, effluent corrosion, and hydrogen consumption. They might cause buildup of CO/CO_2 in recycled gases. Appropriate catalyst choices and proper renewable feedstock storage and handling are necessary to minimize impacts.

Stand-alone processing of renewable oils is possible in a unit appropriately designed to accommodate the stocks.

Running renewable oils in a refinery is economically challenging. The supply of these oils is tight and the price elasticity is low. Still, we can expect to see more of them in refineries to help meet renewable fuel mandates in the future.

Other Unconventional Feeds

A refinery may, from time to time, see other feedstocks in low volumes that can impact refinery operations. We will not explore all the possible stocks but will touch on the key issues experienced with two alternative feeds: finished or waste lube oil and transportation mixes (pipeline interface or off-spec products).

Lube Oil Re-refining

It is not advisable to take a finished or spent lube oil into a conventional refinery in any concentration. Re-refining lube oil involves several operations that are not available in most refineries. You might be able to run it in the coker; but otherwise, there are lube oil re-refiners set up to handle the unique issues.

Specific problems you will see with lube oils include:

- Calcium and other metals/semimetals from lube oil additives (soaps)
- Solids and other contaminants (sludge) introduced during use – like carbon particles, iron from engine wear and tear, etc.
- Residual fuel contamination

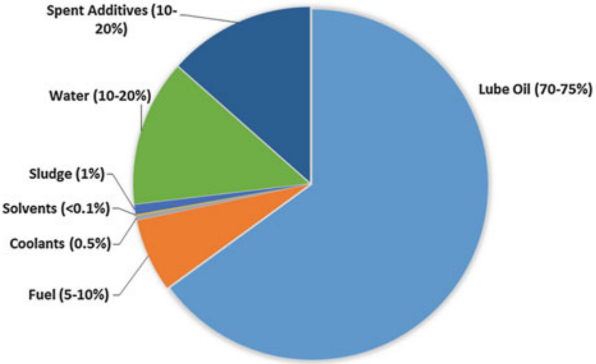


Fig. 17 Used lube oil contents and contamination (Data source: *Re-refining Used Lube Oil*, http://www.sequoia-global.com/re-refining-used-lube-oil.html, 2013)

- Water introduced during use
- Engine coolant contamination, with additives
- Solvent contamination

Figure 17 shows what you might find in a used lube oil.

Figure 18 illustrates one re-refining scheme for lubes to address the various issues. The re-refining steps here include:

- Rejecting sludge and other accumulated materials – gums and solids
- Rejecting water
- Vacuum distilling out VGO
- Dealing with potential catalyst poisons (adsorption or absorption)
- Evaporation of raw lube stock
- Hydrotreating the raw stock
- Separation of the treated product into neutral oils

Generally, it is best to leave used lube oil re-refining to the specialized facilities designed for it.

Transmix and Tank Farm Stocks

Transmix is used here as a general term for oil that comes for transportation and sometimes remote tank operations.

Most commonly, in a pipeline, there is always an interface between two commodities, where the commodities are intermixed. Normally this interface is managed by downgrading the relatively small amount of the transmix to a product that can tolerate the material – usually the heavier of the two commodities. For instance, an interface between gasoline and diesel would be used as diesel, assuming the diesel specs could be met.

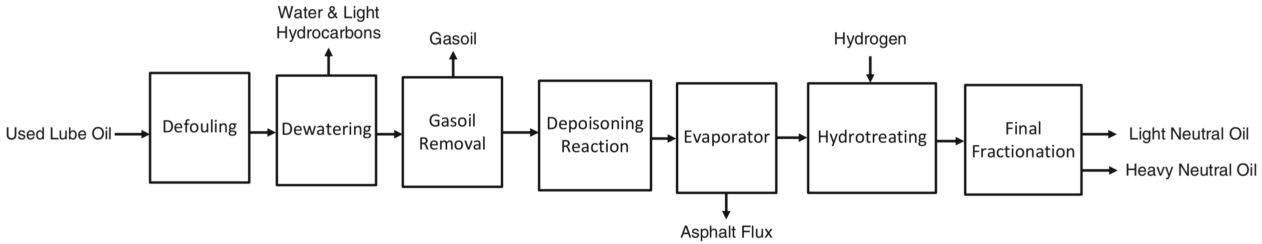


Fig. 18 CEP technology process for waste lube oil re-refining (Data source: Park and Magnabosco 2012)

However, sometimes the interface amount is too large or can't be managed locally and it must be sent elsewhere for reprocessing. If the commodities are still blendstocks without additives, it is not a major problem to reprocess the material through a refinery – it just consumes crude capacity. If the material has been additized, then this becomes a bigger problem. If one of the materials is an oxygenate, like FAME, additional process and storage issues can be created.

Similar issues can occur in trucking when two commodities get mixed and there is no way to manage them without reprocessing. In the case of the trucks, you would be dealing with fuels that have already been additized. The impact of the additives needs to be considered. Ethanol in gasoline may present a minor issue compared to other additives.

Another stock that sometimes appears is heel or off-spec products from a tank farm. A refinery is often asked to take tank heels from a product tank farm when tanks must undergo maintenance. If the products are just blendstocks that have not been contaminated or additized, they can normally just be rerun in the refinery with or without a crude rate penalty. If contaminated, rerunning has to be approached carefully and planned.

One glitch with some tank farm stocks may result from bacterial action in the tanks. Bacteria love to grow in distillates, especially those that might have esters (e.g., FAME) added. If a tank farm is not monitoring and managing the microbiological growth, it will get out of control (white to green slime) and a tank would have to be removed from service for cleaning. The oil in the tank will be contaminated with bacteria that can then be transferred to the refinery's clean tanks, where bacterial growth can start.

The best advice in dealing with transmix or any other product from marketing or transportation that you are considering rerunning is to be sure you understand the origins of the material: why is it surplus or why does it have to be rerun? You may just be buying into someone else's problems. Get samples of the material and look for contaminants and additives. Have a plan for how you will manage the oil before you receive it and have an alternative in case the material received causes unforeseen problems. There have been plenty of experiences with almost negligible amounts of some odd stock causing major problems in the main refinery processes.

References

American Chemical Society, Item: Oil Sands, ACS Fuel Chemistry Division – ACS Outreach, http://www.ems.psu.edu/~pisupati/ACSOutreach/Oil_Sands.html. Accessed Nov 2013

B. Boundy, et al. *Book: Biomass Energy Data Book – 2011*, U.S. Department of Energy, Oak Ridge National Laboratory (2011), http://cta.ornl.gov/bedb/pdf/BEDB4_Full_Doc.pdf. Accessed Nov 2013

Canadian Crude Quality Monitoring Program, Several assays used, www.crudemonitor.ca. Accessed Nov 2013

caplinepipeline.com, *Crude Oil Quality Assay Reports*. Accessed Nov 2013

Cenovus, Western Canadian Select (WCS) Fact Sheet, http://www.cenovus.com/operations/doing-business-with-us/marketing/western-canadian-select-fact-sheet.html. Accessed Nov 2013

B. Christolini, (UOP, 2006), Item: catalytic cracking of vegetable oils and greases, UOP, Technology & More, Winter 2006

Darpro Solutions, Material safety data sheet for beef tallow (2012), www.darpro.com, July 10, 2012. Accessed Nov 2013

Draft Supplemental Environmental Impact Statement, Keystone XL Project, March (2013)

European Biofuels Technology Platform, (unknown date), Item*:* Fatty Acid Methyl Esters (FAME), www.biofuelstp.eu

J.C. Garner, et al. (Washington State University, 2010), Proceedings of the Sustainable Feedstocks for Advanced Biofuels Workshop, Soil and Water Conservation Society: Chapter 8: Oilseed and Algal Oils as Biofuel Feedstocks, http://www.swcs.org/documents/resources/1_All_Chapters__Sustainable_Feedsto_8A410A56233E6.pdf. Accessed Nov 2013

F. Gregg, (unknown date), Article: fuel properties of various oils and fats, SVO: powering your vehicle with straight vegetable oil, http://bunkum.us/svo/fuel_property.html. Accessed Nov 2013

Jensen, H.B., et al. (U.S. Department of the Interior, Bureau of Mines, 1971), Paper presented to the American Chemical Society Meeting in Los Angeles in March 1971: Characterization of a Shale Oil Produced by In-Situ Retorting, Laramie Energy Research Center, Laramie, WY, http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/15_1_LOS%20ANGELES_03-71_0113.pdf

T. Kalines, et al., Article: Green Diesel Production by Hydrorefining Renewable Feedstocks, Biofuels Technology (~2008), http://www.biofuels-tech.com/view_topic.aspx?intTID=36. Accessed Nov 2013

G. Knothe, Article: a technical evaluation of biodiesel from vegetable oils vs. algae: will algae-derived biodiesel perform?, Green Chemistry, 2011, 13, 3048–3065, Royal Society of Chemistry, UK (2011), http://pubs.rsc.org/en/Content/ArticleLanding/2011/GC/C0GC00946F#!divAbstract. Accessed Nov 2013

S.A. Lordo, B. Mason, (Nalco Energy Services, 2012), Paper presented to 3rd Opportunity Crudes Conference: *Shale and Tight Oil . . . The New Frontier*, Hydrocarbon Publishing Company, P.O. Box 661, Southeastern, PA 19399 (USA)

M. Espinoza da Cunha, et al., Paper: beef tallow: biodiesel produced in a pilot scale, Fuel Processing Technology Journal, Elsevier B.V. (2009), http://www.slideshare.net/EvaneideFerreira/beef-tallow-biodiesel-produced-in-a-pilot-scale, January 2009. Accessed Nov 2013

National Renderers Association Inc. (2008), Pamphlet: pocket information m: a buyer's guide to rendered products, http://assets.nationalrenderers.org/pocket_information_manual.pdf. 2008, Accessed Nov 2013

J. Park, L. Magnabosco, (CEP, 2012), Article: used oil re-refining: improvements in CEP technology make economics more attractive, Lube Magazine, No.111, Oct 2012

Princeton University (1980), Item: An Assessment of Oil Shale Technologies, http://www.princeton.edu/~ota/ns20/alpha_f.html

S. Sayles, (KBC Advanced Technologies, 2012), Paper presented to AFPM Question and Answer Session: *Shale or Tight Oil Processing*, http://www.slideshare.net/kbc_at/kbc-io-e-webinar-shale-or-tight-oil-processing. 2 Oct 2012

Sequoia Global (2013), Item: re-refining used lube oil, http://www.sequoia-global.com/re-refining-used-lube-oil.html, 201. Accessed Nov 2013

Stauffer, H.C. & Yanik, S. J., (Gulf Science and Technology Company, 1978), Paper presented to the American Chemical Society Meeting in Miami, FL in September 1978: Shale Oil: An Acceptable Refinery Syncrude, https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/23_4_MIAMI%20BEACH_09-78_0002.pdf

K. Turini, et al. (Fluor Enterprises, 2011), Paper presented at 2011 AIChE Spring Meeting: *Processing Heavy Crudes in Existing Refineries*, http://www.aiche-fpd.org/listing/112.pdf

Tyson (2007), Material safety data sheet for beef tallow, 23 July 2007

Yi Pan, et al. (Liaoning Shihua University, Liaoning Fushun 113001, China, 2012), Paper: A Review of Technologies for Oil Shale Surface Retort, J. Chem. Soc. Pak., Vol. 34, No. 6, 2012, pp. 1331–1338, http://jcsp.org.pk/PublishedVersion/80b8ee64-0d43-4305-8ac2-603ce6ac62d1Manuscript%20no%201,%201st%20Gally%20proof%20of%209183%20_Yi%20Pan_.pdf

Biorefineries

Stanley J. Frey and Geoffrey W. Fichtl

Contents

Abstract

Relatively recent interest in biofuels is rooted in the growing concern over rising global greenhouse gas emissions, energy independence, and support of agricultural industries. Although biofuels are still a small segment of the fuels industry, technologies that convert biomass into biofuels are widely being developed for industrial-scale application, and are expected to play an increasingly important role going forward. This chapter gives a broad overview of the major biofuels conversion pathways including fermentation both from plant sugars and

---

S.J. Frey (✉) • G.W. Fichtl
UOP, A Honeywell Company, Des Plaines, IL, USA
e-mail: stan.frey@honeywell.com; geoffrey.fichtl@honeywell.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_30

lignocellulose-derived sugars, biodiesel, hydroprocessing of vegetable and animal oils, gasification, pyrolysis, and liquefaction. Special attention is given to hydrotreating and hydroisomerization of vegetable and animal oils due to its prevalence in industry, and its strong relationship with similar petroleum hydroprocessing covered in other chapters in this handbook. Life cycle analysis, measurement of biologically-derived carbon, and issues of integration of biofuels into fuel supplies that are still largely petroleum-based are also discussed.

Keywords
Biofuels • Hydrotreat • Deoxygenation • Renewable • Fermentation • Lignocellulose • Ethanol • Biodiesel • Triglyceride • HEFA • SPK • Life Cycle Analysis

Introduction

This chapter is somewhat different than the others in this handbook in that this chapter is really about a feedstock type rather than a specific conversion technology. That feedstock type is material directly derived from plant and, in some cases, animal matter rather than petroleum oil. Fuels produced from these feedstocks are commonly known as "biofuels," and the feedstocks are known as "renewable" because they can be reproduced in a short period of time, from annually to over the course of a few decades in the case of trees. Note that petroleum is essentially also derived from plant and animal matter; however, it has been transformed from its initial biological chemical form into hydrocarbons via geologic processes that take millions of years. In these processes, the biological matter is subjected to subterranean environments that confine the biological material to high pressures and temperatures in anaerobic conditions and result in products that are hydrocarbons quite absent of certain elements that are found in all life (petroleum.co.uk 2013). These elements include oxygen, phosphorus, nitrogen, alkali and alkali earth metals, and chlorine. The elimination of these elements makes the resulting petroleum much easier to process to fuel products. Conversely, it is the inclusion of these elements in the biofuel feedstocks that makes converting plant and animal feedstocks to hydrocarbons more challenging.

Motivation to Produce Biofuels

Foundational to the interest in converting renewable feedstocks to fuels is the recent concern beginning significantly in the 1990s regarding the earth's rising atmospheric CO_2 concentration. This has caused national governments around the globe to take action in the form of fuel regulations, targeted tax incentives (both credits and new taxes), and subsidies to move toward renewable feedstocks and away from petroleum. Additionally, governments also cite energy security, improved international trade balances, and improved domestic rural economies as other reasons to support production of biofuels over petroleum-sourced fuels. The push by governments to produce biofuels has resulted in substantial growth of petroleum fuel substitutes and additives over the last decade, most notably, ethanol and fatty acid methyl ester (FAME or biodiesel).

New Carbon

Carbon from petroleum is commonly called old carbon to distinguish it from new carbon. New carbon is already at the surface of the earth and is currently used in biological processes by all living things. Old carbon found in petroleum is almost entirely composed of the carbon-12 isotope (^{12}C), as this is the primary stable naturally occurring carbon isotope. New carbon has a greater amount of carbon-14 (^{14}C) isotope than does old carbon. The new-old carbon composition of a hydrocarbon can be determined by analyzing a sample for its isotopic makeup (e.g., by ASTM D6866-10). Thus, the portion of a hydrocarbon sample that is derived from biological versus petroleum sources can be quantified, which can be useful in compliance with regulations requiring that fuel blends be composed of a specific amount of renewably sourced fuel.

Life Cycle Analysis

In order for biofuels to result in reduced emissions of carbon dioxide, the total emissions of CO_2 for the entire biofuel production and use process must be lower than the CO_2 emitted by producing and using equivalent petroleum-derived fuels. Life cycle analysis is essentially an accounting methodology to keep track of all the emissions along these pathways from beginning to end, or cradle to grave. The life cycle of petroleum fuels includes extraction of oil from the earth's crust, transportation of the oil to a refinery, refining into fuels, transportation from refinery to fueling stations, and combustion in the end user's vehicle. Similarly, the life cycle of biofuels includes production of the energy crop, transportation of the oil-bearing crop to an extraction plant, extraction and refining of the oil, transportation of oil to a biofuel production facility, conversion of the oil into a biofuel, transportation to a fueling station, and combustion in the end user's vehicle. Each step along these pathways has associated emissions that must be taken into account. The cultivation and land-use practices of energy crops are especially important, as significant emissions can result if improper techniques are applied, such as razing forest lands to make room for energy crop plantations. Land-use-related emissions can be minimized by growing energy crops in rotation with other crops. For example, the camelina energy crop can be grown in rotation with wheat without dramatically changing the use of the land or disrupting the production of wheat. After land-use-change emissions are properly accounted for, the fuel consumed in farm tractors to cultivate crops and the trucks used to transport oils and fuels between facilities, as well as the fuel gas burned to fire the heaters in a biofuel production plant, are all examples of cradle-to-grave emissions along the biofuel production pathway that must also be taken into account. If these upstream contributors to life cycle emissions are adequately managed, biofuels have an advantage compared to petroleum-derived fuels in that the end-user combustion-related net emissions are essentially zero for biofuels. Of course, the combustion of fuels, whether bio or petroleum derived, results in immediate local emissions of CO_2. For biofuels, these emissions are part of a larger carbon recycle loop, in which every mole of CO_2 released in combustion is eventually removed from the atmosphere and used in the growth of new plants that will be used for production of an equivalent amount of biofuels. In this simple loop, there is no net increase in the amount of CO_2 in the open atmosphere. A similar carbon recycle loop does not exist for CO_2 emissions from petroleum fuels. Thus, having no natural means to be removed from the atmosphere, every mole of petroleum-based carbon used as a fuel results in a mole of CO_2 added to the atmosphere. When the full life cycle of biofuels is managed properly, the greenhouse gas emission reductions can be significant. For example, life cycle analysis of camelina grown in rotation with wheat has been shown to reduce greenhouse gas emissions by as much as 80 % when compared with equivalent petroleum fuels (Shonnard et al. 2010).

Feedstocks and Conversion Routes

The biological feedstocks used to produce biofuels come in three general forms: sugars and starches, lipid oils (including triglyceride and free fatty acids), and lignocellulosic materials. Sugars and starches are most commonly derived from grains or sugar cane and are converted to biofuels via fermentation to ethanol. Ethanol produced by fermentation is by far the world’s largest source of biofuels. Triglycerides are the fats found in plants and animals and are most commonly obtained from plant seeds via crushing and extraction and also in wood pulp processing plants in a product referred to as tall oil. These triglycerides are converted to FAME via transesterification with methanol. Hydroprocessing the triglycerides and free fatty acids results in deoxygenation of the triglycerides and free fatty acids to paraffins that make excellent diesel and jet fuel components. Finally, the third biological feedstock, lignocellulosics, compromises the bulk of plant matter. It is the material that makes up the stem, stalk, trunk, branches, leaves, and roots of any plant material. Three distinct polymers comprise lignocellulosics: cellulose, hemicellulose, and lignin. Cellulose is a polymer of glucose and provides the bulk of the material for the plant. The hemicellulose, a polysaccharide shorter than cellulose, is made up of multiple saccharide unit types and strengthens the cell walls in the plant. Lignin is an irregular polymer of aromatic units connected by ether linkages which strengthen the plant and provide for water transport within the plant. Conversion of lignocellulosics to transport fuels, at the time of this writing, is done on a relatively small-volume basis as these processes are still early in their development and industrial application. Some of the most promising process routes include gasification with subsequent reaction of the synthesis gas to hydrocarbons via Fischer-Tropsch or mixed alcohol reactions, pyrolysis to liquids with subsequent conversion to hydrocarbons by deoxygenation via hydroprocessing or by coprocessing in a refinery FCC unit, and conversion of cellulose to sugars via hydrothermal and enzymatic processes with subsequent fermentation of those sugars to ethanol.

The term "biorefining" is defined by the International Energy Agency's Bioenergy Task 42 group on biorefineries as follows: "Biorefining is the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, and/or materials) and bioenergy (biofuels, power and/or heat)" (Biorefining n.d.). Given that this book focuses on the production of transportation and other liquid fuels, discussion of the multitude of chemicals and products produced by the forest products and other biologically sourced specialty chemical niche industries is outside the general scope of this book. Moreover, most energy produced today in what is considered a biorefinery is found in the combined power and heat integration inside a pulp and paper mill technology that has been in place for decades (Rajgor 2013). The contribution of wood-derived fuels has held steady at just less than 1 % of the total electricity demand in the United States for the last two decades (United States 2013a). Therefore, we will use the following definition of biorefining: "the conversion of biomass primarily for the production of transportation fuels." We will restrict our survey to only the largest volume production processes currently in practice producing transportation fuels. Those are (in approximate descending order of commercial capacity):

1. Fermentation of plant sugars and starches to ethanol
2. Transesterification of vegetable and animal oils to fatty acid methyl esters (FAME or biodiesel)
3. Hydrotreating of vegetable and animal oils to paraffins (renewable diesel and renewable jet fuel)
4. Thermochemical/enzymatic conversion of lignocellulosics to simple sugars followed by fermentation to ethanol
5. Gasification of biomass to synthesis gas and subsequent conversion to Fischer-Tropsch liquids, higher alcohols, or dimethyl ether
6. Pyrolytic and pyrolytic/catalytic processes of lignocellulosics to gasoline and diesel
7. Hydrothermal liquefaction

Of these multiple reaction routes to generate hydrocarbons from biological matter, few have found their way into a process that would fit into a petroleum refinery. The processes that have been used at largest capacity outside a refinery context will first be briefly surveyed as they, in fact, comprise the production of almost all biofuels today. To date, there has only been one process that has been implemented at large scale in a petroleum refinery context, hydroprocessing of triglycerides to diesel, jet fuel, and naphtha. A description of the hydroprocessing of triglycerides will be the focus of this chapter as it is presently the largest scale manufacturing method of fully fungible transport fuels into the existing petroleum-based delivery systems. We now consider general overviews of the other paths first.

Commercialized Biofuel Production Processes

Fermentation of Starches and Sugars to Ethanol

Production Capacity

Bioethanol is by far and away the largest volume transportation biofuel worldwide with a total production at 500–550 million barrels per year (bpy). Over 85 % of the production of bioethanol is confined to two countries, the United States and Brazil. Production has grown rapidly in the United States (United States 2013b) primarily due to the Energy Policy Act of 2005 (United States 2005) and Energy Independence and Security Act of 2007 (United States 2007) mandating the use of ever increasing billions of gallons of renewable fuel through the year 2022. At the time of institution of the laws, the only renewable fuels in substantial production were ethanol and FAME, and hence, their production accelerated rapidly. Figure 1 shows the growth in production of US ethanol over the subsequent years leveling off around 320 million bpy for the years 2010–2012. Almost all of this ethanol production was based on fermentation of corn starch to ethanol. Prior to these changes in public policy in the United States, Brazil had undertaken an aggressive expansion of bioethanol from fermentation of cane sugar. In response to the oil

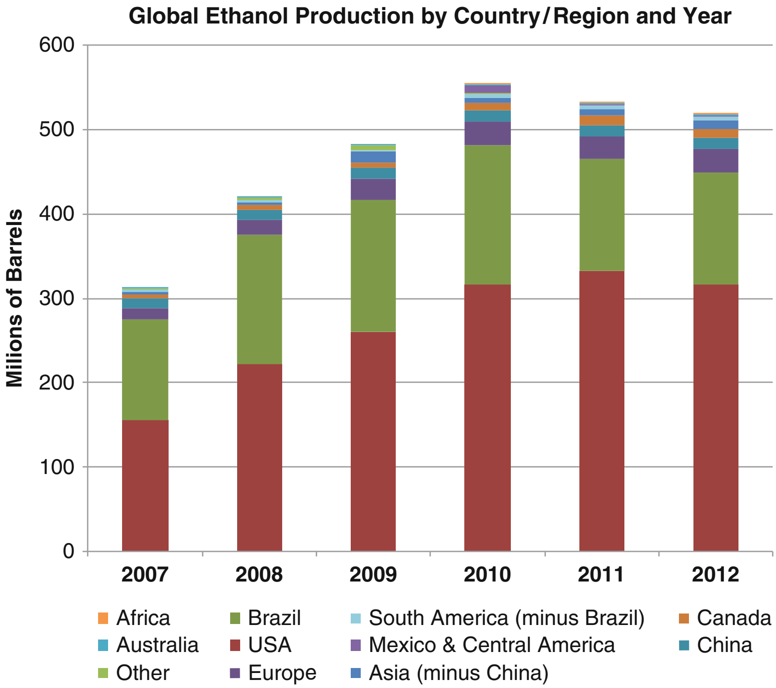


Fig. 1 Global fuel ethanol production

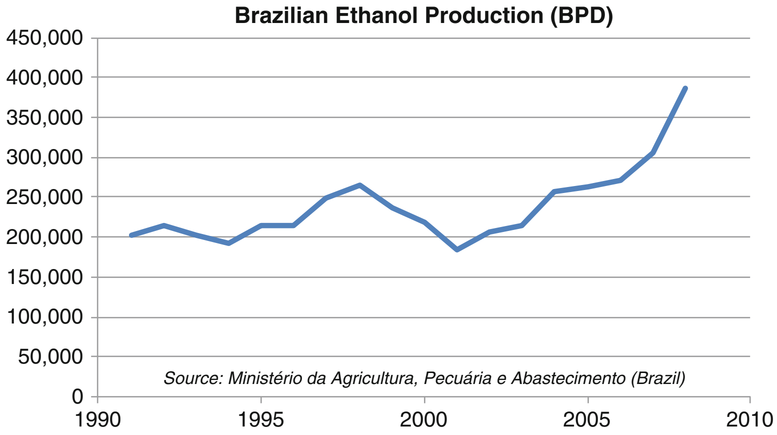


Fig. 2 Brazilian ethanol production since 1991

embargo of the 1970s, Brazil pushed forward with the domestic sugar cane industry to greatly increase production of ethanol until it was between 190,000 and 260,000 bpd from 1990 until 2003 when production again jumped, finally peaking at 450,000 bpd in 2010 (Walker 2011) (Fig. 2).

The plateau in US ethanol production was reached in 2013 when the declining gasoline market compounded by the increasing renewable fuel mandates hits a point at which ethanol production could not be absorbed into the gasoline pool without exceeding the 10 vol% ethanol blending limit previously set. The opinion of many in the fuels and automobile industries is that increasing the ethanol content above this limit brings the mechanical integrity of the fuel delivery infrastructure and automobile fuel systems into question.

Fermentation Process Technology

The fermentation process of corn starch is defined by two methods, wet milling and dry milling (How ethanol is made n.d.). In wet milling (shown in Fig. 3), the whole corn kernel is steeped in dilute sulfurous acid (solution of sulfur dioxide) for 1 or 2 days to separate the gluten and starches from the protein, fiber, and oil (Ibid. 10). This preserves the corn kernel for further processing to make by-products that are useful for animal consumption and edible corn oil (O'Brien and Woolverton 2010). The starches in the steep liquid are enzymatically converted to glucose and then fermented to ethanol. This is contrasted to dry milling (shown in Fig. 4) where the corn kernel is first ground and then subjected to enzymatic saccharification (or liquefaction) to break down the starches to sugars, then the whole mash is fermented for approximately 2 days, and the ethanol is distilled off of the fermented slurry (known as "beer"). Both dry and wet corn milling result in a distilled ethanol product that contains approximately 5 % water as the distillation is limited by an azeotrope. A variety of methods are used to dry the ethanol down to <1 % water (Kumar et al. 2010).

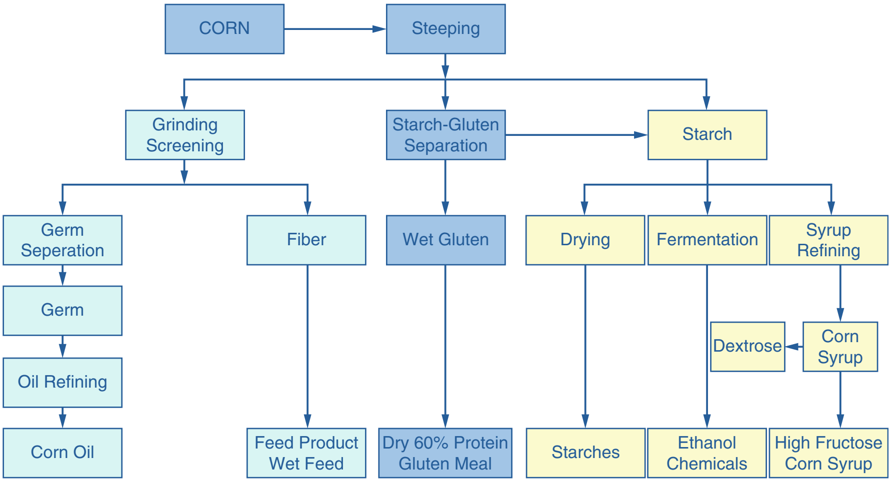


Fig. 3 Wet milling ethanol process (Used with permission of the Renewable Fuels Association)

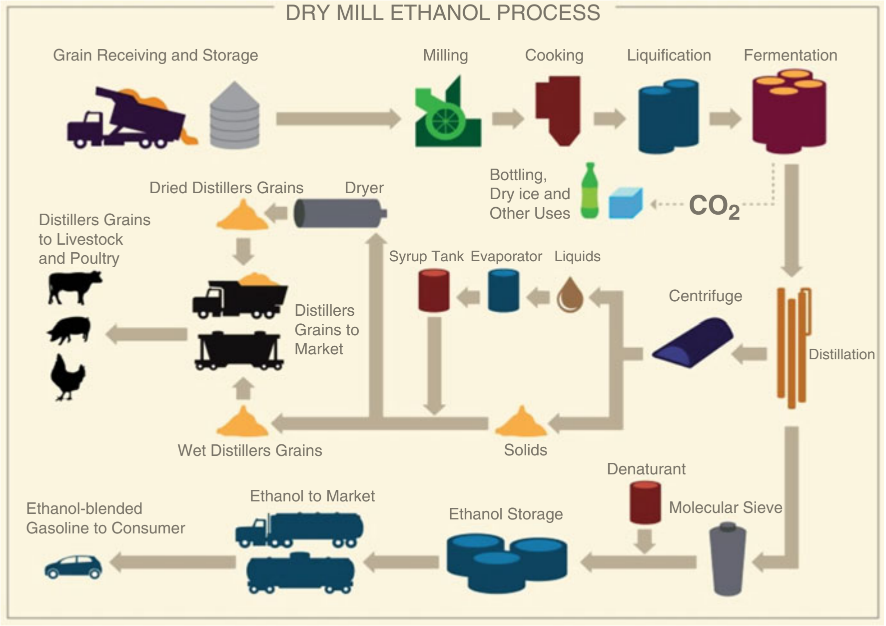


Fig. 4 Dry milling ethanol process

Blending of Ethanol into the Gasoline Fuel Pool

Due to the infinite solubility of ethanol in water, it is required that ethanol be blended into the gasoline pool at the terminal near the point of final sale. Liquid fuel pipelines in the United States do not accept ethanol into the pipeline due to concerns with phase separation due to water seepage into the pipeline, compatibility with other fuels in the pipeline, and corrosion (Whitehead 2012; Kane 2012; Beavers et al. 2009). There is a history of stress corrosion cracking of steel in piping and other components that have been exposed to fuel-grade ethanol. The inability to include ethanol in the primary long-distance transportation network for liquid transport fuels, that is, pipelines, hinders the efficiency with which it can be distributed relative to fully fungible, oxygen-free fuels.

To avoid the issues of water solubility, some companies are engaged in production of butanol, instead of ethanol, by fermentation of starches and sugars. The first commercial-scale operation of this technology was by Gevo in May 2012 at a revamped ethanol plant which has a stated capacity of 430,000 bpy (Gevo 2011, 2012).

Certainly, the use of ethanol in transport fuels has provided benefits in complete combustion of fuels (albeit primarily on vehicles with substandard emission controls) (Gething et al. 1989) and enhances the octane of the blend. However, due to the dissimilar nature of the highly polar ethanol into the nonpolar gasoline petroleum base, the effective Reid vapor pressure (RVP) of the ethanol is quite high. This has limited fuel blender's use of lighter hydrocarbon components (butanes and pentanes) in the gasoline mix to comply with EPA RVP specifications, especially in the high-demand summer season. EPA RVP specifications are primarily in place to limit evaporative emissions from the gasoline during fueling to combat locally high atmospheric ozone levels.

Transesterification of Vegetable and Animal Oils to Fatty Acid Methyl Ester (FAME or Biodiesel)

Production Capacity

In 2012, a total of 111 production facilities in the United States produced 52 million barrels of FAME, more commonly known as biodiesel, via transesterification of vegetable and animal oils using methanol. Worldwide production in 2011 was 147 million barrels. As shown in Fig. 5, production of biodiesel is much more evenly distributed between countries than is ethanol with the top five producers accounting for only about half of the total production (U.S. Energy Information Administration n.d.).

Conversion of vegetable oils to FAME is conducted at low temperature, and the processing is primarily in the liquid phase making production much more accessible to small-scale operations allowing for diverse and distributed production. Producers range from homeowners and farmers that produce biodiesel for their own use to multinational agribusinesses at their soybean processing operations. While vegetable oils also can be used directly for fuel in diesel engines (Pryde 1983), the transesterification of the triglycerides to FAME produces a fuel that has a molecular weight and cold flow properties much closer to petroleum diesel making insertion into the existing engine and delivery infrastructure much more amenable. Similar to ethanol, government biofuel mandates and incentives drive the majority of biodiesel production. In the United States, the primary source of triglycerides is from soybean, and in Europe, the primary source is rapeseed.

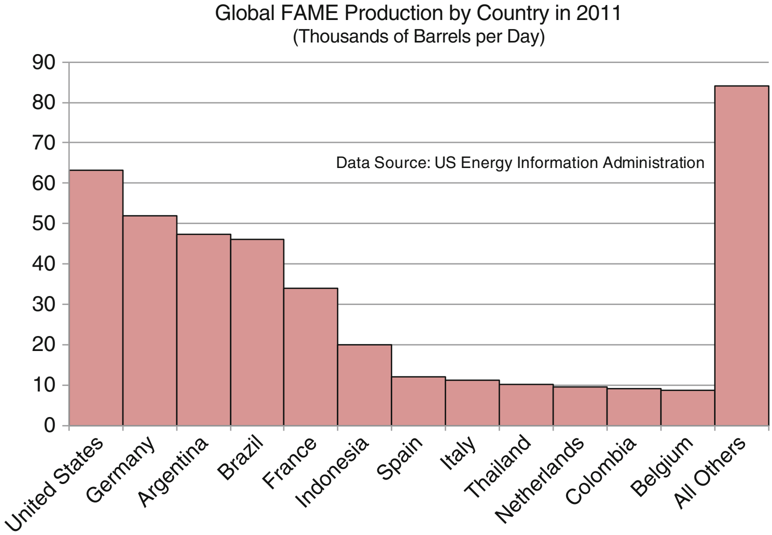


Fig. 5 World biodiesel production by country

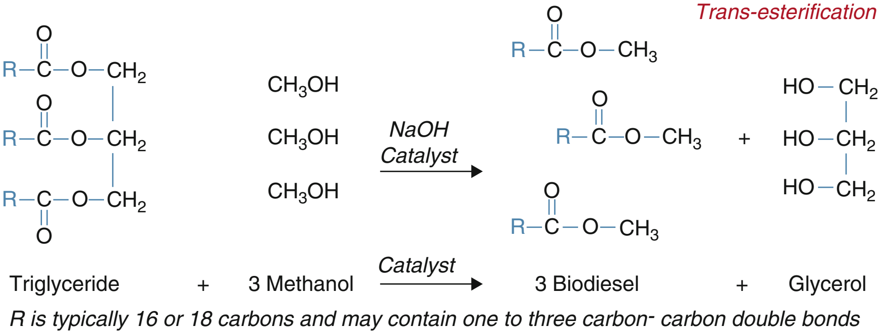


Fig. 6 General chemistry for transesterification reaction to produce FAME

Transesterification Process Technology

The transesterification of triglycerides is typically carried out using base catalysis. The net reaction is as follows (Fig. 6):

Methanol is used as the transesterification reactant. While methanol has a wide availability and low cost, it is derived primarily from natural gas and therefore somewhat reduces the improvement on fossil-based CO_2 emissions when burned in a diesel engine. As can be seen from the stoichiometry, one mole of glycerol is produced for every mole of triglyceride transesterified. Glycerol has many commercial applications as a sweetener, soap component, cosmetic additive, and pharmaceutical component to name a few (Christoph et al. 2002). Even though the large by-product volume of glycerol caused by the huge increase in biodiesel

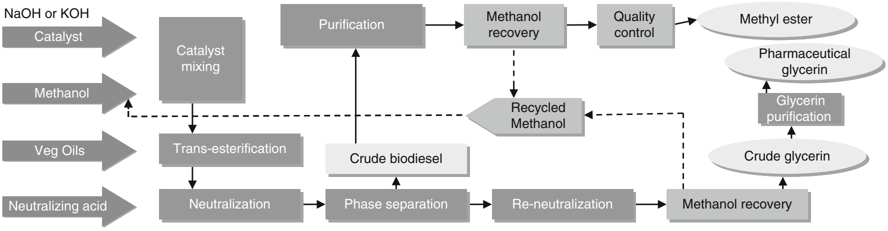


Fig. 7 Typical biodiesel plant schematic

production has created a glut of glycerol to be available, its low price has allowed it to displace other more expensive components in many applications creating a demand to balance the production (Pagliaro and Rossi 2010) (Fig. 7).

While much work is conducted on heterogeneous catalysis systems to promote the transesterification reaction, homogenous sodium hydroxide or potassium hydroxide systems are most common due to the open availability of the catalyst.

The use of used cooking oil and low-grade vegetable oils containing high levels of free fatty acid is an attractive feedstock option over the use of food-grade oils as these oils are lower priced and avoid food versus fuel controversy. However, the use of high free fatty acid feedstock requires additional processing to avoid soap production when contacted with the mineral base catalyst (National Renewable Energy Laboratory 2004).

Blending of FAME into the Diesel Fuel Pool

Similar to ethanol, almost all biodiesel is blended with petroleum diesel near the distribution point. However, the reasons for not sending biodiesel down a pipeline are different than for ethanol. Biodiesel contamination with jet fuel is a main concern. As pipelines typically run batches of various fuels, jet fuel typically follows diesel fuel in a pipeline. If the diesel includes biodiesel, it is common that traces of biodiesel contaminate the jet fuel. Jet fuel typically has a specification of <5 ppm FAME due to the requirement for very-low-temperature freeze points for jet fuel (ASTM D7566-12a). Biodiesel typically is ratio blended (in-line blending with good mixing) with diesel at the fuel terminal. In the early application, some blending was done as “splash blending” which was just to put the biodiesel into a vessel of diesel often unmixed. Due to the nonhomogeneity inherent in this method, it has been mostly abandoned.

Blends of biodiesel are typically between 5 % and 20 % with the higher blend rates promoted in some US states. Several automobile manufacturers still do not warrantee their engines and fuel systems for diesel blends with over 5 % biodiesel; however, most major truck manufacturers do (OEM Statement Summary Chart 2014).

Emissions from diesel that is blended with biodiesel are typically improved over petroleum diesel alone with the exception of nitrogen oxides (NOx) (Hoekman and Robbins 2012). The blending cetane index of biodiesel is typically around 50, and the cloud point of soy-derived biodiesel is near −5 °C. Palm oils produce higher cloud point and rapeseed oil lower cloud points due to the relative amounts of saturated C16 palmitic acid hydrocarbon chains in the various plants (Ibid. 25).

Lignocellulosic Conversion

Feedstock Sources

The conversion of lignocellulosic biomass is one of the two most likely routes (the other being algae) to biofuels that has the potential to replace petroleum-derived fuels on a large scale based on a total annual mass growth. Annual growth of usable lignocellulosic biomass is estimated to be 600–1,300 million metric tons per annum between 2017 and 2030 (U.S. Department of Energy 2011). The major challenges to conversion of lignocellulosic biomass are twofold. The first is logistical: how to economically gather low-density, widely dispersed biomass to a single processing location in an energy and cost-efficient manner (Sokhansanj et al. 2006). This efficient gathering of biomass is already accomplished in the forestry industry. Wood has the advantage of being a dense biomass source with large unit size. This is why many lignocellulosic conversion projects are centered on wood as the feedstock. In addition, the forestry, lumber, and pulp and paper industries have already developed an infrastructure to systematically grow, harvest, and transport the wood to centralized processing locations. Many of the lignocellulosic-derived demonstration and small-scale commercial plants are part of a larger existing pulp and paper or lumber operation to take advantage of the existing utility and labor infrastructure and the already concentrated biomass in one place.

The second major challenge in lignocellulosic conversion is the difficulty of converting the biomass to hydrocarbon molecules useful in internal combustion engines. LC biomass is highly refractory to biological conversion and needs to be mechanically, thermally, and/or chemically modified to reduce the polymer chain lengths to something that can be deoxygenated. Figures 8 and 9 show diagrams of cellulose and lignin which make up LCs. The cellulose has six carbons in a chain before there is an oxygen ether linkage to the next glucose unit. Note that the average gasoline molecule has more than this chain length so conversion of cellulose to conventional gasoline and diesel requires a chain growth mechanism. Hemicellulose is similar to cellulose except that instead of strictly glucose linkages, it contains a variety of anhydrous sugar units such as xylose, galactose, and mannose. These also contain six carbons or less per unit chain, so the same requirement of chain growth pertains to this component of LC biomass.

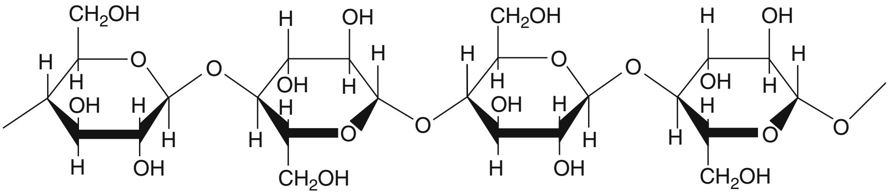


Fig. 8 Diagram of chemical composition of cellulose

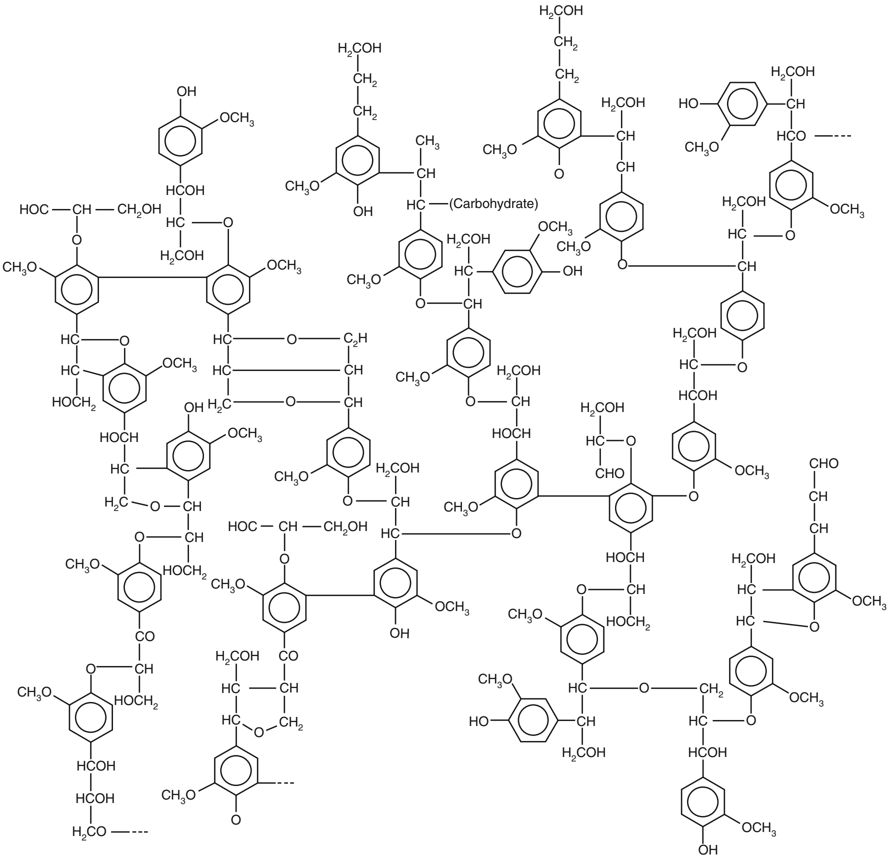


Fig. 9 Diagram of chemical composition of lignin (From: Glazer et al. 1995)

Lignin on the other hand is an irregular polymer made up primarily of hydroxylated propylbenzene groups connected by ether linkages. The basic polymer unit of lignin fits nicely into a gasoline range fuel (Figs. 8 and 9).

Breaking the cellulose-hemicellulose-lignin structure is accomplished primarily in one of four ways, by order of reaction intensity and temperature they are:

1. Chemical hydrolysis and mechanical diminution and enzymatic conversion to sugars
2. Hydrothermal liquefaction
3. Pyrolysis and pyrolysis with catalysis
4. Gasification

We will now briefly review the basic components of each of these methods and their most advanced commercial status in the production of biofuels.

Thermochemical Hydrolysis, Mechanical Diminution, and Enzymatic Conversion to Sugars

Acid hydrolysis of wood to alcohols has been practiced for centuries (Goldstein 1983). The state-of-the-art processes do not use added mineral acids however but generate acids from the biomass itself in various steam explosion or near-critical or supercritical treatments to continue the hydrolysis. The first step in this process as well as any of the lignocellulosic (LC) feedstock conversion methods is mechanical size reduction of the biomass. Of course, this is a more intense operation for wood than for straws or grasses, but in any case, sizes below 3 cm are necessary for almost all processing; this is for conveyance into the process as well as reducing mass transfer resistance of the biomass to any of the fluid treatments described.

The most commercially advanced process of this type is the Proesa™ (trademark of Beta Renewables S.p.A.) technology practiced by Beta Renewables in Crescentino, Italy. The Crescentino plant has a nameplate capacity of 320,000 bpy with expandability to almost 500,000 bpy and began production in October 2013 and is based on using rice and wheat straw in addition to *Arundo donax* as LC feedstocks. This process uses a pretreatment step which Beta Renewables calls "smart cooking" to break the bonds interconnecting the three LC components using water and steam. Purportedly, this first step enables a drastic reduction in the amount of enzyme required for the hydrolysis of the cellulose and hemicelluloses to a mixture of fermentable sugars. The Proesa process enables simultaneous saccharification (hydrolysis) and cofermentation (SSCF) of the LC biomass. The ethanol is distilled from the fermentation mixture and then the lignin is separated where a certain amount of the lignin can be used to generate power and steam for the process (Proesa-the scientific research; Cellulosic ethanol proesa n.d.). Other technologies that are near start-up of commercial-scale production are by POET in Emmetsburg, Iowa (475,000 bpy) (Project liberty – a decade n.d.); Abengoa in Hugoton, Kansas (600,000 bpy) (Abengoa Energy S.A. n.d.); and DuPont in Nevada, Iowa (700,000 bpy) (Du Pont n.d.), all of which are based upon feedstocks from agricultural residues from corn production such as cobs and stover.

Hydrothermal Liquefaction

Hydrothermal liquefaction is the medium-temperature, high-pressure depolymerization and deoxygenation of biomass to simpler molecules. Many of these molecules however are quite unstable and polymerize to form larger molecules. Because the process results in substantial dehydration of the biomass, the product hydrocarbons are quite deficient of hydrogen (i.e., aldehydes and olefins) and participate in chain growth reactions. Advantages of hydrothermal liquefaction over other LC conversion methods are that the feedstock can be wet as water is actually a key reactant in the process, temperatures are moderate (280–370 °C), and a large amount of deoxygenation does occur providing a product that will be closer to typical petroleum fuels. Disadvantages are that upgraded metallurgy is often required, and the process requires very high pressures (1,500–4,000 psi) (Toor et al. 2011). Moreover, the product is typically not useful for a standard fuel application and is not suitable for direct insertion into a petroleum refinery often due to its acidity and chlorides in the product. Product yields and improved product characteristics can be accomplished with the use of alkaline catalysts.

Much work in hydrothermal liquefaction has been done by Pacific Northwest National Laboratory (PNNL). Their research includes evaluation of various catalysts, feedstocks, and operating conditions (Pacific Northwest National Laboratory 2009).

Hydrothermal liquefaction has recently found particular application in conversion of algal biomass to transportation fuels. Initially almost all investigators in algae were attempting to extract the lipids from the algae and then converting that to biodiesel or otherwise processing it to make diesel or jet fuel. It was found that this provided unacceptably low yields. In response to this challenge, some companies such as Sapphire Energy have reverted to hydrothermal liquefaction as a means to get all of the algal biomass including all of the lipids into a liquid that can be processed in a petroleum refinery (Goodall et al.; Cranford et al.; Sapphire energy 2013). The ability to make a substance that can be processed in existing petroleum refining infrastructure gives any conversion of biological material a great advantage in the use of existing capital and integration into the transportation delivery infrastructure.

Pyrolysis

Due to the resistance of lignocellulosic (LC) biomass to decomposition, more extreme thermal treatments are often used to convert it to gaseous or liquid products. Pyrolysis is a type of thermal treatment that has generated great interest due to its ability to produce a liquid product. Pyrolysis is the heating of biomass in the absence of oxygen to temperatures of 300–550 °C causing thermal decomposition of the LC biomass to an array of oxygenated fragments and producing a liquid as the primary product. The liquid is commonly referred to as a "pyrolysis oil."

The chemical composition of pyrolysis oil is quite different from other oils like triglycerides or petroleum. Pyrolysis oil is a complex mixture of pyrolytic fragments of cellulose, lignin, and extractives, all of which contain oxygen. These oxygenated compounds are miscible with water in certain concentrations (Sipila et al. 1998; Wildschut et al. 2009). The compounds in pyrolysis oil include anhydrous sugars, light carboxylic acids, aldehydes, ketones, glycols, syringols, cresols, furans, and light to heavy multi-ring phenols in a mixture containing 20–30 % water. Pyrolysis oil is acidic, typically having a pH less than 3. Most interestingly, due to its aldehyde and phenol content, it will form solid polymers within minutes upon heating to $>150\,^{\circ}$ C. Due to its unique characteristics, pyrolysis oil, in and of itself, does not make a suitable transportation fuel. However, it can be directly combusted in a furnace as a heat source.

To produce a liquid pyrolysis oil, temperatures near 500 ° C are used and heating must be done on the order of seconds to avoid high production of char and gas. This rapid heating, commonly referred to as fast or flash pyrolysis, is commonly done by intimate contacting with a fluidized heat carrier, typically sand. This technology typically results in >70 % pyrolysis liquid yield, 10–20 % char, and the remaining

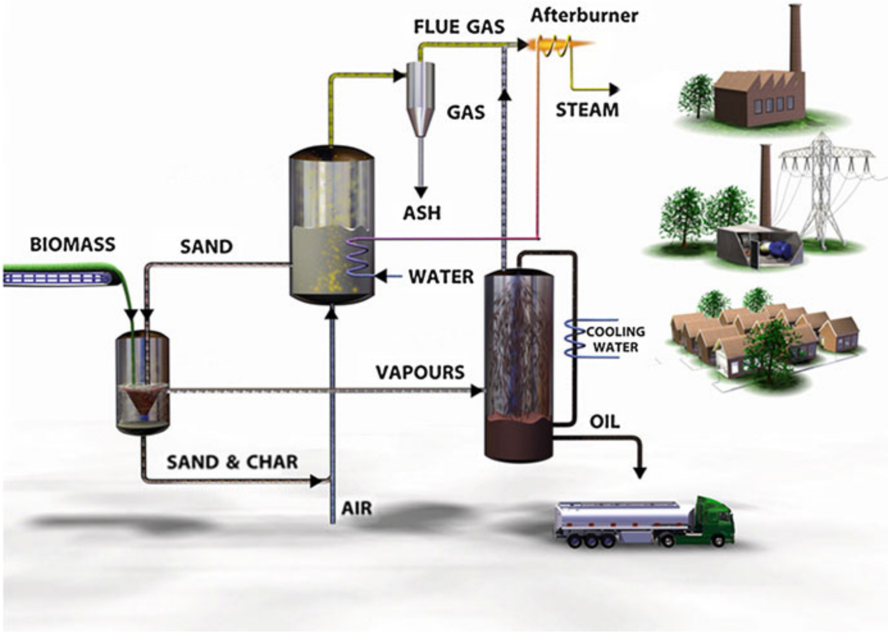


Fig. 10 BTG rotating cone pyrolysis process flow scheme (Source: BTG Bioliquids)

CO- and CO_2-rich gas. There are two leading methods currently offered for pyrolysis to effect the contact of the fluidized heat carrier and the movement of the biomass. The first is by mechanical agitation via mechanical energy input. The second is by heat medium contact with the biomass in a fluidized transport regime affected by entrainment in a gas stream.

BTG Biomass Technology Group BV (BTG) in the Netherlands uses technology that mixes the heat carrier (commonly sand) with the biomass in a rotating cone reactor (Wagenaar et al. 1994; Fast pyrolysis n.d.). The rotating cone reactor avoids the need for any motive fluid to move and mix the biomass and heat carrier. The sand is reheated by burning the char. The first construction of a 25 MWth commercial-scale unit to produce electricity, process steam, and fuel oil is expected to be completed by the end of 2014 (Empyro energy and materials n.d.) (Fig. 10).

Ensyn Corporation licenses a technology called Rapid Thermal Processing or RTP™ (trademark of Ensyn Corporation) which uses the entrained gas to contact and transport the heating media and biomass. This technology feeds biomass to a vertical riser in which sand is flowing upward in an entrained gas stream. The entrained gas is produced by the process and is simply recirculated noncondensables generated by the pyrolysis reaction. The char generated by the process is burned to reheat the sand which is recirculated to the entraining gas in the riser. This technology avoids the use of moving mechanical equipment to contact and move the sand and the biomass. Ensyn has several commercial units in operation, dating back to 1989 (Ensyn history n.d.).

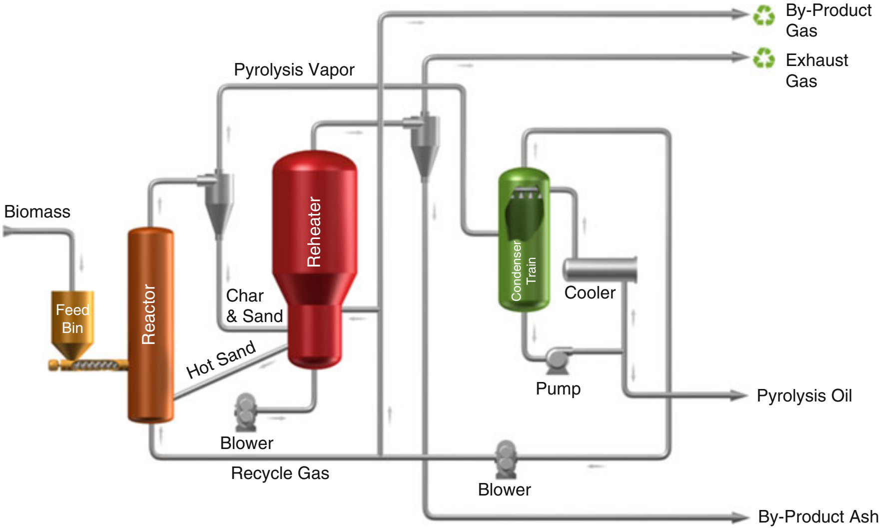


Fig. 11 Envergent RTP process flow scheme (Source: Envergent)

RTP units for the production of biomass-derived pyrolysis oil for energy and subsequent conversion to transportation fuels are sold through Ensyn's JV with Honeywell/UOP, Envergent (Hassett and Baird 2014) (Fig. 11).

As mentioned previously, pyrolysis oil is not suitable for direct use as a transportation fuel and requires further upgrading before it can be used as such. Several pathways have been proposed to convert pyrolysis oil to hydrocarbons, including hydroprocessing, coking, and catalytic cracking. Hydroprocessing and catalytic cracking are the two that have had the most development to date.

Hydroprocessing of pyrolysis oils has been investigated by several entities including PNNL, NREL, University of Twente, University of Groningen, and UOP LLC (de Miguel Mercader 2010). In short-term fixed bed or stirred autoclave tests, hydrocarbon yields of 30 % on feed that originally contained 50 % oxygen have been obtained. This is quite an encouraging result potentially making the final product cost competitive with petroleum-derived fuels. However, the primary difficulty in hydrotreating pyrolysis oil at commercial scale is that the reactors are typically fixed bed down flow filled with extruded catalyst particles. This reactor type is highly susceptible to plugging when even tiny amounts of solids are generated. This has proven very difficult to avoid while hydrotreating. Many studies have examined the competition between polymerization and hydrodeoxygenation of the pyrolysis oil to prevent solid formation (Ibid. 50; de Miguel Mercader et al. 2011; Ardiyanti et al. 2012). The primary method employed to avoid reactor plugging is a two-stage system where the first hydrotreatment step can be operated at conditions that promote mild hydrogenation of the components most prone to cause polymerization before going to a second, higher temperature stage to complete the deoxygenation or to send the stabilized liquid from the first stage to a

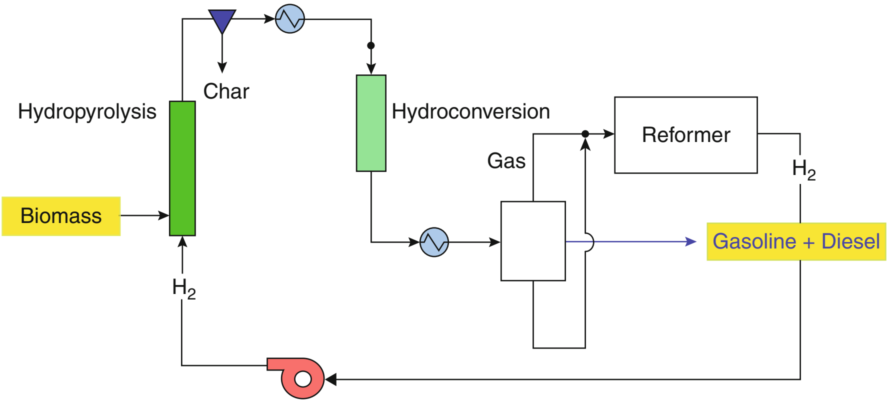


Fig. 12 Flow scheme of the IH^2 process (Source: GTI, in “Biomass to Gasoline and Diesel using Integrated Hydropyrolysis and Hydroconversion” report for U.S. DOE Award DE-EE-000287)

petroleum refining unit such as a diesel hydrotreater or fluidized catalytic cracker and coprocess with a petroleum feedstock. Until a very low solid generating system can be devised, commercialization of hydrotreatment of pyrolysis oil in a conventional fixed bed reactor will not occur.

The Gas Technology Institute has developed a hydroprocessing technology that attempts to avoid the fixed bed fouling issue by hydrotreating the pyrolysis oil in a fluidized transport reactor. This process known as $IH^{2®}$ (trademark of Gas Technology Institute) consists of two stages of hydrodeoxygenation. As shown in Fig. 12, the first stage has a riser transport phase reactor where catalyst is contacted with biomass at temperatures of 340–470 °C and less than 500 psig pressure with hydrogen to promote hydropyrolysis and hydrodeoxygenation reactions (CRI Catalyst Company 2012). The product vapors flow through a char removal system and are cooled with steam generation before entering a fixed bed hydrotreating reactor to eliminate the remainder of the oxygen. By conducting the first stage of hydrodeoxygenation in the transport phase riser reactor, IH2 avoids the plugging problem that was mentioned earlier in fixed bed hydrotreater reactors. The second-stage hydrotreater completes the deoxygenation producing finished, oxygen-free gasoline and diesel blendstocks. To eliminate the need for outside hydrogen input, hydrogen is generated via reforming the light hydrocarbons produced in the process. This process is yet to be constructed at commercial scale, but years of pilot plant testing have shown promise. The IH2 process is licensed through CRI Catalyst Company (Ibid 54).

KiOR has developed a process called Biomass Fluid Catalytic Cracking (BFCC). For the most part, the flow scheme is similar to a petroleum FCC unit with solid biomass replacing the gas oil feed seen in petroleum units. The BFCC process converts solid biomass to a low-oxygen-content oil. This oil is then sent to a fixed bed hydrotreating reactor to complete the conversion to pure hydrocarbon products. The process also has a biomass pretreatment step before feeding to the BFCC riser reactor. KiOR has obtained many pretreatment patents ranging from impregnating biomass with salts, mixing catalyst with biomass, and liquefying, to torrefying, slurrying with hydrocarbon and then contacting with catalytic materials before feeding to the reactor (Bartek et al.; Yanik et al.; Bartek et al.). KiOR constructed a $213 million dollar 500 bone dry ton per day biomass facility in Columbus, MS, with a nameplate production capacity of 937 bpd (assuming an estimated 330 operating days per year basis) of finished products. KiOR is unique in having delivered the largest volumes of pure hydrocarbon transportation fuels from lignocellulosic materials to date from non-Fischer-Tropsch methods, amounting to 16,425 barrels of gasoline and diesel in 2013 (Technology 2014; Production facilities 2014; KiOR expects 2013). It should be noted that this total is only a little over a 2-week operating volume equivalent of the nameplate production. Start-up difficulties are impacting the viability of the KiOR Corporation (cellulosic fuels company KiOR reveals “substantial doubts” about its viability, funding needed by 1 April 2014).

Cool Planet has developed a technology that employs sequential thermal and catalytic decomposition of the biomass, first to gases and then converting the evolved fractions with on-purpose catalysts. These catalysts are different for different functions: dehydration, aromatization, and so forth (http://www.coolplanet.com/how-it-works/overview). In this way, the Cool Planet process avoids the problem of producing the multitude of oxygenated organic compounds generated by bulk thermal and catalytic methods. The Cool Planet approach is to evolve certain chemical types from the biomass and use appropriate catalysis for that type to convert them to hydrocarbons or other valuable products as shown in Fig. 13 (Cheiky and Malyal). Cool Planet has a 720 bpsd facility in construction (Ibid 64).

A similar sequential approach is also being followed by Renmatix that has resulted in their Plantrose™ process. This process first converts the hemicellulose to C5 sugars and separates them from the solids and then converts the cellulose to C6 sugars under more severe supercritical hydrolysis conditions as shown in Fig. 14 (PlantroseTM process n.d.).

Gasification

As opposed to the other methods of lignocellulosic conversion, gasification provides a route to make a very predictable simple intermediate product, synthesis gas or syngas (also known as producer gas) which has just a few simple chemical compounds. Fundamentally, gasification is partial combustion of the biomass to carbon monoxide, carbon dioxide, hydrogen, and water (i.e., syngas). Much lesser amounts of tars and char are also produced. Eliminating the tars from the syngas stream is necessary for clean gas to be converted in downstream processes via Fischer-Tropsch (FT) processes and catalysts. Methods for addressing the char and tar have been the subject of much research over the years and will continue to be so in the future (Wolfesberger et al. 2014; Hansen et al. 2014; Simell et al. 2014; Felix et al. 2014; Dayton and Gupta 2014). The FT product is quite paraffinic however also quite waxy. Typically, the product needs to be converted through a hydroprocessing step called “dewaxing” to make the paraffin suitable for diesel or jet fuel applications.

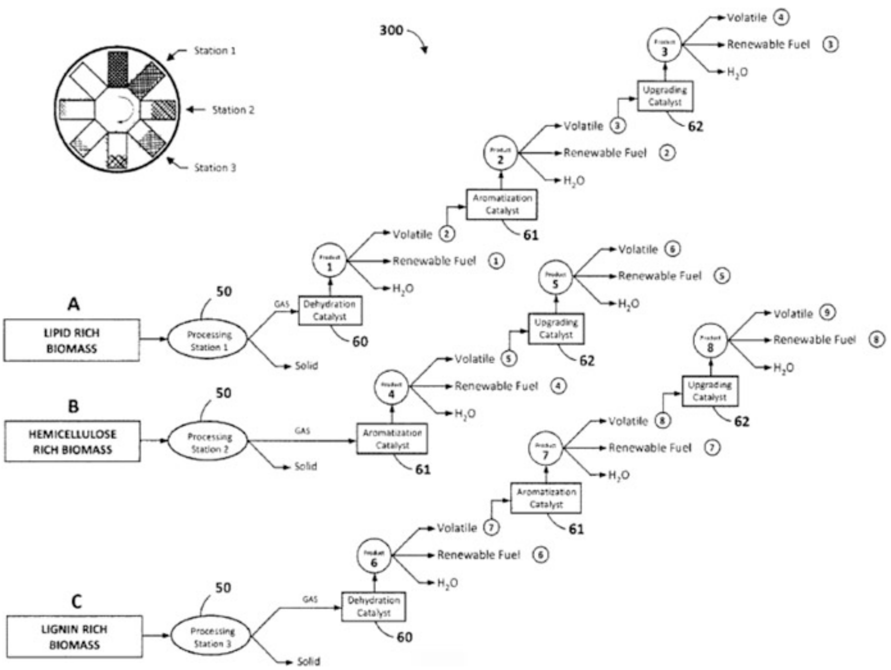
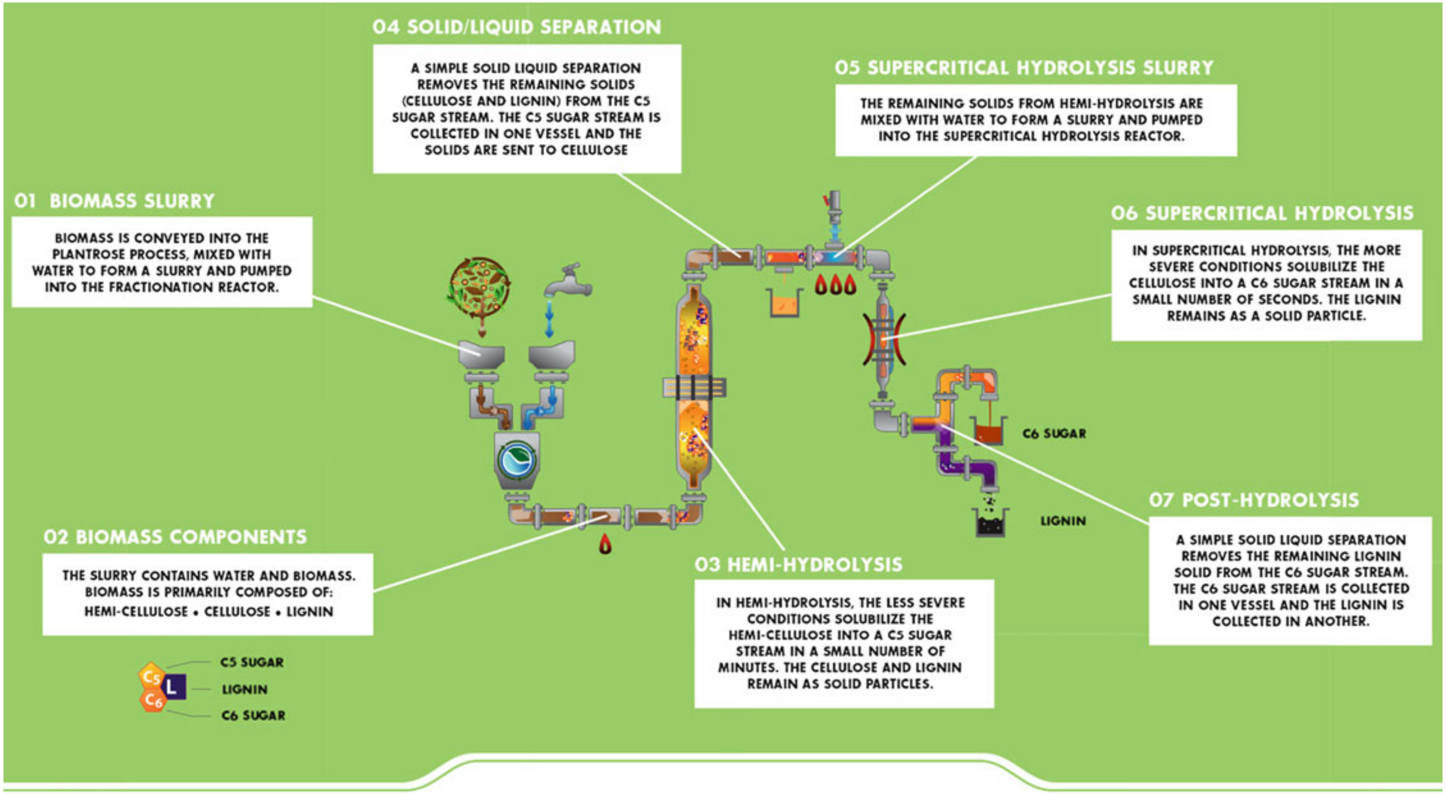


Fig. 13 Conceptual diagram of Cool Planet process (Source: U.S. Patent 8383049)

Two primary routes are used to perform the gasification: air gasification at pressures of 350–1,000 psig and gasification with enriched or pure oxygen. While there are significant costs associated with producing enriched oxygen, much of the capital spent on the air separation plant is recovered by savings in lower-pressure gasification and easier gas cleanup, and providing the possibility to recycle as the nitrogen from the air will not accumulate in the recycle loop (nitrogen is an inert in the gasification and FT processes) (van Steen et al. 2008). Gasification and FT conversion are well-known processes and have been operated at large scale by Sasol, Shell, and ExxonMobil using natural gas and coal feedstocks. Studies have shown that gasification using biomass rather than coal or gas incurs additional catalyst costs of some 60 % above that for the gas-based plant due to the solid feedstock handling, slag formation from the alkali metals in biomass, additional oxygen requirement, and requirement for deeper gas cleaning (Boerrigter 2006).

As alluded to earlier, gasification is an excellent process to convert carbonaceous materials with many difficult contaminants (such as alkali metals, chloride, heavy metals, and high oxygen content) to a hydrocarbon after FT because the unwanted contaminants are efficiently removed in the ash from the gasification step. Also, the gasification route provides great opportunity for electricity cogeneration from the waste heat from the gasifier and from the syngas itself by sending a fraction to a furnace to produce power or more heat. In this way, gasification projects can have both a stationary energy and a transport fuel revenue stream to support the project.



01 BIOMASS SLURRY

BIOMASS IS CONVEYED INTO THE PLANTROSE PROCESS, MIXED WITH WATER TO FORM A SLURRY AND PUMPED INTO THE FRACTIONATION REACTOR.

02 BIOMASS COMPONENTS

THE SLURRY CONTAINS WATER AND BIOMASS. BIOMASS IS PRIMARILY COMPOSED OF: HEMI-CELLULOSE • CELLULOSE • LIGNIN

03 HEMI-HYDROLYSIS

IN HEMI-HYDROLYSIS, THE LESS SEVERE CONDITIONS SOLUBILIZE THE HEMI-CELLULOSE INTO A C5 SUGAR STREAM IN A SMALL NUMBER OF MINUTES. THE CELLULOSE AND LIGNIN REMAIN AS SOLID PARTICLES.

04 SOLID/LIQUID SEPARATION

A SIMPLE SOLID LIQUID SEPARATION REMOVES THE REMAINING SOLIDS (CELLULOSE AND LIGNIN) FROM THE C5 SUGAR STREAM. THE C5 SUGAR STREAM IS COLLECTED IN ONE VESSEL AND THE SOLIDS ARE SENT TO CELLULOSE

05 SUPERCRITICAL HYDROLYSIS SLURRY

THE REMAINING SOLIDS FROM HEMI-HYDROLYSIS ARE MIXED WITH WATER TO FORM A SLURRY AND PUMPED INTO THE SUPERCRITICAL HYDROLYSIS REACTOR.

06 SUPERCRITICAL HYDROLYSIS

IN SUPERCRITICAL HYDROLYSIS, THE MORE SEVERE CONDITIONS SOLUBILIZE THE CELLULOSE INTO A C6 SUGAR STREAM IN A SMALL NUMBER OF SECONDS. THE LIGNIN REMAINS AS A SOLID PARTICLE.

07 POST-HYDROLYSIS

A SIMPLE SOLID LIQUID SEPARATION REMOVES THE REMAINING LIGNIN SOLID FROM THE C6 SUGAR STREAM. THE C6 SUGAR STREAM IS COLLECTED IN ONE VESSEL AND THE LIGNIN IS COLLECTED IN ANOTHER.

Fig. 14 Renmatix Plantrose process flow scheme (Source: Renmatix, Inc.)

The process and equipment difficulties due to the use of biomass in gasification include the special metallurgy and refractory requirements in the gasification step necessitated by the natural-occurring inorganic contaminants. Biomass gasification typically has a high yield of methane which is also an inert in the gasification-FT process (Ibid. 72). To make use of the methane, a steam reforming step is often employed to convert the methane to more syngas; however, this adds even more capital cost. Given all of this, however, the most common major issue in any project is one of achieving economic scale (Ibid. 73). Gasification-FT processing has a large combined cost, so making the process economically feasible requires large scale with capital expenditures in the neighborhood of 1–2 billion US dollars. A plant this size might only produce 10–20,000 bpd of fuels. Reducing the cost of the gasification-FT system, especially to enable smaller-scale production, has been the focus of some development with companies such as Rentech and Velocys (Paisley; McDaniel 2013).

Major commercial activity in biomass gasification to transport fuels has progressed mainly in Europe. Choren developed a reactor system called Carbo-V which is now being included in the design of the Forest BtL project in Finland to produce renewable diesel via FT by 2016 (Landalv 2014a). Chemrec completed operation of a demonstration plant that made up to 4 tons/day of dimethyl ether (a fuel that can be used in modified diesel systems) via gasification in 2011. Commercialization for a few larger, commercially viable projects has been on hold due to the combination of two reasons: large capital investment and an uncertainty of the commitment of governments to firm legislation mandating or incentivizing the use of biofuels (Landalv 2014b).

Hydroprocessing Conversion

Fatty Acid, Triglyceride, and Tall Oil Conversion to Hydrocarbon Biofuels

Except for coprocessing bio-liquids in existing refinery units, the technologies surveyed thus far are not easily amenable to incorporation into a petroleum refinery. This is primarily due to the fact that they deal with large volumes of solid biomass or produce biofuels that must be blended on the downstream side of fuel distribution pipelines near their point of use. Fuel products from petroleum refineries must be pipeline fungible with all the products of the pipeline and be compatible with the pipeline materials of construction. Typically, this is a challenge to oxygen-containing biofuels as mentioned in the sections on ethanol and FAME. Hydroprocessing, on the other hand, in which feed is reacted with hydrogen over a catalyst at elevated temperature and pressure to replace contaminants with hydrogen, has a long and successful track record among nearly all the world's petroleum refineries. Recently, hydroprocessing technology has been applied to renewable fatty acid, triglyceride, and tall oils to produce biofuels. Biofuels produced by hydroprocessing technologies differ from other processes that use similar feeds, such as FAME production processes, in that the oxygen of the renewable oil is treated as a major feed contaminant to be removed from, rather than incorporated into, the resulting biofuel. Biofuels produced by hydrotreating renewable oils are fully hydrocarbon, fully fungible, and are considered prime blending components due to their enhanced properties in middle distillate fuel pools. The following section details fatty acid and triglyceride hydrotreating conversion to biofuels.

Hydroprocessing of Fatty Acids and Triglycerides

Introduction

Although biofuels can be made from a wide variety of feed sources, from wood chips to cooking grease to corn, the rest of this chapter focuses on biofuels made from primarily triglyceride (or triacylglycerols) and free fatty acid (FFA) feed sources, with only brief mention of tall oils.

To understand why fatty acid-based feeds are useful for production of drop-in biofuels, it is important to know the general composition of the petroleum-based fuels that biofuels are intended to supplement or replace. Fatty acids, triglycerides, and tall oils are most commonly used to produce diesel and jet fuel (middle distillates) because their fatty acid carbon chains roughly match the carbon number profiles of typical petroleum diesel and jet fuels. If fatty acid carbon chains could be isolated and saturated with hydrogen and converted into paraffins, they would substitute the petroleum-based fuel quite well because the paraffins derived from fatty acids are virtually chemically indistinguishable from major components of petroleum diesel and jet fuels.

Several process technologies based on the concept of triglyceride, free fatty acid, or tall oil hydrotreatment have been developed to convert plant- and animal-based oils into biofuels. The following discussion reviews the major process steps required to complete this conversion, including the production of primarily triglyceride oils via typical vegetable oil refining, deoxygenation to produce fully hydrocarbon *n*-paraffins, and isomerization and cracking of *n*-paraffin to make biofuels. Several commercial installations have started up over the past few years that produce renewable diesel from triglyceride, free fatty acids, or tall oil feed sources, as shown in Table 1 (Cleaner solutions 2014; Production capacity 2014; Lane 2012, 2013; Schill 2009; Dynamic Fuels n.d.; Egeberg et al. 2014; Diamond Green Diesel n.d.; Italy's largest refiner to use 2012).

Triglycerides and Fatty Acids

Triglycerides are molecules composed of three fatty acids bound to a glycerol backbone by an ester linkage. Triglycerides are the fundamental unit of fats in living organisms and are used to store energy. Unbound fatty acids are called free fatty acids (FFA), comprised of a nonpolar hydrocarbon chain with a polar carboxylic acid functional group. Tall oil is primarily composed of free fatty acids and

Table 1 Commercial triglyceride, FFA, and tall oil hydroprocessing installations

Company name	Capacity (BPD)	Technology	Location	Primary product	Start-up date
Neste	3,900	NEXBTL™	Porvoo, Finland (1)	Diesel	2007
	3,900	NEXBTL™	Porvoo, Finland (2)	Diesel	2009
	16,600	NEXBTL™	Singapore	Diesel	2010
	16,600	NEXBTL™	Rotterdam, the Netherlands	Diesel	2011
Dynamic Fuels	5,000[a]	Bio-Synfining™	Geismar, LA, USA	Diesel	2010
Preem	10,000 (30 % RTD[b] co-feed)	HydroFlex™	Gothenburg, Sweden	Diesel	2010
Diamond Green Diesel	10,000	Ecofining™[c]	Norco, LA, USA	Diesel	2013
ENI	7,200[a]	Ecofining™[c]	Venice, Italy	Diesel	2014

[a] Denotes production capacity rather than feed capacity

[b] Raw tall diesel is a derivative of tall oil, in which the fatty acids of tall oil are esterified to make fatty acid methyl esters. The rosin acids of tall oil are largely inert to esterification

[c] "Ecofining™" refers to the UOP/ENI Ecofining process

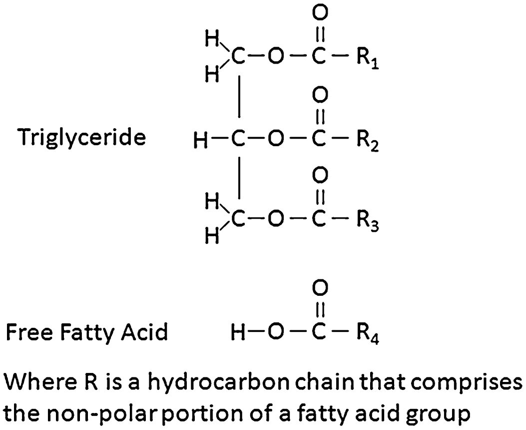


Fig. 15 General structure of triglyceride and free fatty acid molecules

rosin acids and is a commercial by-product of wood pulping. General structures for triglycerides and free fatty acids are shown in Fig. 15. The fatty acid carbon chain length and the degree of hydrogen saturation can vary significantly, usually depending on the organism. For example, coconut triglycerides are rich in lauric (12:0) and myristic (14:0) fatty acids, whereas soybean triglycerides are rich in oleic (18:1), linoleic (18:2), and linolenic (18:3) fatty acids. As is apparent in these two examples, fatty acids are nearly exclusively found in nature with even-numbered carbon chains of approximately 8–22 carbon atoms. The variety of

Table 2 Common fatty acids found in plants and animals

The common fatty acids of animal and plant origin		
Systematic name	Trivial name	Shorthand
Saturated fatty acids		
Ethanoic	Acetic	2:0
Butanoic	Butyric	4:0
Hexanoic	Caproic	6:0
Octanoic	Caprylic	8:0
Decanoic	Capric	10:0
Dodecanoic	Lauric	12:0
Tetradecanoic	Myristic	14:0
Hexadecanoic	Palmitic	16:0
Octadecanoic	Stearic	18:0
Eicosanoic	Arachidic	20:0
Docosanoic	Behenic	22:0
Monoenoic fatty acids		
cis-9-hexadecenoic	Palmitoleic	16:1(n-7)
cis-6-octadecenoic	Petroselinic	18:1(n-12)
cis-9-octadecenoic	Oleic	18:1(n-9)
cis-11-octadecenoic	*cis*-vaccenic	18:1(n-7)
cis-13-docosenoic	Erucic	22:1(n-9)
cis-15-tetracosenoic	Nervonic	24:1(n-9)
Polyunsaturated fatty acids[a]		
9,12-octadecadienoic	Linoleic	18:2(n-6)
6,9,12-octadecatrienoic	γ-linolenic	18:3(n-6)
9,12,15-octadecatrienoic	α-linolenic	18:3(n-3)
5,8,11,14-eicosatetraenoic	Arachidonic	20:4(n-6)
5,8,11,14,17-eicosapentaenoic	EPA	20:5(n-3)
4,7,10,13,16,19-docosahexaenoic	DHA	22:6(n-3)

[a] All the double bonds are of the cis configuration.

fatty acid combinations that can make up a triglyceride varies widely among all organisms and can even vary, to a lesser extent, within the same organism, depending on the season of the year, region of the world, or strain of organism. In general, most animal-derived triglycerides are more saturated than plant triglycerides. The shorthand to describe fatty acids is carbon number followed by the number of double carbon-carbon bonds, also known as the degree of unsaturation, separated by a colon (carbon number: degree of unsaturation). Table 2 (Christie 2013) shows nomenclature, carbon chain length, and degrees of unsaturation for several common fatty acids. Table 3 (Sanford et al. 2009) shows common triglyceride oil compositions in terms of the concentration of fatty acids.

Triglyceride Oil Production

Production of primarily triglyceride oils has a long history, much of which is closely tied to food, illumination, and medicine. Triglyceride oils from plants

Table 3 Fatty acid composition of common triglyceride oils

Feedstock	C8 : 0	C10 : 0	C12 : 0	C14 : 0	C15 : 0	C16 : 0	C16 : 1	C17 : 0	C17 : 1	C18 : 0	C18 : 1
Algae 1				0.6		6.9	0.2			3.0	75.2
Babassu	0.5	3.8	48.8	17.2		9.7				4.0	14 2
Beef tallow			0.2	2.9	0.6	24.3	2.1	1.2	0.4	22.8	40.2
Borage						9.3				3.8	17.1
Camelina oil						5.0				2.2	17.7
Canola oil						3.8	0.3			1.9	63.9
Castor[a]						0.9				1.1	3.1
Choice white grease				1.3		21.6	2.8	0.2	0.3	9.0	50.4
Coconut	6.3	6.0	49.2	18.5		9.1				2.7	6.5
Coffee						11.0	0.5			3.4	70.0
Com						12.1	0.1		0.1	1.8	27.2
Cuphea viscosissima				4.7		18.2				3.5	46.9
Evening primrose						6.0				1.8	6.6
Fish			0.2	7.7		18.8	9.3	0.3	0.3	3.9	15.0
Hemp						5.2				2.4	13.1
Hepar, high IV			*0.2*	1.0		20.7	-	0.2	0.3	8.9	46.7
Hepar, low IV		0.1	0.1	1.5		28.0	1.9	0.3	0.2	20.2	36.1
Jatropha						12.7	0.7			5.5	39.1
Lesquerella fendleri[a]				0.1		0.9	0.3			1.7	13.0
Linseed						4.4				3.8	20.7
Moringa oleifera[a]						5.5	1.2			5.8	76.3
Mustard						2.6	0.2			1.2	20.6
Neem						14.9	0.1			20.8	43.9
Palm			0.2	0.5		43.4	0.1			4.6	41.9
Perilla seed						5.3	0.1			2.2	16.6
Poultry fat			0 1	1.0		19.6	3.2	0.3	0.2	7.5	36.8
Rice bran				0.3		12.5				2.1	47.5
Soybean						9.4				4.1	22.0
Stillingia			0.4	0 1		7.5				2.3	16.7
Sunflower						4.2				3.3	63.6
Tung						1.8				2.1	5.3
Used cooking oil			0.1	0.1		11.8	0.4	0.1	0.1	4.4	25.3
Yellow grease			0.1	0.5		14.3	1.1	0.3	0.2		35.6

[a] In the GC/FID chromatogram, the hydroxy ester peaks were missing. The quantity of the hydroxy ester peaks was estimated from the hydroxyl value with the assumption that all the hydroxy value was the primary hydroxy acid in the sample

C18 : 1n − 9(OH)	C18 : 2	C18 : 3	C18 : 39c, 11t, 13t	C20 : 0	C20 : 1	C20 : 1n − n(OH)	C20 : 2	C20 : 5	C22 : 0	C22 : 1	C24 : 0	C24 : 1	Unknowns
	12.4	1.2		0.4					0.1				
	18												
	3.3	0.7		*0.2*	0.6								0.5
	38.7	26.1							0.2	2.5		1.5	0.8
	18.0	37.9		1.4	9.8		1.6		0.4	4.5	*0.3*	0.2	1.0
	19.0	9.7		0.6					0.4		0.2	0.2	
90.3	4.0	0.6											
	12.2	1.0		0.2	0.5					0.3			0.2
	1.7												
	12.7	0.8		0.6	0.1				0.2		0.1		0.6
	56.2	1.3		0.4					0.2				0.6
	22.8	2.3		0.6					0.4		0.6		
	76.3	9.0		0.3									
	4.6	0.3		0.2	1.4			25.1	0.7	1.3		0.4	10.5
	57.1	20.0		0.7					0.5		0.3		0.7
	15.6	0.5		0.2	0.8		1.3		0.2	0.4		0.1	0.1
	9.7	0.3		0.2	0.7		0.4			0.3			
	41.6	0.2		0.2									
	5.8	10.6		0.7		66.5					0.1	0.4	
	15.9	54.6		0.2					0.3				
	0.7			3.1	2.0				4.2		0.4		0.8
	20.6	13.3		0.9	10.7		1.0		0.5	25.5	0.2	1.5	1.1
	17.9	0.4		1.6					0.3		0.3		
	8.6	0.3		0.3					0.1				
	13.7	62.1											
	28.4	2.0		0.1			0.1		0.3	0.4			
	35.4	1.1		0.6					0.3		0.2		
	55.3	8.9							0.3				
	31.5	41.5											
	27.6	0.2							0.7		0.4		
	68	0.7	72.2	0.2			0.1				10.4		0.4
	49.5	7.1		0.3					0.4	0.3	0.1		
	35.0	4.0		0.3					0.3	0.2		0.1	

Table 4 Global plant triglyceride commodity oil production

						May
	2009/2010	2010/2011	2011/2012	2012/2013	2013/2014	2014/2015
Production, million metric tons						
Coconut	3.52	3.71	3.41	3.66	3.45	3.43
Cottonseed	4.59	4.96	5.21	5.21	5.07	4.99
Olive	3.08	3.25	3.24	2.38	3.1	3.19
Palm	46.07	48.76	52.01	55.97	58.77	62.35
Palm kernel	5.6	5.73	6.13	6.52	6.83	7.23
Peanut	4.89	5.33	5.31	5.54	5.63	5.84
Rapeseed	22.55	23.47	24.12	24.98	25.9	26.02
Soybean	38.79	41.3	42.6	42.82	44.65	46.34
Sunflower seed	12.28	12.42	14.87	13.45	15.83	15.52
Total	141.38	148.93	156.9	160.52	169.23	174.89

Totals may not add due to rounding. Data as of May 2014

and – for the wealthy – whales have been used as fuels for heating and lighting, though fossil sources nearly entirely displaced this use from the late nineteenth century forward (Yergin 1991). The current global production of major commodity triglyceride oils derived from plants is shown in Table 4 (Foreign Agricultural Service 2014). Relatively recently, triglyceride oils have seen a resurgence in use in production of fuels. Triglyceride oils are typically derived from oilseeds, beans, or fruits of oil-producing crops or rendered fats from animal sources. Refining processes have been developed to extract and clean the oil of undesirable contaminants. This section overviews vegetable oil extraction and refining processes as they are typically configured. For the purpose of preparing triglyceride oils for downstream hydroprocessing to produce fuels, some of these steps may be modified or even removed. Ultimately, the triglyceride oil extraction and refining processes must produce oil that is consistent with the feed specifications for its intended use, whether for food, fuels, cosmetics, or medicines. The standard for vegetable oil processing is refining, bleaching, and deodorizing (RBD). The major processing steps of RBD vegetable oil production are summarized in Fig. 16.

Once oil crops are harvested, they must first be prepared for oil recovery. This preparation typically involves a cleaning step to remove solids, such as seed pods, leaves, soil, metals, and stems. A drying step removes moisture to the appropriate level to minimize tendency of the oil seeds to deteriorate via oxidation or enzymatic decay during transport or storage. After a seed hull cracking and flaking step, the flakes typically are processed through an expander, optionally followed by an extruder. In the expander, the flakes are exposed to steam that ruptures the oil sacks to allow for easier recovery. Extruders increase the density of the expander effluent, which allows for increased solvent extraction capacity. The most common method for recovering crude oil is solvent extraction, though mechanical means of recovery via pressing and polishing are also sometimes employed. In solvent

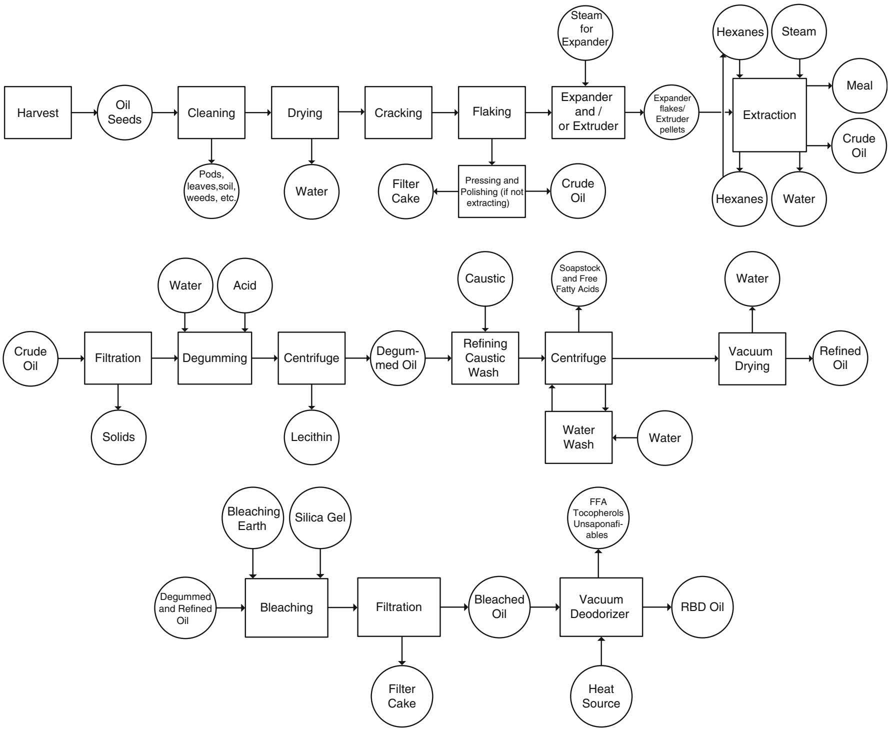


Fig. 16 Typical triglyceride oil production processing steps

extraction, a mixture of hexane isomers is contacted with the effluent flakes or pellets from the expander and/or extruder. The solvent-oil mixture, also known as miscella, is separated in an evaporator that is typically heated with steam. The evaporator distillate product is hexane, which is recycled to the solvent extractor. The evaporator bottoms product is dried in a stripper, where water and more solvent are removed from the crude oil. The stripper bottoms product is the crude oil that is directed onward to degumming. Solids that accumulate in the solvent extraction step are typically treated in the toaster desolventizer, where steam and/or heat is applied to remove residual solvent from the solids and to cook the solids. The desolventized and cooked solids form the meal product, and the hot effluent solvent is most often used as an additional heating medium in the evaporator before being recycled to the solvent extractor. The meal product is typically used as industrial animal feed.

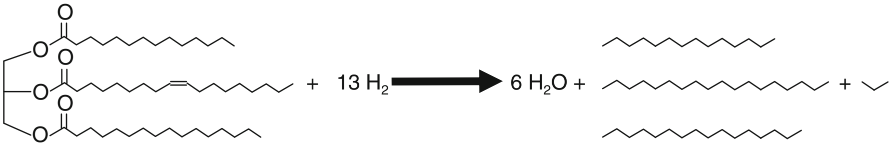
After extraction, the crude oil is processed either through chemical or physical refining, but most often chemical. Chemical refining involves several steps, including degumming, caustic refining, bleaching, and deodorizing. The degumming step contacts the crude oil with acid followed by water and centrifugation to remove phospholipids, also known as phosphatides. The heavy centrifuged product, upon additional processing, forms the lecithin product, which is most often used in production of food products. The light centrifuged product is the degummed oil, which is then processed through the caustic refining step. The caustic refining step contacts the degummed oil with sodium hydroxide to neutralize free fatty acids (FFA). The neutralized oil is typically water washed and then centrifuged, where the light product forms a soap stock-FFA mixture, and the heavy product is the oil. The oil is vacuum dried to remove water, and the resulting product is caustic-refined oil, which is processed further in the bleaching step. The bleaching process contacts the oil with diatomaceous bleaching earth (or clay) to remove color bodies, such as chlorophyll, as well as other impurities, such as metals and peroxides. Further silica gel treatment can remove residual phosphatides and soaps. The bleached oil is filtered and then processed through the deodorization step. The deodorization step heats the bleached oil under vacuum to remove volatile compounds that have an impact on the flavor and odor of the oil, such as FFA, aldehydes, ketones, peroxides, tocopherols, sterols, unsaponifiables, or monoglycerides/diglycerides. The resulting oil is then considered refined, bleached, and deodorized (RBD) oil and is ready for downstream uses, such as food or biofuel production. RBD oil is largely composed of triglycerides, with only trace impurities. The end use of the oil must be considered in the application of typical vegetable oil refining steps. In some cases, especially in the case of food production, additional processing steps beyond RBD may be required, such as interesterification, hydrogenation (less so recently due to concerns over trans fat), or fractionation. There may also be opportunities to adjust the severity or even omit some of the refining steps, depending on the acceptable level of trace impurities and FFA for the intended downstream use of the oil (Anderson 2005; Akoh and Lai 2005).

Deoxygenation and Saturation

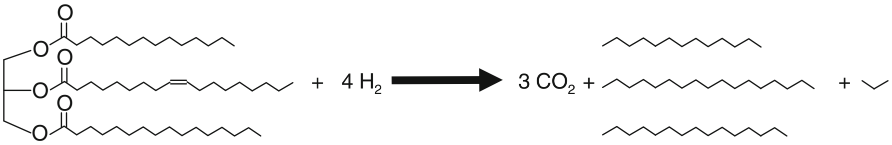
Petroleum-derived middle distillate fuels do not contain oxygen or olefin (alkene) species. However, each triglyceride molecule contains six oxygen atoms and possibly unsaturated carbon-carbon double bonds among its three fatty acids. Therefore, removal of oxygen, or deoxygenation, and saturation of double bonds are important chemical reactions in the conversion of triglycerides to biofuels that resemble their petroleum counterparts.

Deoxygenation and saturation are typically done at elevated temperature and pressure over base metal catalyst in the presence of excess hydrogen (Egeberg et al. 2014). The triglyceride oil feed is mixed with hydrogen, heated to reaction temperature, and contacted with the catalyst in the reactor, and the reactor effluent is cooled and separated. Saturation reactions occur most rapidly, where hydrogen deficiencies along the fatty chains are hydrogenated. Deoxygenation can occur via two major pathways, where the oxygen atoms of the triglyceride either combine with available hydrogen to form water (H_2O), known as hydrodeoxygenation, or retain their linkage to the first carbon of the fatty chain and convert to carbon dioxide (CO_2) or carbon monoxide (CO), known as decarboxylation and decarbonylation, respectively. Hydrodeoxygenation and decarboxylation/decarbonylation occur simultaneously, and both result in the fatty acids breaking their links to the three-carbon backbone of the triglyceride, such that water, carbon oxides, and propane are evolved. With CO, CO_2, H_2O, and H_2 simultaneously present, the water-gas shift reaction will shift CO_2 and H_2 into CO and H_2O, or vice versa, depending on the catalyst selection and reaction conditions. Once deoxygenated and saturated, the fatty acid chains of the original triglyceride have been converted to long linear paraffin chains (normal alkanes) that are fully hydrocarbon. The saturation and deoxygenation reactions both consume hydrogen and evolve significant heat. Commercial-scale production facilities must be designed to manage reactor exotherm to keep operating temperatures within equipment constraints and minimize thermal fouling that could result in buildup of deposits that lead to reactor plugging. Reactions 1 and 2 show the reaction scheme for hydrodeoxygenation and decarboxylation on a model triglyceride molecule composed of myristic (14:0), palmitic (16:0), and oleic (18:1) acids. Reaction 3 shows the water-gas shift reaction.

Reaction 1



Reaction 2



Reaction 3

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

The reactor effluent mixture is directed to downstream cooling equipment, which condenses water and heavier hydrocarbons, and then onward to separation equipment, where the gaseous effluents (CO_2, CO, excess H_2, and propane) are disengaged from the liquid products. The gaseous products are treated to recover propane, remove carbon oxides, and purify hydrogen. The hydrogen is recycled to the reactor for further deoxygenation and saturation. The CO_2 is usually removed by amine scrubbing. Propane is sold as a light fuel or burned in heaters to provide heat input to the process. The bulk of the water product is separated from the paraffin product by density difference. Table 5 shows the theoretical range of products and by-products that would be expected at various levels of hydrodeoxygenation and decarboxylation of camelina oil. While hydrodeoxygenation prevails

Table 5 Theoretical deoxygenation product profile of camelina oil at various levels of hydrodeoxygenation (HDO) and decarboxylation/decarbonylation (DeCOx)

Fraction HDO	Mole frac.	0.1	0.5	0.9
Fraction $DeCO_x$	Mole frac.	0.9	0.5	0.1
Consumed H_2	Mass%	2.2	3.0	3.8
H_2O	Mass%	1.2	6.0	10.9
$CO + CO_2$	Mass%	13.3	7.4	1.5
Propane backbone	Mass%	4.9	4.9	4.9
Naphtha + jet + diesel *n*-paraffins	Mass%	82.7	84.6	86.5

relative to decarboxylation/decarbonylation, the yield of paraffinic product increases. This is because hydrodeoxygenation retains the entire fatty acid carbon chain intact and converts it to an even-number *n*-paraffin, whereas decarboxylation/decarbonylation shortens the fatty acid chain by one carbon in making CO_2 or CO and converts it to an odd-number *n*-paraffin. The yield advantage of hydrodeoxygenation is counteracted by the greater consumption of hydrogen relative to decarboxylation/decarbonylation. The deoxygenation/saturation operation must be managed to complete the deoxygenation, saturate all carbon-carbon double bonds, and reduce trace contaminants that could poison the isomerization section catalyst or lead to off-specification products.

As deoxygenation is the first catalytic process step in the conversion of renewable oils to biofuels, if feedstock quality is not properly managed, it can cause operational, stability, and product specification problems. Mitigation measures must be taken via feedstock quality management or engineering controls to ensure that the integrity of deoxygenation section and its catalysts is maintained. In particular, metals and chlorides are known to be present in some renewable oils. Other contaminants may include free fatty acids (FFA), sterols, and unsaponifiables.

Nickel (Ni) and vanadium (V) are common metal contaminants found in petroleum oils and are known to be poisons to hydrotreating catalysts. In contrast, renewable triglyceride oils more often contain trace levels of different metals: iron (Fe), calcium (Ca), magnesium (Mg), potassium (K), and sodium (Na). Additionally, phosphorous (P), typically from residual phosphatides, is a common elemental contaminant. These “bio-metals” can be deoxygenation catalyst poisons. Methods to deal with such contaminants may include more rigorous triglyceride oil refining, especially in the bleaching step, or use of demetalization catalysts similar to those used in petroleum hydrotreating to remove metals upstream of the deoxygenation/saturation catalyst. If feed metals and phosphorous are allowed to break through the entire process, they can cause the final products to be off-specification. This can particularly be a problem for jet fuels derived from triglyceride oils. For example, the ASTM D7566 specification (ASTM D7566-12a) for renewable jet fuels has a tight limit of 0.1 mass-ppm on all individual metals and phosphorous.

Acids and chlorides cause corrosion of process equipment and piping metallurgy if not handled properly. Chlorides, especially in the presence of liquid water, are

Table 6 Freezing point of common *n*-paraffins resulting from deoxygenation/saturation of triglycerides and free fatty acids

Species	Carbon no.	Freezing point, deg C
n-nonane	9	−54
n-decane	10	−30
n-undecane	11	−26
n-dodecane	12	−10
n-tridecane	13	−5
n-tetradecane	14	6
n-pentadecane	15	10
n-hexadecane	16	18
n-heptadecane	17	22
n-octadecane	18	28
n-nonadecane	19	32
n-eicosane	20	36

particularly aggressive toward inadequate metallurgies. Proper metallurgy selection and management of the occurrence of liquid water in the deoxygenation/saturation section must be carefully considered to avoid chloride-induced corrosion. Similarly, excessive free fatty acids in triglyceride oils may lead to corrosion of process metallurgy. If the FFA content of the feed is controlled to be within the corrosion resistance of the metallurgy, FFA can be successfully converted to *n*-paraffins by the same deoxygenation and saturation reactions discussed above. Many times, reduction of chlorides and FFAs can be accomplished in triglyceride oil refining steps, such that expensive metallurgies in the deoxygenation and isomerization sections of the plant can be minimized.

Upon completing deoxygenation/saturation, the normal paraffin product is already chemically similar to middle distillate fuels (jet and/or diesel). Both petroleum jet and diesel fuels typically contain significant amounts of normal paraffins, among several other species. Normal paraffins alone perform poorly when cooled to ambient temperatures because they readily crystallize into wax. Table 6 (Reference Data for Hydrocarbons and Petro-Sulfur Compounds 1974) shows the freezing points of several pure normal paraffins.

For example, *n*-hexadecane, with freezing point of about 18 °C (64 °F), is a very common deoxygenation product from several plant and animal oils. Ambient temperatures nearby or colder than *n*-hexadecane's freezing point are common throughout most regions of the world during at least part of the year. The use of normal paraffins as fuel would be impractical due to the fuel freezing in tanks and filters. Therefore, triglyceride-derived normal paraffins require further processing so that they can be used at typical ambient temperatures. The well-established refinery process known as dewaxing via isomerization is used to improve the cold temperature performance of the fuel.

Isomerization and Cracking

The *n*-paraffins that result from deoxygenation/saturation of animal and plant triglyceride oils are most often of carbon number 15 (nC_{15}, *n*-pentadecane) through

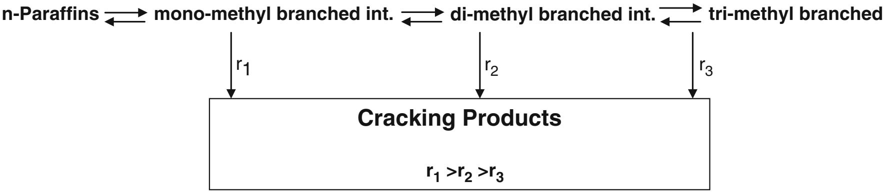


Fig. 17 Isomerization and cracking reaction pathway via branched intermediates (int.) on bifunctional catalyst

18 (nC_{18}, *n*-octadecane). In terms of boiling points, the *n*-paraffins bracketed by nC_{15} and nC_{18}, with normal boiling points of 270 °C and 316 °C, respectively, fall firmly in the typical diesel boiling range (140–370 °C) and nearby the typical jet boiling range (140–300 °C). However, as discussed above, waxing of *n*-paraffins at normal ambient temperatures precludes them from serving as drop-in diesel or jet fuels in most situations. Therefore, some amount of dewaxing via isomerization and cracking is required to convert the *n*-paraffins into usable diesel and/or jet fuels composed of normal and isoparaffins.

Isomerization and cracking reactions can be carried out over various types of catalysts, such as bifunctional noble metal-acid catalysts and base metal-acid sulfided catalysts. Isomerization and cracking are done at elevated temperature and pressure in the presence of hydrogen. As the *n*-paraffin rearranges to form branched isomers (isoparaffins), the more-branched isomers have increased susceptibility to cracking. Therefore, as the reaction conditions are adjusted to increase isomerization, inevitably the amount of cracking also increases. The process conditions must be managed to balance the isomerization and cracking reactions to suit the biofuel production goals. Figure 17 shows the general reaction pathway for isomerization and associated cracking on a bifunctional catalyst (Egeberg et al. 2014; Weitkamp and Ernst 1990; Girigis and Tsao 1996; Beecher and Voorhies 1969; Calemma et al. 2000).

In the production of diesel, it is generally the best practice to operate the isomerization-cracking section such that just enough isomerization occurs to meet the target cold flow properties, such as cloud point, without allowing any more cracking than necessary. Cracking converts paraffins that are already appropriate carbon number for diesel (e.g., nC_{15}–nC_{18}) into paraffins that are only suitable for lighter products, such as jet, naphtha, or lighter by-products. On the other hand, if the goal is to produce jet fuel, then adjusting the process conditions toward increased severity to allow more cracking is desirable. However, as severity is increased, there is a point where cracking reactions that form naphtha and lighter by-products begin to dominate and the benefit of increasing reaction severity is diminished due to jet and diesel yield losses. Paraffinic naphtha derived from hydrocracking of long-chain paraffins makes a poor gasoline pool blending component because it is low in octane number. The paraffinic naphtha is better suited for thermal cracking to produce olefins, but this generally provides a lower value compared to distillate fuels. Therefore, for the biofuel producer intending to

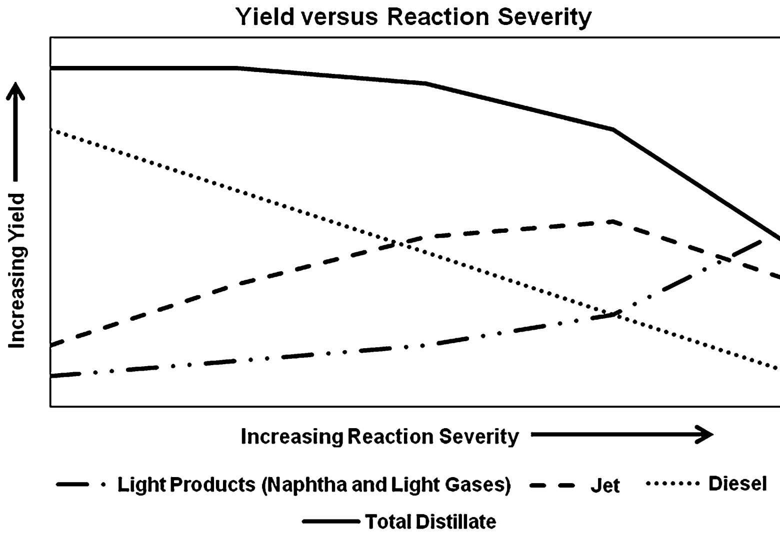


Fig. 18 Theoretical yield profile for isomerization and cracking of *n*-paraffins at various reaction severities

produce diesel or jet fuel, over-cracking is doubly disadvantaged and must be carefully managed. Figure 18 illustrates the effect on yield of major products as reaction severity is adjusted.

The combination of isomerization and cracking of triglyceride-derived normal paraffins can have a dramatic effect on the cold temperature performance of the biofuel products. As a paraffin molecule of a given carbon number is rearranged to have branches, the freezing point generally decreases relative to the normal paraffin of the same carbon number. This suppression of freezing point generally occurs to a greater extent as the degree of branching of a molecule increases. Table 7 shows the freezing points of several pure paraffin isomers of nonane (C_9H_{20}). Conversion of long-chain paraffins into cracked products also helps improve the cold temperature performance of a fuel because lower carbon number paraffins have lower freezing points than longer paraffins with similar degrees of branching. Table 8 shows the freezing points of several isoparaffins that could result from long-chain paraffins isomerizing and then cracking (Reference Data for Hydrocarbons and Petro-Sulfur Compounds 1974).

Fuel Nomenclature

After tuning the isomerization and cracking section to meet the biofuel production goal, usually jet, diesel, or both, the resulting biofuels are separated by fractionation. Biofuels derived from hydrotreated and hydroisomerized/cracked triglycerides are commonly called hydrotreated vegetable oil (HVO) or hydroprocessed

Table 7 Freezing points of isomers of nonane

Species	N/I	Freezing point, deg C
n-nonane	Normal	−53
2-methyloctane	Iso	−81
2,2-dimethylheptane	Iso	−113
2,2,4-trimethylhexane	Iso	−120
2,2,3,4-tetramethylpentane	Iso	−121

Table 8 Freezing points of isoparaffin cracking products

Species	Carbon no.	Freezing point, deg C
Isobutane	4	−159
Isopentane	5	−160
2-methylpentane	6	−154
2-methylhexane	7	−118
2-methylheptane	8	−109
2-methyloctane	9	−81
2-methylnonane	10	−74

esters of fatty acids (HEFA). The jet fuel fraction may sometimes be called renewable jet (RJ), green jet, hydroprocessed renewable jet (HRJ), or HEFA synthetic paraffinic kerosene (HEFA-SPK). Another type of jet fuel, Fischer-Tropsch SPK (FT-SPK), is produced by an entirely distinct technology and feed source, so it is important when using the SPK nomenclature to appropriately specify HEFA or FT. Similarly, the diesel fraction is commonly called renewable diesel, green diesel, hydroprocessed renewable diesel, hydroprocessed vegetable oil (HVO), or HEFA diesel. It is important to emphasize the difference between HEFA diesel and biodiesel, as they are inherently distinct fuels, both in terms of chemical makeup and physical properties. “Biodiesel” is reserved for fatty acid methyl ester (FAME) diesel blending component, and thus, referring to HEFA diesel as “biodiesel” is incorrect. The naphtha fraction of the product is casually called green naphtha. Some weaknesses in nomenclature as described above are clear. For example, the term “renewable diesel” on its own is inherently unspecific, even though HEFA diesel is the understood meaning, because biodiesel and HEFA diesel are both renewable in the sense that they are both derived from triglyceride feeds. Indeed, the nomenclature of biofuels evolves quickly as new processing pathways emerge, so special attention is warranted to ensure the description of the fuel is unambiguous.

HEFA Biofuel Properties

As previously noted, biofuels produced by hydroprocessing are entirely hydrocarbon, making them fully fungible with their petroleum counterpart fuels in storage and distribution infrastructure. There is typically no limit to how much HEFA diesel can be blended with petroleum diesel, unlike FAME biodiesels, which are typically limited to maximum 5 vol% blends. HEFA diesel fuel typically has very high cetane number, usually between 60 and 80, compared with petroleum diesel cetane number between about 40 and 60. The cetane number is a measure of the fuel's tendency to ignite in a compression ignition engine. HEFA diesel's high cetane number makes it an excellent diesel pool blending component. HEFA jet fuel blends are currently limited to 50 vol% in the ASTM D7566 specification (ASTM D7566-12a). This limitation is mainly due to HEFA jet fuel's paraffinic nature, which causes it to have lower density than petroleum jet fuel, and, by nature, very low content of aromatic compounds. Aromatic compounds are needed in jet fuel to maintain elastomer seals in aircraft fuel systems. HEFA jet fuel is blended with petroleum jet fuel, which typically has naturally occurring aromatic compounds and higher density, such that the final blend is within the density and aromatics content windows in jet fuel specifications. Aside from these manageable differences, HEFA biofuels are nearly indistinguishable from their petroleum fuel counterparts in terms of their physical properties and how they perform in service.

References

2G Hugoton Project General Information, in *Abengoa Energy* (Abengoa Energy S.A. n.d.), Web 5 Jan 2014. http://www.abengoabioenergy.com/web/en/2g_hugoton_project/

About, in *Dynamic Fuels* (Dynamic Fuels, n.d.), Web 15 May 2014. http://www.dynamicfuelsllc.com/about.aspx

C.C. Akoh, O.-M. Lai, Healthful lipids, in *Production, Processing, and Refining of Oils*, ed. by E. Hernandez (AOCS Press, Urbana, IL, 2005), pp. 48–64 (2005)

D. Anderson. A primer on oil processing technology, in *Bailey's Primer on Pretreatment – Bailey's Industrial Oil and Fat Products*, 6th edn, vol. 6 Set (Wiley, Hoboken, NJ, 2005)

A.R. Ardiyanti, S.A. Khromova, R.H. Venderbosch, V.A. Yakovlev, I.V. Melian-Cabrera, H.J. Heeres, Catalytic hydrotreatment of fast pyrolysis oil using bimetallic Ni-Cu catalysts on various supports. Appl. Catal. Gen. **449**, 121–130 (2012)

ASTM D6866-10, *Standard Test Methods for Determining the Biobased Content of Solid, Liquid, and Gaseous Samples Using Radiocarbon Analysis1* (ASTM International, West Conshohocken, PA, 2010)

ASTM D7566-12a, Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons (ASTM International, West Conshohocken, PA, 2012). Table A2.1

R. Bartek, M. Brady, D. Stamires, U.S. patent 8236173

R. Bartek,, M. Brady, D. Stamires, S. Yanik, P. O'Connor, J.C. Rasser, U.S. patent 8288600

J. Beavers, N. Sridhar, C. Zamarin, Effects of steel microstructure and ethanol-gasoline blend ratio on SCC of ethanol pipelines, in *NACE – International Corrosion Conference Series*, 2009, Corrosion 2009; 22 Mar 2009–26 Mar 2009; National Association of Corrosion Engineers International, Houston, TX, Print

R. Beecher, A. Voorhies Jr., Ind. Eng. Chem. Prod. Res. Dev. **8**(4), 366 (1969)

Biorefining – 'sustainable processing of biomass into a spectrum of marketable biobased products and bioenergy', in *IEA Bioenergy* (International Energy Agency, n.d.), Web 9 May 2014

H. Boerrigter, Biomass-to-liquid (BTL) plants – an engineering assessment, in *Energy Research Centre of the Netherlands (ECN),* May 2006. Web 15 May 2014. https://www.ecn.nl/publications/

V. Calemma, S. Pertatello, C. Perego, Hydroisomerization and hydrocracking of long chain *n*-alkanes on Pt/amorphous SiO2-Al2O3 catalyst. App. Catal. Gen. **190**, 207–218 (2000)

Cellulosic ethanol proesa, in *Biochemtex* (Biochemtex SpA, n.d.), Web 5 Jan 2014. http://www.biochemtex.com/proesaeng.html

Cellulosic fuels company KiOR reveals 'substantial doubts' about its viability; funding needed by 1 April, *Green Car Congress*, BioAge Group, LLC, 19 March 2014, Web 26 Apr 2014

M. Cheiky, R. Malyal, U.S. patent 8383049

W. Christie, What is a lipid?, in *The Common Fatty Acids of Animal and Plant Origin*, The AOCS Lipid Library, 25 July 2013. Web 7 May 2014. http://lipidlibrary.aocs.org/Lipids/whatlip/index.htm

R. Christoph, B. Schmidt, U. Steinbrunner, W. Dilla, R. Karinen, *Glycerol. Ullman's Encyclopedia of Industrial Chemistry*, vol 17, (Wiley-VCH, Hoboken, NJ, 2002), p. 79. Web 15 Apr 2006

Cleaner solutions, in *Neste Oil* (Neste Oil, n.d.) Web 15 May 2014. http://www.nesteoil.com/default.asp?path=1,41,11991,22708,22709

R.J. Cranford, A.M. Aravanis, S.G. Roussis, US patent application publication no. US20120190872 A1

CRI Catalyst Company, Transportation fuels from biomass via IH^2 technology. in *IEA Bioenergy Conference*, IEA Task 39 (Vienna, 2012). Web 14 May 2014. http://task39.org/files/2013/05/SessionIX4-McLeod-CRI.pdf

D.C. Dayton, R. Gupta, Biomass gasification tar cracking technology development, in *tcbiomass2009 Conference*, tcbiomass2009 Gasification II presentations, Gas Technology Institute, Web 14 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2009/04_tcb2009_Gasification_II.pdf

F. de Miguel Mercader, Pyrolysis oil upgrading for co-processing in standard refinery units (2010), Doctoral dissertation, University of Twente, Enschede, The Netherlands

F. de Miguel Mercader, P.J.J. Koehorst, H.J. Heeres, S.R.A. Kersten, J.A. Hogendoom, Competition between hydrotreating and polymerization reactions during pyrolysis oil hydrodeoxygenation. AICHE J **57**(11), 3160–3170 (2011)

DuPont Nevada site cellulosic ethanol facility, *DuPont Biofuels Solutions* (Du Pont, n.d.), Web 5 Jan 2014. http://biofuels.dupont.com/cellulosic-ethanol/nevada-site-ce-facility/

R. Egeberg et al., Industrial-scale production of renewable diesel, *PTQ Q3 2011* www.eptq.com (Haldor Topsoe, n.d.), Web 15 May 2014. http://www.topsoe.com/business_areas/refining/~/media/PDF%20files/Refining/paper_industrial_scale_prod_of_renewable_diesel.ashx

R. Egeberg et al., Novel hydrotreating technology for production of green diesel, in *Research Technology Catalysts* (Haldor Topsoe, n.d.), Web 15 May 2014. http://www.topsoe.com/business_areas/refining/~/media/PDF%20files/Refining/novel_hydrotreating_technology_for_production_of_green_diesel.ashx

Empyro energy and materials from pyrolysis (Empyro Project Consortium, n.d.), Web 13 Apr 2014. http://www.empyroproject.eu/

Ensyn history, in *Ensyn* (Ensyn, n.d.), Web 13 Apr 2014. http://www.ensyn.com/about-ensyn/ensyn-history/

Fast pyrolysis, in *Biomass Technology Group* (BTG Biomass Technology Group & Blue Bear, n.d.), Web 13 Apr 2014. http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis

L. Felix, C. Choi, D. Rue, L. Weast, Robust glass-ceramics catalysts for decomposing tars produced in fluid-bed biomass gasification, in*tcbiomass2009 Conference*, tcbiomass2009 Gasification II presentations, Gas Technology Institute, Web 14 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2009/04_tcb2009_Gasification_II.pdf

Foreign Agricultural Service. U S. Department of Agriculture, Table 03: Major Vegetable Oils: World Supply and Distribution (Commodity View), 9 May 2014. Web 17 May 2014. http://apps.fas.usda.gov/psdonline/psdReport.aspx?hidReportRetrievalName=Table+03%3a+Major+Vegetable+Oils%3a+World+Supply+and+Distribution+%28Commodity+View%29+++++++++++++++++++++&hidReportRetrievalID=533&hidReportRetrievalTemplateID=5

J. Gething, J. Welstand, J. Horn, Are the reductions in vehicle carbon monoxide exhaust emissions proportional to the fuel oxygen content? SAE technical paper 890216, Warrendale, PA, 1989

Gevo. *Gevo Announces Successful Startup of World's First Commercial Biobased Isobutanol Plant*. *Gevo*. Gevo, 24 May 2012. Web 5 Jan 2014. http://ir.gevo.com/phoenix.zhtml?c=238618&p=irol-newsArticle&ID=1699401&highlight

Gevo. *Gevo Begins Retrofit of World's First Commercial-Scale Biobased Isobutanol Plant*. *Gevo*. Gevo, 31 May 2011. Web. 5 Jan. 2014. http://ir.gevo.com/phoenix.zhtml?c=238618&p=irol-newsArticle&ID=1568917&highlight

M.J. Girigis, Y.P. Tsao, Ind. Eng. Chem. Res. **35**, 386 (1996)

A.W. Glazer, H Nikaido, *Microbial Biotechnology*: *Fundamentals of Applied Microbiology* (San Francisco: W. H. Freeman, New York, NY, 1995), p. 340

I.S. Goldstein, Acid processes for cellulose hydrolysis and their mechanisms, in *The wood and agricultural residues – research on use for feed, fuels, and chemicals*, ed. by E.J. Soltes (Academic, New York, 1983). Pg 315 in

B.L. Goodall, G.A. Aravanis, R.J. Behnke, D.J. Cranford, L. Sajkowski, US patent application publication no. US2012120116138 A1

J.B. Hansen, P.E.H. Nielsen, N.B. Jacobsen, Tar reforming and ammonia decomposition enabling technologies for thermochemical biomass conversion. *tcbiomass2009 Conference*, tcbiomass2009 Gasification I presentations, Gas Technology Institute, Web 14 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2009/04_tcb2009_Gasification_I.pdf

P.F. Hassett, L. Baird, Practical application of bio-based pyrolysis oil, *tcbiomass2013 Presentations and Posters*, Gas Technology Institute, Web 9 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2013/03-Hassett-tcbiomass2013-presentation-Thur.pdf

S.K. Hoekman, C. Robbins, Review of the effects of biodiesel on NOx emissions. Fuel Process. Technol. **96**, 237–249 (2012). Print

Home, *Diamond Green Diesel* (Diamond Green Diesel, n.d.), Web 15 May 2014. http://www.diamondgreendiesel.com/Pages/default.aspx

How ethanol is made, in *Renewable Fuels Association* (Renewable Fuels Association, n.d.) Web 9 May 2014. http://www.ethanolrfa.org/pages/how-ethanol-is-made

Ibid. 54

Ibid. 64

Ibid. 10, p. 8

Ibid. 25, p. 25

Ibid. 50, pg 69-70

Ibid. 72, Pg 655

Ibid. 73, Pg 5

Italy's largest refiner to use Honeywell's UOP/Eni Ecofining™ process technology at Venice refinery, *Honeywell* 2012 Web 15 May 2014. http://honeywell.com/News/Pages/Italy%E2%80%99s-Largest-Refiner-To-Use-Honeywell%E2%80%99s-UOP-Eni-Ecofining-Process-Tech-At-Venice-Refinery.aspx

R.D. Kane, Update on eSCC case studies and guidelines for SCC prevention, *NACE – International Corrosion Conference Series*, vol. 1, 2010, 722–733, 2012, *NACE International – Corrosion Conference and Expo 2012*, 11 Mar 2012–15 Mar 2012, National Association of Corrosion Engineers International. Print, Houston, TX.

KiOR expects to produce 920K gallons of cellulosic biofuels by year end; short-term focus on economics, in *Green Car Congress* (BioAge Group, LLC, 2013), Web 26 Apr 2014. http://www.greencarcongress.com/2013/12/20131224-kior.html

S. Kumar, N. Singh, R. Prasad, Renew. Sustain. Energy Rev. **14**, 1830–1844 (2010)

I. Landalv, Status report on demonstration plants for advances biofuels production – thermochemical pathways, in *European Biofuels Technology Platform, 5th Stakeholder Plenary Meeting*, European Biofuels Technology Platform, Brussels, Belgium, 6–7 Feb 2013. Web. 15 May 2014. http://biofuelstp.eu/spm5/pres/landalv.pdf

I. Landalv. Two years experience of the BioDME project – a complete wood to wheel concept, in *tcbiomass2013 Presentations and Posters*, Gas Technology Institute, Web 9 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2013/03-Landalv-tcbiomass2013-presentation-Wed.pdf

J. Lane, Neste oil: biofuels digest's 5-minute guide, in *Biofuels Digest*, 6 Nov 2012 Web 15 May 2014. http://www.biofuelsdigest.com/bdigest/2012/11/06/neste-oil-biofuels-digests-5-minute-guide/

J. Lane, Albemarle: biofuels digest's 5-minute guide, in *Biofuels Digest*, 29 Jan 2013 Web 15 May 2014. http://www.biofuelsdigest.com/bdigest/2013/01/29/albemarle-biofuels-digests-5-minute-guide/

J. McDaniel, Smaller scale FT enables biomass-to-liquids, in *Gasification Technologies Conference 2013*, Gasification Technologies Council, Colorado Springs, CO, 13–16 Oct 2013. Web 15 May 2014. http://www.gasification.org/uploads/downloads/Conferences/2013/8-3-McDaniel-Velocys.pdf

National Renewable Energy Laboratory, in *Biodiesel Production and Technology*, ed. by J. Van Gerpen, B. Shanks, R. Pruszko, D. Clements, G. Knothe (National Technical Information Service, U.S. Department of Commerce, Springfield, 2004), pp. 52–55. Subcontractor Report under Contract NREL/SR-510-36244

OEM statement summary chart, *Biodiesel*, National Biodiesel Board, Web 3 Jan 2014. http://www.biodiesel.org/using-biodiesel/oem-information/oem-statement-summary-chart

D. O'Brien , M. Woolverton, Updated trends in U.S. wet and dry corn milling production, *Agricultural Marketing Resource Center Newsletter,* Agricultural Marketing Resource Center, Feb 2010, Web 27 December 2013. http://www.agmrc.org/renewable_energy/ethanol/updated-trends-in-u-s-wet-and-dry-corn-milling-production/

M.A. Paisley, U.S. patent 6613111

Pacific Northwest National Laboratory, in *Catalytic Hydrothermal Gasification of Lignin-Rich Biorefinery Residues and Algae*, ed. by D.C. Elliott, G.G. Neuenschwander, T.R. Hart, L.J. Rotness Jr., A.H. Zacher, D.M. Santosa, C. Valkenburg, S.B. Jones, S.A. Tjokro Rahardjo (National Technical Information Service, U.S. Department of Commerce, Springfield, 2009). Report PNNL-18944

M. Pagliaro, M. Rossi, *The future of glycerol*, 2nd edn. (Royal Society of Chemistry, Cambridge, 2010). Chapter 10

petroleum.co.uk (petroleum.co.uk, n.d.) Web 22 Dec 2013. http://www.petroleum.co.uk/formation/

Plantrose^{TM} process, in *Renmatix* (Renmatix, Inc., n.d.), Web 15 May 2014. http://renmatix.com/technology/plantrose-process/

Production capacity, in *Neste Oil* (Neste Oil, n.d.) Web 15 May 2014. http://www.nesteoil.com/default.asp?path=1,41,11991,22708,22720

Production facilities, in *KiOR* (KiOR, Inc., n.d.), Web 26 Apr 2014. http://www.kior.com/content/?s=6&s2=56&p=56&t=Production-Facilities

Products & technology, *Cool Planet Energy Systems* (Cool Planet Energy Systems, n.d.), Web 15 May 2014. http://www.coolplanet.com/how-it-works/overview

Proesa-the scientific research, *Beta Renewables* (Beta Renewables S.p.A., n.d.), Web 5 Jan 2014. http://www.betarenewables.com/proesa/scientific-research

Project liberty – a decade of cellulosic research, in *Poet-DSM Advanced Biofuels* (Poet-DSM Advanced, n.d.), Web 5 Jan 2014. http://poetdsm.com/liberty

E.H. Pryde, JAOCS J. Am. Oil Chem. Soc. **60**(8), 1557–1558 (1983)

G. Rajgor, Renewable power generation – 2012 figures, in *Renewable Energy Focus USA* (Reed Elsevier, 18 November 2013), Web 9 May 2014

Reference data for hydrocarbons and petro-sulfur compounds, Petrochemical and Supply Division Chemicals Group, Phillips Petroleum Company, OK, 1974

S.D. Sanford et al., *Feedstock and Biodiesel Characteristics Report*, Renewable Energy Group, Inc., www.regfuel.com (2009)

Sapphire energy and Phillips 66 to advance commercialization of algae crude oil, in *Sapphire Energy* (Sapphire Energy, Inc., 2013). Web 5 Jan 2014. http://www.sapphireenergy.com/press-article/1986963-sapphire-energy-and-phillips-66-to

S. Schill, Hydroprocessing goes small scale, *Biodiesel Magazine*, 19 Aug 2009. Web 15 May 2014. http://www.biodieselmagazine.com/articles/3666/hydroprocessing-goes-small-scale

D.R. Shonnard, L. Williams, T.N. Kalnes, Camelina-derived jet fuel and diesel: sustainable advanced biofuels. Environ. Prog. Sustain. Energy **29**, 382–392 (2010). doi:10.1002/ep.10461

P. Simell, E. Kurkela, I. Haavisto, J. Jarvenpaa, The development of a gas cleanup process: lessons learned, in *tcbiomass2009 Conference*, tcbiomass2009 Gasification II presentations, Gas Technology Institute, Web 14 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2009/04_tcb2009_Gasification_II.pdf

K. Sipila, E. Kuoppala, L. Fagernas, A. Oasmaa, Characterization of biomass-based flash pyrolysis oils. Biomass Bioenergy **14**(2), 103–113 (1998). Print

S. Sokhansanj, A. Kumar, A.F. Turhollow, Development and implementation of integrated biomass supply analysis and logistics model (IBSAL). Biomass Bioenergy **30**, 838–847 (2006). Print

Technology, in *KiOR* (KiOR, Inc., n.d.), Web 26 Apr 2014. http://www.kior.com/content/?s=11&t=Technology

S.S. Toor, L. Rosendahl, A. Rudolf, Hydrothermal liquefaction of biomass: a review of subcritical water technologies. Energy **36**, 2328–2342 (2011). Print

U.S. Department of Energy, *U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry* (Oak Ridge National Laboratory, Oak Ridge, 2011), p. xxiii. R.D. Perlack and B.J. Stokes (Leads), ORNL/TM-2011/224. 227p

U.S. Energy Information Administration (U.S. Department of Energy, n.d.), Web 4 Jan 2014. http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=79&pid=81&aid=1&cid=regions&syid=2007&eyid=2011&unit=TBPD

United States. *Public Law 109-58, 109th Congress* (GPO, Washington, DC, 2005), p. 1069, Web 8 Aug 2005. http://www.gpo.gov/fdsys/pkg/PLAW-109publ58/pdf/PLAW-109publ58.pdf

United States. *Public Law 110-140, 110th Congress* (GPO, Washington, DC, 2007), p. 121. Web. http://www.gpo.gov/fdsys/pkg/PLAW-110publ140/html/PLAW-110publ140.htm

United States. US Energy Information Administration/Monthly Energy Review, December 2013a, p. 95

United States. US Energy Information Administration/Monthly Energy Review, November 2013b, p. 141

E. van Steen, M. Claeys, Fischer-Tropsch, Catalysts for the biomass-to-liquid process. Chem. Eng. Technol. **31**(5), 655–666 (2008)

B.M. Wagenaar, W. Prins, W.P.M. Van Swaaij, Pyrolysis of biomass in the rotating cone reactor: modelling and experimental justification. Chem. Eng. Sci. **49**(24B), 5109–5126 (1994)

G.M. Walker, J. Inst. Brew. **117**(1), 3–22 (2011)

J. Weitkamp, S. Ernst, in *Guidelines for Mastering the Properties of Molecular Sieves*, ed. by D. Barthomeuf, E.G. Derouane, W. Holderich (Plenum, New York, 1990), p. 343

S. Whitehead, Colonial Pipeline Company – moving the energy that moves America, North Carolina General Assembly, in *North Carolina House Select Committee on Energy Independence and Alternative Fuel*, Presentation at the 8 Feb 2012 Meeting, Raleigh, Web. http://www.ncleg.net/DocumentSites/Committees/HSCEIAF/Meetings/2012%20February%208/Presentations%20and%20Handouts/Whitehead%20-%20Colonial%20Pipeline%202-8-12.pdf

J. Wildschut, F.H. Mahfud, R.H. Venderbosch, H.J. Heeres, Hydrotreatment of fast pyrolysis oil using heterogeneous noble-metal catalysts. Ind. Eng. Chem. Res. **48**, 10324–10334 (2009)

U. Wolfesberger, I. Aigner, H. Hofbauer, Tar content and composition in producer gas of fluidized bed gasification of wood – influence of temperature and pressure, in *tcbiomass2009 Conference, tcbiomass2009 Gasification I Presentations* (Gas Technology Institute), Web 14 May 2014. http://www.gastechnology.org/tcbiomass2013/tcb2009/04_tcb2009_Gasification_I.pdf

S. Yanik, P. O'Connor, R. Bartek, U.S. Patent 8288599

D. Yergin, *The Prize* (Free Press, New York, 1991, 1992), p. 22

Part III

Support Systems

Process Controls in Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments, LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_16

Abstract

This chapter focuses on the control systems which support the refining processes. This is not a definitive work on control systems, but paints the applications of control systems in a modern refinery with a broad brush. The material in this chapter starts with a discussion of control system architecture and continues with detailed descriptions of the major types of parameters controlled: flow, temperature, pressure, level, and composition. Additional material is provided on specific, common control situations. There is a brief discussion of control theory and there are procedures provided for sizing control valves. Numerous references are available for further information.

Keywords

Refinery • Process • Control • Distributed control system • Advanced control • SIS • DCS

Introduction

This chapter focuses on the control systems which support the refining processes. This is not a definitive work on control systems, but paints the applications of control systems in a modern refinery with a broad brush. More detailed treatment of process controls can be found in instrumentation and controls references, some of which are noted at the end of each section of this chapter.

The discussion includes:

- Definitions
- Control system types and architectures
- Specific discussion of each type of parameter monitoring and controls:
  - Flow
  - Temperature
  - Pressure
  - Level
  - Composition
- Discussion of special control situations commonly encountered:
  - Surge
  - Reflux
  - Steam generation
  - Column pressure control
  - Safety instrumented or integrated systems

Definitions

We will start with a few basic definitions that will be encountered frequently in control systems discussions.

Advanced process control (*APC*). A control system overlaying the DCS or basic process control system that performs more complex control functions for a process unit. It analyzes and coordinates several loops to obtain an optimum operation with the limitations of the refinery unit. The solution and changes are passed back to the DCS or other control system for implementation.

Basic process control (BPC). This is the workhorse control system that takes input from the process variables, compares the input to the set points, and outputs the appropriate control moves to the control elements in the field.

Cascade control. A control system with two or more controllers. The "master controller(s)" provides a set point to the "slave controller."

Control element. A device that performs a control function, such as a control valve or variable-speed controller.

Control loop. The basic device arrangement from process sensing element in the field to the process controller to the final field control element (like a control valve).

Control system architecture. Refers to essentially a map of how the process control system is assembled. Architecture would include what devices are tied into the process control system or network.

Control valve. A final control element that introduces a variable pressure drop into a flowing line. The pressure drop causes the flow rate in the line to change in a characterized and predictable way.

Control valve response. The minimum time that should be allowed between HLL and LLL to permit the control valve to respond effectively to changes in level. Typical values are:

CV size, inches	Response, sec
1	6
2	15
3	25
4	35
6	40
8	45
10	50

The above times allow for air signal lags and for operating at a proportional band of about 50 %.

Data historian. An electronic data storage system that collects data periodically from the process control systems and laboratory for archiving and analysis.

Dead time (*dead band*). The amount of time before a process starts changing after a disturbance or control action in the system.

Derivative. A control mode where the controller output is determined by the rate of change of the deviation from the set point. Acts like a dampening term. Normally used as a fine-tuning parameter in a proportional control mode.

Distributed control system (*DCS*). This is a computer-based control system used for basic process control. The basic control loops are in the background. The DCS displays the process and control loop information for the operator. It also records the information and communicates with any advanced control systems. The operator and APC change the settings in the DCS, which then sends the moves on to the process loops. DCS is the most common type of control system today in refineries.

dP cell. A diaphragm device for measuring small differences in pressure with the higher pressure on one side of the diaphragm and the lower pressure on the other side. The difference may be directly indicated or may be transmitted.

Enterprise control. An overall control system that factors in economics, market, and other factors to optimize and coordinate several refinery units simultaneously.

Error. This is usually defined in process control as the difference between the set point and the process variable or measurement.

Feedforward control. A control scheme where changes in an upstream variable initiate changes in downstream controls in anticipation of upcoming deviations. For example, if the feed rate to a unit changes, the appropriate controllers can also be changed downstream so they are set correctly for the new feed rate.

Input. The measured parameter or parameters provided to a controller. These may be direct readings, 3–15 psi pneumatic signals, 4–20 ma electrical signals, or digital.

Instrumentation. Typically, this term applies to the physical elements of the control system. It is usually considered separately from the actual controls.

Integral. A control mode where the controller output is determined by the deviation from the set point and how long that deviation has existed. Acts like an amplification term. Normally used as a fine-tuning parameter in a proportional control mode.

Level control range. This is the distance between the high liquid level (HLL) and the low liquid level (LLL) in the vessel. When using a level controller, the signal to the control valve at HLL will be to fully open the valve. At LLL the signal will be to fully close the valve.

Output. The signal coming from a controller to the field control device. These may be 3–15 psi pneumatic signals, 4–20 ma electrical signals, digital, or some other form.

Process control. Management of process operating conditions to meet product objectives safely and efficiently within equipment limitations.

Programmable logic controller (*PLC*). An electronic control system that uses programmed logic to carry out repetitive, sequential process tasks. Outputs from the PLC are used to control field elements. It may interface with other control systems but is intended to perform its function stand-alone.

Proportional. A control mode where the controller output is determined by the deviation from set point times a constant. See proportional band.

Proportional band. This determines the response time of the controller. Normally a proportional band is adjustable between 5 % and 150 %. The wider the proportional band, the less sensitive is the control. If a slower response time is required, a wider proportional band is used.

Reset. The rate at which a control system makes changes to a process. A high reset rate will make more frequent changes to the system. In a PID or PI controller, this may result in windup of controller output which causes it to overshoot the set point. A low reset rate may never reach its target.

Safety integrated system (*SIS*). AKA safety integrity system. This is a system that takes secure process information parallel to other control systems and applies specific limits to the measured variables. If one of the variables goes outside the predefined limits, the system first alarms at low deviation and then takes a predefined set of emergency actions at high or sustained deviation. The system is similar to a PLC but is normally triple redundant to ensure high integrity.

Sensing element. The field device that measures a physical or chemical property to be used in controlling the process. The most common elements measure things like flow, temperature, pressure, and level.

Set point. The desired value of a process variable that is provided to a controller. The controller tries to make the process measurement match the set point.

Supervisory control. Essentially basic process control.

Surge volumes. This is the volume of liquid between the normal liquid level (NLL) and the bottom (usually the tangent line) of a vessel.

Control System Types and Architectures

Evolution of Control System Types

Control systems can be viewed from several perspectives. Controls have evolved from simple control valves that were manually manipulated to sophisticated, enterprise-wide systems found in some companies today. Most refineries have some semblance of each evolution of control systems in operation today.

A control system can be viewed as a hierarchy of control layers, one on top of the other. Each layer has increasing amounts of information available to it and can perform increasingly complex control functions. This hierarchy is illustrated in Fig. 1, with the most basic level system at the bottom and progressing upward in sophistication.

The most basic process control is accomplished by simple hand valves manually controlled by the operator. Until the early twentieth century, this was the primary control method for chemical processes. We still see manual control used in refineries in devices such as "hand valves" in large steam turbines. These manual valves control the number of steam orifices through which steam impacts the turbine blades.

In the next control evolution, the manual valves were automated to control a specific variable directly and continuously. This is a simple loop control and it is common in refineries. An example would be a pressure regulator. A relief valve is

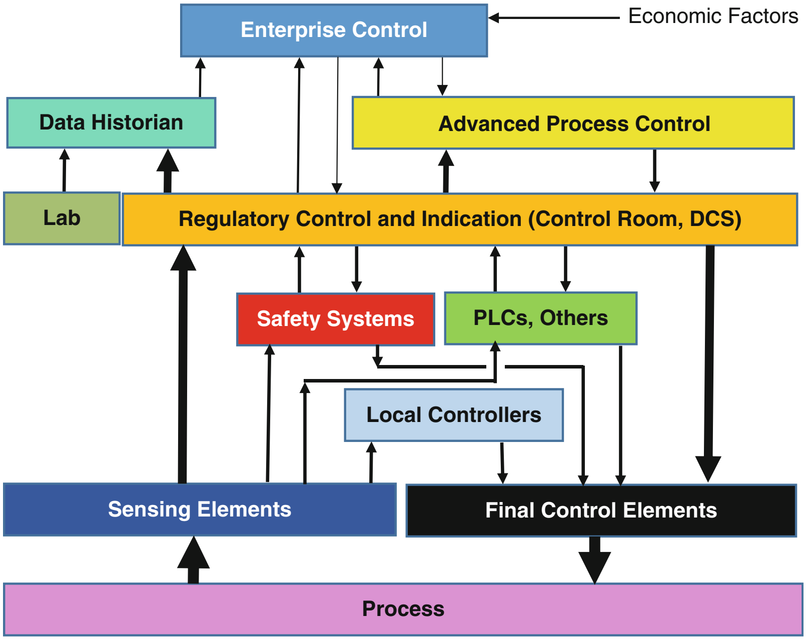


Fig. 1 Control system hierarchy

also a special case of this type of control with an on/off action. In a simple loop, illustrated by Fig. 2, a sensing element directly controls a process variable at a set value. The controls may be mechanical or pneumatic.

Simple loops lead to single loop controls, Fig. 3, where a sensing element sends a signal to a controller (local or in a control room). The controller has a set point target. The controller compares the set point to the measured variable and outputs a signal to a field control device to adjust the device and bring the variable closer to the set point. This type of controller normally has additional logic beyond the simple loop to enable it to keep the process variable under tighter control over a wider range of variation than a simple controller and to enable an operator to change set points easily. Single control loops are among the most common controls you will encounter in a refinery. In single loops here, we will also include indicator

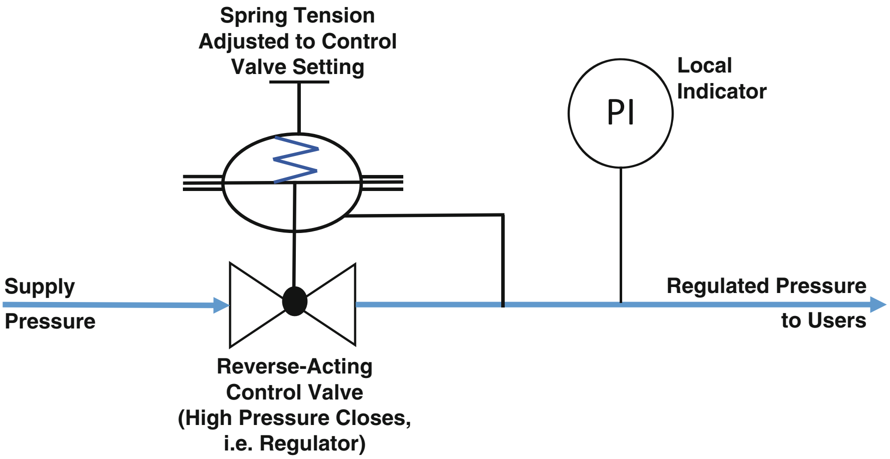


Fig. 2 Simple direct control – pressure regulation

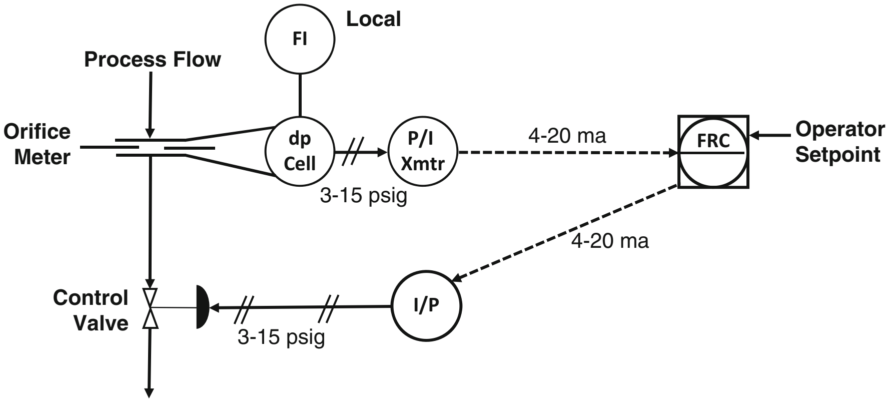


Fig. 3 Single-flow control loop with DCS controller

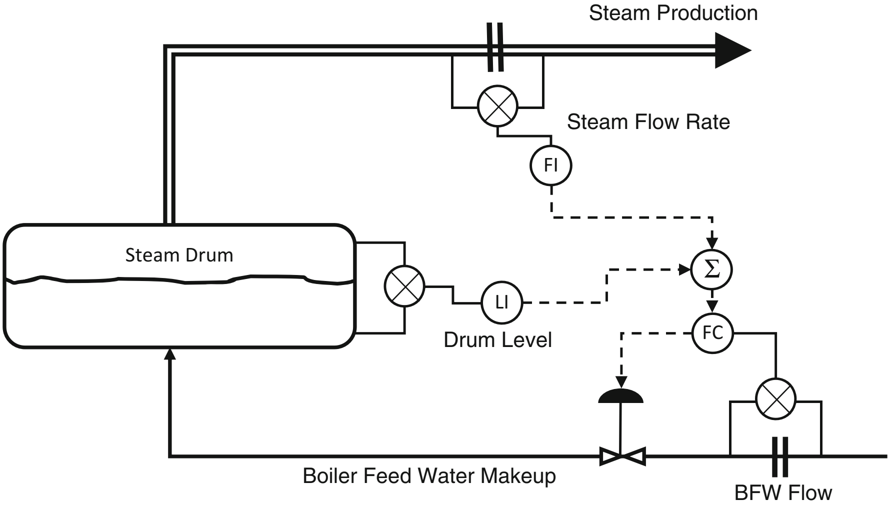


Fig. 4 Basic three element boiler control

loops, which may have no control function but provide data to the operator. More sophisticated controls are built upon a foundation of loop controls.

Multiple control loops can be coordinated using several schemes, such as using one control loop to look at more than one variable and then provide set points to other control loops based on its evaluation. See Fig. 4. Examples of this include cascading one loop to another and 3-element boiler control.

In the example in Fig. 4, the steam flow rate and the steam drum level changes are both added together to determine the total water demand for the steam generation system. The control system then sends a set point to the boiler feed water flow controller indicating how much water the system wants. The controller compares the set point with the current BFW flow rate and adjusts the BFW control valve to provide the required amount of water.

Multiple single loop controls are normally pulled together into a control room. The control room may have individual loop controllers (that may be pneumatic or electronic) or may have a distributed control system (DCS), which is computer based. You will find numerous mixtures and variations between these extremes. The layer of individual control or sensing loops, however, remains as a foundation. More sophisticated controls rely on this foundation layer. The compilation of data from all the loops in one system enables operating data to be retained and archived for analysis, opening up a whole range of operation improvements. The archived data is stored in a “data historian” for access by plant personnel.

Above the loops, DCS and other control systems enable better coordination of the controls and more sophisticated control schemes. Having a DCS can be viewed as the investment required for smarter controls. A common example would be advanced process control (APC), found in most refineries today. An APC application, for instance, can be used to control several loops around a fractionator to target specific product properties off the fractionator and optimize the energy consumed making these products all at the same time. APC can be used in a hydrotreater to control the multiple individual bed temperatures to optimize catalyst and energy use.

The “highest” level of control currently seen we will call “enterprise” control, which factors market considerations into control decisions. A facility using this approach economically optimizes the entire facility within facility and market constraints. The system knows what each product is worth and what each feed or utility costs. Then it finds a solution that makes the most money. This is like a refinery LP but is run more frequently and can more immediately impact the operation.

From a practical standpoint, APC and higher control applications are “slow loops”; that is, they are normally “tweaking” controls or are providing information on a much lower frequency than the normal loop controllers. They may make a move once an hour or once a day. The operator is usually given the option to accept or reject the control solution from the more sophisticated systems. This interface is needed because the advanced applications may not have current information about a refinery’s capability and status at any given time.

Control System Architecture

Control system architecture refers to essentially a map of how the process control system is assembled. Architecture would include what devices are tied into the process control system or network. Figure 1 indicates the general architecture layers possible.

In a simple refinery control architecture, the loops are connected to unit control rooms where they are displayed, monitored, and controlled. In this configuration, the system ends with the “Regulatory Control and Indication” layer. Data from the process is recorded, at some frequency, manually on a data sheet for review and analysis by the refinery staff. Up until the advent of computer or DCS systems, this was the refinery norm.

A modern refinery architecture would still look somewhat like the simple architecture, with a control loop level, but the loops are tied to a DCS with advanced control overlaying the control loops and optimizing the loops. Data from the control system and the laboratory information system are collected in a data historian. The refinery staff, and remote users, can access the data for analysis. There may still be some manual readings taken to cover in instruments that are not part of the system and to help ensure operators monitor specific equipment on some frequency. This is the architecture you would find most commonly today.

The enterprise layer of the system is not yet common, but growth in this area is expected.

Special Control Systems

There are two categories of devices that are common in facilities today and have special purposes within control systems. These are programmable logic controllers (PLCs) and safety integrated systems (SIS). While these may interface with the normal process control systems, they have dedicated functions and operate much like very complex control loops.

Programmable Logic Controllers

Programmable logic controllers are used where a clearly defined complex control must be implemented continuously and repeatedly. A simple example of this type of control would be an instrument air-dryer which senses the moisture in the instrument air and switches to its regeneration cycle based on the moisture content. The controller then sequences the dryer regeneration cycle. A more sophisticated example would be the antisurge controller for a large centrifugal compressor, which analyzes the compressor performance and distance away from surge continuously and limits or shuts down the compressor if it approaches surge.

Another application for PLCs is found in pressure swing adsorption units where a PLC controls and monitors the valve sequences and pressures required to operate the PSA. More sophisticated PSA systems will also contain diagnostics and fallback operations if something goes amiss in the PSA. The system prevents damage to the PSA.

Safety Integrated Systems

Also known as safety integrity systems, these are normally triple-redundant logic solvers (essentially parallel PLCs) that monitor specific variables and take specific override actions if the data indicate that a process unit is headed toward a major process safety incident. The requirement for an SIS originates in Process Hazards Analysis of a process unit. A Layers of Protection Analysis (LOPA) is used to define the requirements and adequacy for an SIS design. The types of events the system is targeted to avoid would include fire, explosion, loss of containment, or any other serious incident.

An example where an SIS is employed is monitoring a hydrocracker for potential loss of positive reactor temperature control (runaway), which can lead to rapid overheating of equipment and subsequent failure accompanied by fire and/or explosion. An SIS in this service can detect the incipient runaway and, after pre-alarms, would automatically shutdown the unit and vent the hydrogen pressure to the flare at a high rate. These actions are designed to eliminate runaway risk. While the unit is shutdown by the actions, this is safer than a loss of containment incident.

SIS systems normally have their own, separate, dedicated, multiple sensing elements in the process unit. They may communicate information to the DCS but operate outside and separately from the DCS. There are specific requirements for design, analysis, installation, redundancy, modification review and approvals, testing frequency, and maintenance of the SISs. How rigorous the requirements are is determined by the severity of the possible consequence.

Flow Measurement and Control

Flow is one of the most common and important measurements in a refinery. From an overall standpoint, crude oil, feedstocks, and refined products are normally bought and sold by volume, hence volumetric flow directly affects a facility's economics. On a day-to-day basis, flows in and around each unit must be measured and managed. Material balancing is important for monitoring and controlling units and flow measurements are required to develop a balance.

This section is intended to be survey of flow measurement and control. More detailed information on this topic is available from many sources, including those listed as references.

We will review the basics of:

- Flow sensing elements and their characteristics
- Typical arrangements
- Control elements

Flow Elements and Their Characteristics

Rate gauging by changes in tank or drum levels is probably the most basic and direct method for determining flow rates. This method relies on changes in level within a known, calibrated vessel. While this is technically a determination of flow rate, it is not continuous and is not our subject in this section. Our focus here is on elements that continuously measure flow rate for use in controlling a process.

Table 1, 2 and 3 provides a listing of many common types of flow metering elements currently commercially available. The table summarizes the measurement principle, application characteristics, advantages, disadvantages, typical locations used, and other factors relevant to refinery applications.

Note that there is no truly successful method for metering two-phase flows, so this should generally be avoided.

Within the chemical industry, the prevalence of meters by type is represented in the following, after G. Livelli of ABB, Inc. Refining would be a subset of the chemical industry in this regard.

Meter type/principle	Percentage of meters
Differential pressure	29
Magnetic	20
Direct mass	18
Positive displacement	9
Turbine	8
Ultrasonic	7
Anemometer	5
Swirl, vortex, other	4

Table 1 Common types of flow elements and their characteristics

Principle	Differential pressure			Magnetic
Meter type	Orifice plate	Venturi tube	Pitot tube	Magnetic
Applications	Clean liq, gas, steam	Clean liq, gas, some dirt, slurry	Clean gas or liquid	Clean or dirty liquids, sulfur
Sizes, inches	>1	>2	>3	>0.1
Accuracy, ±%	0.5–3	0.5–1.5	3	0.5
Turndown	3:1	3:1	3:1	10:1
Min Reynolds # or visc limits	10,000	>100,000	>100,000	None
Max psig	H	L–H	L	M
Δp	H	L	L	L
Meter cost	L	H	L	H
Installation cost	M–H	M	M	H
Maintenance cost	M–H	L	L	M
U/S pipe, dias	10–30	5–10	20–30	5
Output form	Sq.Rt.	Sq.Rt.	Sq.Rt.	Linear
Some advantages	Low cost, excellent history, very common in refinery	Low dP, dirty fluids, short pipe run	Similar to pitot venturi	Good range, zero Δp, insensitive to fluid props
Some disadvantages	High Δp, limited range, wear, density effects	Expensive, limited range, high R_d required	Similar to pitot venturi + very low Δp, taps plug	Expensive, minimum conductivity required

Of the types of flow meters available, the orifice meter is, by far, the most common in refineries. It is simple and reliable for most applications. We will spend most of this section reviewing the equations used for sizing orifice meters and how they are applied.

We will also briefly discuss applications of the other meter types in a refinery. We will specifically discuss custody transfer metering.

Orifice Meters

An orifice meter is simply a designed restriction plate (a plate with a hole through it) in a pipe that produces a pressure drop with a known relationship to the flow rate. The pressure is measured upstream and immediately downstream of the plate where the flow is at the highest velocity (at the vena contracta). Using Bernoulli's principle, the flow rate is a function of the pressure drop.

Table 2 Common types of flow elements and their characteristics

Principle	Oscillatory		Positive displacement		
Meter type	Coriolis	Vortex shedding	Positive displc.	Oval gear	Nutating disc
Applications	Clean or dirty liquids	Clean liq, gas, steam, some dirt	Clean liq, gas, higher viscosity	Clean liq, gas, high viscosity	Clean liq
Sizes, inches	<6	>0.5	>12	1/8–3	5/8–2
Accuracy, ±**%**	0.25	1	0.5–1	0.25	2
Turndown	>25:1	10–20:1	20:1	High	Med
Min Reynolds # or vise limits	None	>10,000	>10 cSt	<50,000 cP	<5,000 cP
Max psig			L	M	L
Δp	M	M	H	H	H
Meter cost	H	M	H	H	M
Installation cost	H	L–M	H	H	M
Maintenance cost	L–M	M	H	H	H
U/S pipe, dias	None	15–25	None	None	None
Output form	Linear	Linear	Linear	Linear	Linear
Some advantages	Direct mass reading, open channel, high accuracy, wide range	Accuracy unaffected by props, high range, high turndown, moderate dP	Custody transfer, high accuracy, wide range, viscous liquids	Similar to PD	Similar to PD
Some disadvantages	Difficult installation, not for gases, expensive	High Reynolds no., visc. <20 cP, not for dirty, corrosive or erosive services	Mechanical, expensive, not good for rates, output affected by viscosity	Similar to PD, small sizes only	Similar to PD, small sizes only

Orifice meters normally used in refineries are the sharp-edged, concentric-type devices. Figure 5 shows the key parts of a typical orifice meter installation using orifice taps. Specific application may use eccentric or segmental-type orifice plates, but these are not common. If another type of plate is used, appropriate changes to the calculations are needed. The taps may also be in other locations around the orifice plate, such as in the pipe upstream and downstream, but these arrangements are not common.

The basic, generalized equation for an orifice meter is:

$$Q = (\pi/48)C\ Y\ {d_o}^2\left[\left(2\rho_f g_c \Delta p\right)/\left(1-\beta^4\right)\right]^{1/2} \tag{1}$$

Table 3 Common types of flow elements and their characteristics

Principle	Turbine	Ultrasonic		Variable area	Thermal
Meter type	Turbine	Doppler	Transit time	Rotameter	Thermal dispersion
Applications	Clean liq, gas, steam	Dirty/ corrosive liq or slurry	Clean/ corrosive liq	Clean liq or gas, some contaminants	Clean/dirty liq or gas, slurry
Sizes, inches	>0.25	>0.5	>0.5	<3	<3
Accuracy, ±%	0.5	2–5	2–5	0.5–5	1–5
Turndown	10–35:1	10:1	10:1	10:1	100:1
Min Reynolds # or visc. limits	2–15 cSt	None	None	<3 cP	None
Max psig	M	M	M	L	M
Δp	M	L	L	M	L
Meter cost	M	M	M	L–M	L–M
Installation cost	M	L	L	L	L
Maintenance cost	M–H	L	L	L	L–M
U/S pipe, dias	None	5–20	5–20	None	10–20
Output form	Linear	Linear	Linear	Linear	Log
Some advantages	Good range, low flow, easy to install	Nonintrusive, low cost, bidirectional	Same as Doppler	Low cost, direct reading	High range, almost any fluid
Some disadvantages	Accuracy affected by wear and fluid props, clean fluids, high cost, gas meters tend high	Needs particles to work, liquids only, low accuracy	Clean liquids only, low accuracy	Expensive larger sizes, fluid props affect accuracy	Sensor fouling affects performance, low accuracy

where:

Q = flow rate for compressible fluids, lb_m/s
C = orifice discharge coefficient (correction factor)
Y = expansion factor (correction factor for compressible fluids)
d_o = orifice diameter in inches
ρ_f = fluid density at upstream flow conditions, lb_m/cft
g_c = gravity constant, 32.174 ft*$\text{lb}_\text{m}/(\text{lb}_\text{f}\ \text{s}^2)$
Δp = pressure drop across the orifice, psi
β = ratio of the diameter of the orifice to the pipeline ID, dimensionless

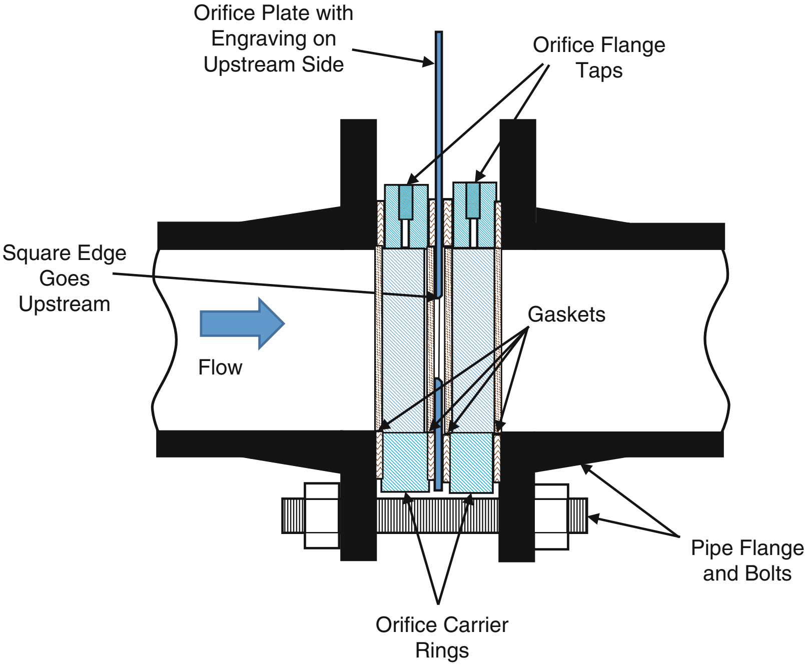


Fig. 5 Orifice meter detail

For incompressible (or nearly incompressible fluids, like liquids), Y = 1. For compressible fluids:

$$Y = 1 - \left(Y_0 d_p\right)/(p_1 k) \tag{2}$$

where:

Y_0 = function depending on tap location. For the normal flange taps
$Y_0 = 0.41 + 0.35\beta^4$
p_1 = absolute pressure of upstream fluid, *psia*
k = ratio of fluid specific heats = C_p/C_v

Now,

$$C = C_\infty + b/{R_d}^{\mathrm{n}} \tag{3}$$

where:

C_∞ = orifice coefficient at infinite Reynolds number

For normal orifice flange taps:

$$\text{Small pipes} \left(\sim 2''\right) : C_{\infty} = 0.5959 + 0.0312\beta^{2.1} - 0.184\beta^{8} + 0.039\beta^{4}/\left(1-\beta^{4}\right) - 0.0337\beta^{3}/d_{p}$$

$$\text{Large pipes} : C_{\infty} = 0.5959 + 0.0312\beta^{2.1} - 0.184\beta^{8} + 0.09\beta^{4}/\left(1-\beta^{4}\right) - 0.0337\beta^{3}/d_{p}$$

$b = 91.71\ \beta^{2.5}$
R_d = Reynolds number of orifice $=12 * d_o * v_o * \rho_f/\mu$
n = 0.75
v_o = fluid velocity through orifice in ft/s
μ = absolute viscosity in lb/(ft*s)

Solving these equations is primarily accomplished using computer programs today, so the task is not as onerous as it might appear.

From a practical operating standpoint, the key observation from the orifice equations is that the mass flow rate through an existing orifice is proportional to the square root of the pressure drop and the fluid density. Flow meters for orifice taps often make the square root conversion for you. The density correction may also be incorporated into the control system but is normally done separately. If density does not change much, the correction is usually ignored except in test runs.

To correct a liquid flow rate from flowing conditions to a standard, base set of conditions:

$$Q_{\text{base}} = Q_{\text{meas}}\left(\rho_{\text{base}}/\rho_{\text{meas}}\right)^{0.5} \tag{4}$$

where:

Q_{base}, Q_{meas} = flow rate, base conditions and measured, respectively
ρ_{base}, ρ_{act} = liquid density at base and actual conditions, respectively

This correction is normally minor, but it may be done for detailed test runs.

To correct a compressible fluid flow rate to a base condition density from actual density, then:

$$Q_{\text{corr}} = Q_{\text{meas}}\left(P_{\text{base}}/P_{\text{act}}\right)^{0.5}\left(M_{\text{base}}/M_{\text{act}}\right)^{0.5}\left(T_{\text{act}}/T_{\text{base}}\right)^{0.5}\left(Z_{\text{act}}/Z_{\text{base}}\right)^{0.5} \tag{5}$$

where:

Q_{corr}, Q_{meas} = flow rate, base conditions and measured, respectively
P_{base}, P_{act} = absolute pressure, base and actual, respectively
M_{base}, M_{act} = molecular weight of fluid, base and actual, respectively

T_{base}, T_{act} = absolute temperature of fluid, base and actual, respectively
z_{corr}, z_{act} = compressibility factor of fluid, base and actual, respectively

Note that by expressing the corrections as ratios, you don't need to deal with conversion of units. You just need to be sure the numerator and denominator of each correction factor are in the same units. Also, note that the pressure and temperature units for the compressible gas corrections are in *absolute* units.

Orifice meters have several cousins:

- Venturi flow meters – These apply the same measurement principles. They have a more smooth flow pattern and recover more head; hence, they have lower pressure drop. Venturis are often used in low-pressure applications where loss of head is expensive.
- Nozzle meters – These are like orifices but use a smooth tube in place of an orifice.
- Wedge or V meters – This type of meter is often used where slurries are processed. The meter consists of a roughly triangular wedge that projects into the flow, with pressure drop measure between the upstream fluid and the narrowest part of the wedge restriction.

Orifice meters, and other meters that depend on pressure drop, enjoy a long history with many applications in refineries. They are handicapped by their limited 3:1 turndown and the pressure drop they impose. They require straight runs of pipe upstream and downstream for good accuracy, which can make the installation physically large, but they can be used for very large flows.

Magnetic Flow Meters

Mag flow meters or magmeters make use of Faraday's law. Faraday discovered that a conductive material moving through a magnetic field will generate a voltage that is directly proportional to the fluid velocity. In a magmeter, a magnetic field is imposed perpendicular to a flowing stream. The voltage generated through the flowing stream is then measured perpendicular to the magnetic field and the stream flow.

The meter calibration is specific to the fluid handled. Density corrections for differences in fluid density are required for the best accuracy. Accuracy can be $\pm 0.2\ \%$ of full scale.

Obviously, this method of measurement requires a conductive fluid to operate. Mag flow meters are "nonintrusive" to the process, i.e., they do not interfere with flow, and they can be built with corrosion-resistant liners to handle corrosive materials. You will find them in refineries when metering molten sulfur, concentrated acids, and other onerous services. They are generally limited to smaller-sized lines by the ability to produce an adequate magnetic field. Installations are fairly small, requiring only short runs of straight pipe.

Oscillatory Meters

There are two common types of oscillatory flow meters in refineries: mass flow and vortex-shedding meters. These meters are expensive but have value in some applications. Mass flow meters require no special pipe runs, but vortex meters require substantial meter runs length. Other types of oscillatory meters include Coanda and momentum exchange meters.

Mass Flow Meters

Mass flow meters are finding increasing use in refinery liquid services. They are generally not suitable for gases. The most common mass flow meter makes use of the Coriolis effect. In this meter, the fluid flows through one or two tubes (usually looped) that are vibrated at their natural resonant frequency by electromagnetic drivers. Fluid flow creates a secondary vibration in the tubes that is a linear function of the fluid flow rate and density. The meter sensors measure the secondary vibration and convert it to flow rate. Accuracy can be ±0.2 % and these meters have an extremely wide operating rate (up to 100:1 turndown). The flow is measured directly as mass.

A volumetric reading from a mass flow meter can be corrected to a base condition using the ratio of base density to measured density. The mass flow reading needs no corrections.

Vortex-Shedding Meters

The vortex-shedding meter depends on the phenomenon that swirls are created downstream of anything inserted into the middle of a flowing stream and the swirl direction oscillates from one side to the other on a frequency that is proportional to the flow rate. This oscillation can be sensed and converted to flow rate. Flow rates from a vortex-shedding meter can be corrected for density to determine actual flow. These meters have ±1 % accuracy and good turndown. They offer little flow resistance.

A high Reynolds number (i.e., turbulent flow) is required for vortex shedding to work best. The fluid needs to be clean and noncorrosive to avoid erosion or corrosion of the “bluff body” that creates the swirls.

Positive Displacement (PD) Meters

PD meters directly measure the volumetric flow of a fluid. Meters in this category include nutating discs, rotary pistons, rotary vanes, reciprocating pistons, lobes, and oval gears. Positive displacement meters can be used for both liquids and vapors. They can handle viscous fluids but may lose accuracy at low viscosities. The standard gas meters on homes are PD meters.

These meters are essentially positive displacement pumps forced to run backward. The rate at which they run is sensed and converted to volumetric flow. Correction of the flow to a base or standard condition requires simple adjustment for density.

These meters tend to be mechanically complex (i.e., reliability issues) and expensive. They are used often for custody transfer because they have high accuracy and wide rangeability. Sizes are limited to about 1,000 gpm or less.

The fluid should be clean to prevent undue wear and tear. They do not like two-phase flows. No pipe meter runs are required for PD meters.

Turbine Meters

Another type of meter commonly applied in refineries, especially for custody transfer, is the turbine meter. Accuracy is good and the meters operate over a wide range of turndown. Cost is moderate. The meters require clean, non-plugging or eroding fluids. Gas turbine meters tend to read high. Corrections for density are required for most accurate work. The meters usually have their own straightening vanes incorporated into them.

Essentially these meters operate by spinning a small turbine or multiblade propeller using the flowing fluid. The turbine speed is linear with the flow rate.

Ultrasonic Meters

Two types of ultrasonic meters are common today: Doppler and transit time (or time of flight). The meters are nonintrusive, relatively cheap, and have no pressure drop. They do require a meter run of straight pipe. Accuracy is 2–5 % at best, so they are used mostly for difficult services or where you need a temporary reading on a line without any other meters. They are often “strap-on”-type meters. They are not for gas streams, but liquids or slurries only.

Doppler Meters

A Doppler meter determines the flow rate by sensing the Doppler frequency shift of an ultrasonic signal imposed on a stream and reflected off particles moving in the stream. This means that the Doppler meter only works on dirty liquids or slurries or liquids with entrained bubbles. The resulting flow signal is linear.

Transit Time or Time of Flight Meters

Converse to a Doppler meter, a transit time meter needs very clean fluid to work properly. In this type of meter, the time for an imposed ultrasonic signal to reach a sensor that is a fixed distance away across the flowing stream is determined. The change in this time is converted to a flow rate. The result is linear with flow rate.

Variable Area Meters

A variable area meter imposes a fixed force set against a flowing stream in an expanding flow tube. The flow pushes against the force and moves it in the tube, increasing the flow area until the flowing force equals the resistance. The most common application of this is the rotameter.

These meters are generally limited in size, with variable accuracy. They can be very small but are limited to about 3″ maximum size. The fluid used must be fairly clean, but some contamination is tolerable. The tubes can be armored to allow higher pressures, but these devices are usually limited to <700 psig.

They are low cost and read flow directly. Fluid properties affect the accuracy. Corrections for fluid density are required for highest accuracy. No meter runs are needed, although a rotameter must normally be installed in a vertical pipe run.

Thermal Meters

There are two common varieties of thermal meters: anemometers and thermal dispersion. These meters are some of the most tolerant of fluid conditions, working with liquids, gases, or slurries. They have a wide turndown range. The primary issue with them would be fouling of the elements. Accuracy is only in the ±1–5 % range, however, and they do need metering runs, which can be expensive in large scale.

Both types of meters determine the heat loss into a flowing stream by various methods. The resulting output is proportional to the log of the mass flow rate. Corrections for density and stream properties would be required.

You might find this type of meter in a flare header, for instance.

Typical Arrangements

Flow Element Installation

The installation of the flow sensing elements in the process depends on the type of element being used.

For the most common elements, a straight section of pipe upstream and downstream of the meter element is required. This is often referred to as the meter run. For large lines, the meter run may require a great deal of space and cost a lot. For instance, a typical orifice meter run in a 24-in. pipe would require 40 f. of undisturbed 24″ pipe upstream and about 8 f. downstream, plus the orifice installation for a total of about 50 f. of straight pipe. Some types of meters do not require meter runs, so have an advantage.

The metering run does not have to be horizontal in most cases. A vertical run will work just as well. In some cases, such as two phase or slurry, a vertical run is preferred.

If there is insufficient room for a good meter run in the piping, straightening vanes can be used to reduce the length of pipe required, but there will be some compromise in accuracy. Poor incoming flow to an orifice meter can result in the meter being off 15–20 %.

Figure 6 illustrates a normal orifice meter installation, including the meter run. We will spend some time reviewing this installation, since it is most common.

Following the inlet meter run, the orifice is installed in specific orifice flanges that have pressure taps incorporated into the flanges. The taps sense pressure upstream of the orifice and immediately downstream of the orifice. These are normally called “flange taps.”

The orifice itself is installed between the orifice flanges, using gaskets upstream and downstream. The orifice will have a tab that protrudes from the flange to indicate the orifice number and size. *The lettering stamped into the tab must point toward the incoming flow for the orifice to correctly measure flow rate*. Errors of 3–10 % are introduced if the orifice is pointed the wrong way.

Downstream of the orifice flanges, there should be about five diameters of straight, undisturbed flow. This is not as important as the upstream meter run, but will introduce inaccuracy if the flow runs immediately into an elbow, for instance.

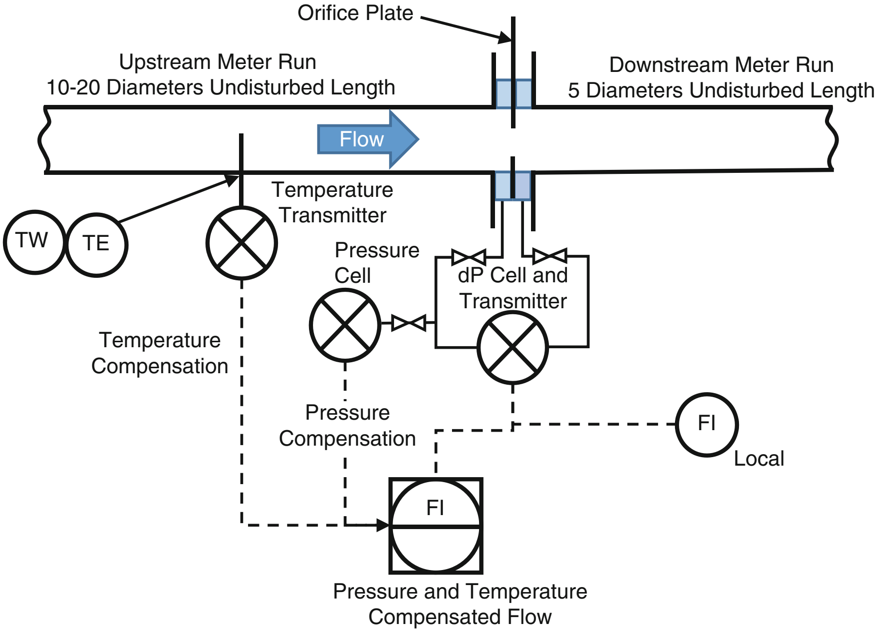


Fig. 6 Orifice meter installation

The taps on the orifice flanges are close-coupled to root valves that comply with the same specification as the piping. These root valves can be used to isolate the flange from the Δp cell that senses the pressure drop for maintenance or if there is a loss of containment from the small piping and tubing connected to the flange. The small piping and tubing are especially susceptible to damage from activity in the area and from vibration.

Piping or tubing from the root valves leads to a differential pressure cell through an inlet instrument manifold. The manifold has its own isolation valves and a bypass valve, as well as calibration connections. It allows the dP cell to be zeroed, spanned, and otherwise maintained. Standard instrument manifolds are available or one can be built from piping, tubing, and instrument valves.

The dP cell is a sensitive instrument that detects the pressure differential between the upstream and downstream orifice taps by the position or strain on a diaphragm with upstream pressure on one side and downstream pressure on the other. The cell may be direct indicating of the pressure drop (or may have a square root scale) or the cell may transmit the dP to the control system. The signal may be pneumatic or electronic and analog or digital.

For flow elements other than orifices, the element installation is somewhat simpler:

- Magnetic and vortex-shedding meters are installed between flanges after appropriate meter runs.

- Coriolis, positive displacement (all kinds), and turbine meters are installed between flanges without any significant meter runs.
- Ultrasonic meters are strapped onto the pipe with an appropriate meter run. They need to be mechanically coupled to the pipe wall to ensure good contact.
- Rotameters are installed into a vertical pipe run.
- Thermal dispersion and pitot tube meters are inserted into the pipe or ducting after an appropriate meter run through a flange using a root valve and packing gland arrangement. They can usually be removed from the line in service and isolated for maintenance.

Most of the non-orifice elements themselves incorporate a sensing system that translates the flow sensor reading into, normally, an electronic signal for transmission to the controller. The signal may be analog or digital and pneumatic or electronic, depending on the control system architecture. For pitot meters, a dP cell is used, similar to an orifice.

While most of the flow sensing elements are connected to the main stream, there are cases where it is impractical to meter the entire stream due to size. In these cases, sidestream metering is an option. For this approach, a smaller branch is created off the main flow line and a known, small pressure drop is incorporated into the main line to cause flow in the branch. The branch flow is metered. The branch flow will be a function of the main line flow rate. In this way, a smaller meter can be used to measure a large stream.

Each refinery and engineering company has its own standards for instrument installation, but most are similar to the above description.

Flow Signal to the Controller

In most cases, the signal from the flow element is transmitted to the controller where the actual conversion to flow rate and any monitoring and control actions are determined. The transmitter may also have its own local flow indication for field operator information.

In some cases, a local controller or indicator is used, but the flow signal is normally sent to the control room for display, recording, and decisions on control action.

Controller Processing

The controller takes the flow signal, compares it to the desired flow rate (set point), and determines the required response, if any. The resulting output from the controller is sent back to the final control element in the field. Controllers are discussed more fully in the section entitled “Controllers”.

Output Signal to the Control Element

The output signal from the flow controller is returned to the appropriate flow control element in the field. The output signal may be electronic or pneumatic.

The most common flow control element in a refinery is the control valve. These will be discussed in detail later.

Another control element that is seeing more application in refineries is the variable-speed controller. More on this element in a while.

The control signal is usually received at the final control element by some sort of signal converter that translates the signal into something the control element can use.

Final Control Elements

There are three final control elements we will discuss here:

- Control valves
- Variable-speed drives
- Variable volume

Control Valves

The most common final control element for flow is the control valve. There are many types of control valves available. The different characteristics of these valves offer the opportunity for optimization. Selection of the valve type appropriate to a service is critical.

By way of definition, a control valve is “a power-operated device forming the final element in a process control system. It consists of a body subassembly containing an internal means for changing the flow rate of the process fluid. The body is linked to one or more actuators which respond to a signal transmitted from a controlling element (controller).”

The major types of control valves and actuators used in refining today are described in Table 4. A detailed discussion of the most common types of control valves and key considerations follows.

Figure 7 shows a conventional control valve which in this case is taken as a double-seated plug-type valve. Like most control valves, it is operated pneumatically by an air stream exerting a pressure on a diaphragm which in turn allows the movement of a spring-loaded valve stem. One or two plugs (the diagram shows two) are attached to the bottom of the valve stem which, when closed, fit into valve seats, thus providing tight shutoff. The progressive opening and closing of the plugs on the valve seats due to the movement of the stem determines the amount of the controlled fluid flowing across the valve. The pressure of the air to the diaphragm controlling the stem movement is varied by a control parameter, such as a temperature measurement, or flow measurement, or the like. In many of the more modern refineries, many control valves are operated electronically.

Figure 8 shows two other types of control valves in common service in the industry. These are the venturi type and the butterfly type. Both these types when pneumatically operated (which they usually are) work in the same way as described above for a plug-type valve. The major difference in these two types is in the valve system itself. In the case of the venturi, the fluid being controlled is subjected to a 90° angle change in direction within the valve body. The inlet and outlet

Table 4 Control valve and actuator options

Control valve categories			
Type of action	Valve type	General description	Typical flow pattern past plug/seat
Linear or rising stem	Single port	Globe-type valve with single plug and seat arrangement. Opens as stem rises	Normally upward. Plug pushes against flow
	Double port	Globe-type valve with two plugs and seats on common stem, one above the other. As stem rises, both seats are opened. Forces balanced by flow action	Both upward and downward past plugs and seats to balance forces
	Balanced plug, cage guided	Plug is contained inside a cage with multiple holes in the cage. As plug rises, more holes are uncovered to increase flow. Balance obtained by arrangement of internals	Flow horizontal through cage walls and then downward. From outside of cage inward
	High capacity, cage guided	Similar to balanced plug, cage-guided principle. Rising stem increases flow	Flow upward toward plug and then horizontally outward through cage
	Reverse acting, cage guided	Similar to balanced plug, cage-guided principle. Rising stem *decreases* flow as holes in cage are covered	Flow horizontal from outside cage through the cage wall and then downward and out through passages in the plug
	Three way	Single-plug proportions flow to two different destinations. May be cage guided. Position of stem changes proportion of flow to different destinations	Normally up flow to one destination and downflow to the other destination
	Angle	Similar to a single-port valve. Rising stem increases flow. For very high-pressure services, this type of valve may have several plugs and seats with part of the dP across each set	Downflow past plug and through each seat
Rotary shaft	Butterfly	Similar to damper. A near-line-sized valve disc is rotated with a center shaft located along the disc diameter. Rotation is 90 ° from full closed to full open	Flow is through the seat and past the disc. Forces on the disc are roughly balanced
	V-notch ball	This is a ball valve with a notch removed from the ball. Greater rotation of the ball exposes more of the wedge-shaped notch, allowing increased flow. Rotation is 90 ° from full closed to full open	Flow passes through the notch in the ball. The seat for the ball surrounds it
	Eccentric plug	Similar to a butterfly valve, but the axis of rotation is offset away from a smaller disc, so that the disc rotates in or out of a seat ring	Flow may go either direction past the eccentric plug or the seat

(*continued*)

Table 4 (continued)

Actuator categories		
Principle	Actuator type	General description
Pneumatic	Direct acting	Control air pressure pushes down on a diaphragm against a spring to move a linear stem down. The stem is connected to the valve. Loss of air supply causes stem to rise
	Reverse acting	Control air pressure pushes up on a diaphragm against a spring to move a linear stem upward. The stem is connected to the valve. Loss of air supply causes stem to drop
	Rotary acting	Linear motion from a diaphragm or piston actuator is converted to rotary motion similar to "locomotion" acting through a cam eccentrically on the rotary stem
	Piston	Air pressure acting on a piston causes linear movement of the piston rod which moves the valve stem. The piston may have a spring return or may be double acting, using air pressure to move in either direction
Electrically operated	Electrohydraulic	An electrically driven hydraulic pump provides oil pressure to actuate a valve. This type of actuator is often used where rapid action is required, like power generation steam turbine controls. Significant amounts of oil can be stored in high-pressure accumulators to provide rapid action. Can be used on very large valves
	Electric motor	Actuation is achieved by a gearbox connected to an electric motor. This type of valve will fail in place normally if no power is available
Manually operated	Manual	Actuation is normally by the operator turning a handwheel. This type of actuator can be used in any type of valve but is hard to use on very large valves. Most other types of actuators can also have handwheels on them to enable control if the primary control actuator fails. A manually actuated valve has no failure position; essentially it fails in place

dimensions are also different, with the inlet having the larger diameter. The valve itself is plug type but seats in the bend of the valve body. Venturi type or angle valves are used in cases where there exists a high-pressure differential between the fluid at the inlet side of the valve and that required at the outlet side.

Butterfly valves operate at very low-pressure drop across them. They can operate quite effectively at only inches of water gauge pressure drop and where the operation of the conventional plug-type valves would be unstable. The action of this valve is by means of a flap in the process line. The movement of this flap from open to shut is made by a valve stem outside the body itself. This stem movement, as in the case of the other pneumatically operated valves, is provided by air and spring loads onto the stem from a diaphragm chamber. The only major disadvantage in this type of valve is the fact that very tight shutoff is difficult to obtain due to the flap-type action of the valve.

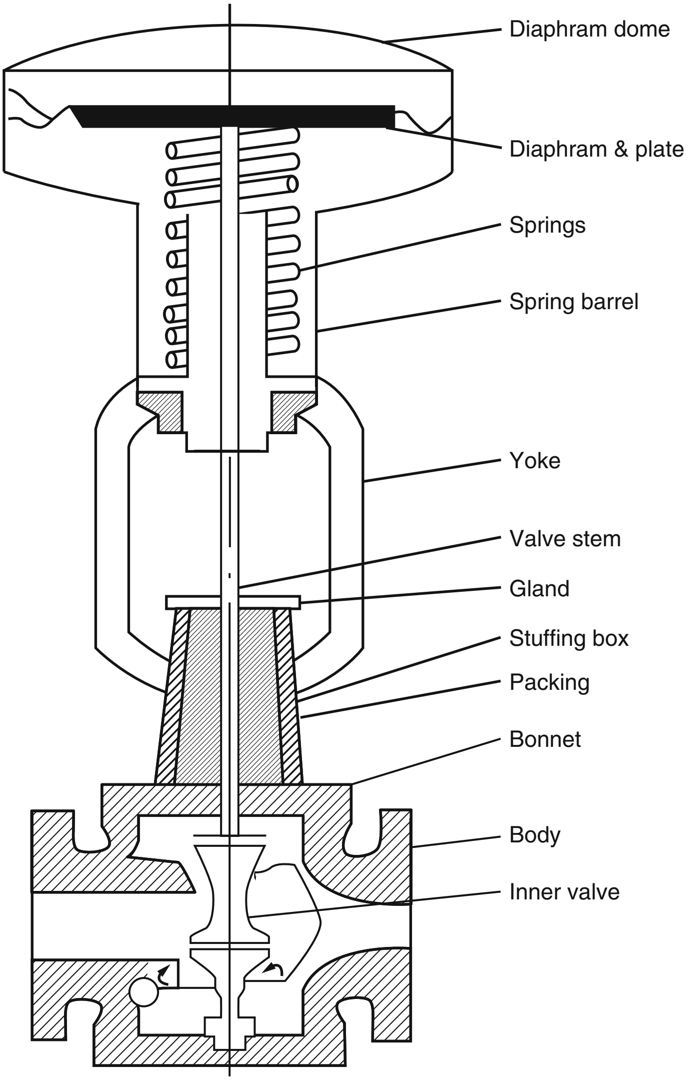
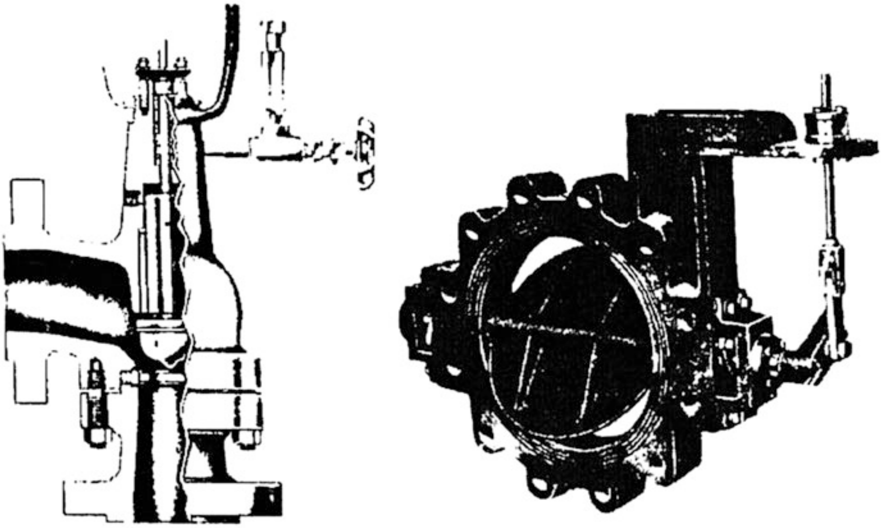


Fig. 7 A conventional control valve

The Valve Plug

There are two types of valve plugs used for the conventional control valve function. These are:

- Single-seated valves
- Double-seated valves



Ventun

Butterfly

Fig. 8 The venturi and butterfly control valves

Single-seated valves are inherently unbalanced so that the pressure drop across the plug affects the force required to operate the valve. Double-seated valves are inherently balanced valves and are the first choice in many services.

The conventional control valves predominantly in use can have either an equal percentage, or linear characteristics. The difference between these two is given in Fig. 9.

With an equal percentage characteristic, equal incremental changes in valve stem lift result in equal percentage changes in the flow rate. For example, if the lift were to change from 20 % to 30 % of maximum lift, the flow at 30 % would be about 50 % more than the flow at 20 %. Likewise, if the lift increases from 40 % to 50 %, the flow at 50 % would be about 50 % more than at 40 %.

With a linear valve having a constant pressure drop across it, equal incremental changes in stem lift result in equal incremental changes in flow rate. For example, if the lift increases from 40 % to 50 % of maximum, the flow rate changes from 40 % to 50 % of maximum. Thus, equal percentage is the more desirable characteristic for most applications and is the one most widely used.

Pressure Drop Across Control Valves

In sizing or specifying the duty of the control valve, the pressure drop across the control valve must be determined for the design or maximum flow rate. In addition, if it is known that a valve must operate at a flow rate considerably lower than the maximum rate, the pressure drop at this lower flow rate must also be calculated. This will be required to establish the rangeability of the valve.

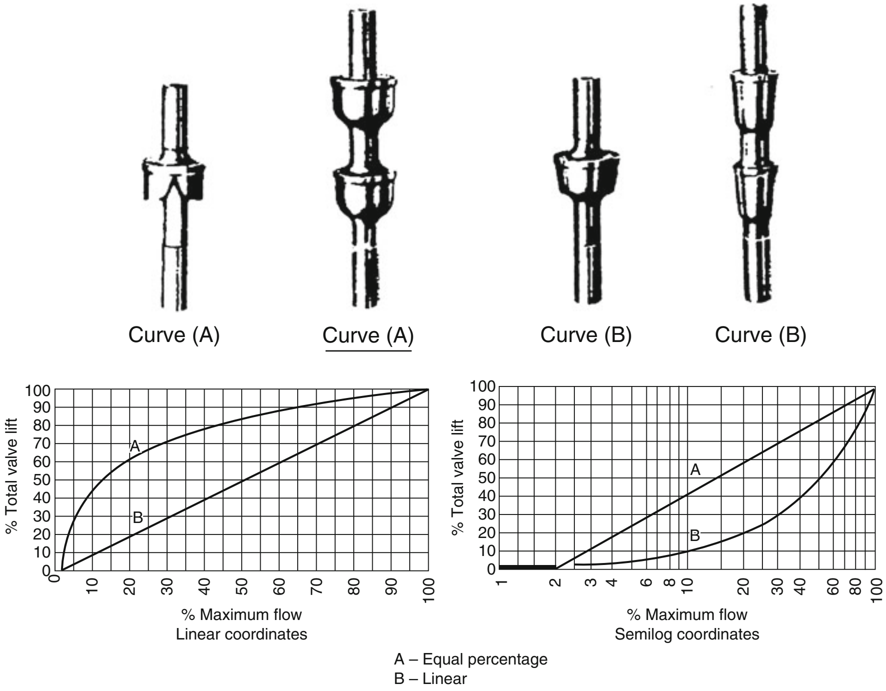


Fig. 9 Control valve characteristics

As a general rule of thumb, the sum of following pressure drops at maximum flow may be used for this purpose:

(a) 20 % of the friction drop in the circuit[1] (excluding the valve).
(b) 10 % of the static pressure of the vessel into which the circuit discharges up to pressures of 200 psig, 20 psig from 200 to 400 psig, and 5 % above 400 psig.

The static pressure is included to allow for possible changes in the pressure level in the system (i.e., by changing the set point on the pressure controller on a vessel). The percentage included for static pressure can be omitted in circuits such as recycle and reflux circuits in which any change in pressure level in the receiver will be reflected through the entire circuit. In some circuits the control valve will have to take a much greater pressure drop than calculated from the percentages listed above. This occurs in circuits where the control valve serves to bleed down fluid from a high-pressure source to a low-pressure source. Examples are pressure control valves releasing gas from a tower or streams going out to tankage from

---

[1] A circuit generally includes all equipment between the discharge of a pump, compressor or vessel, and the next point downstream of which pressure is controlled. In most cases this latter point is a vessel.

vessels operating at high pressure. These are the circumstances where venturi or angle valves are used, as described earlier.

Valve Action on Air Failure

In the analysis of the design and operation of any process or utility system, the question always arises on the action of control valves in the system on instrument air failure.

Should the control valve fail open or closed is the judgment decision based principally on evaluating all aspects of safety and damage in each event. For example: control valves on fired heater tube inlets should always fail open to prevent damage to the tubes from low or no flow through them when they are hot. On the other hand control valves controlling fuel to the heaters should fail closed on air failure to avoid overheating of the heater during the air failure.

The failure position of the valve is established by introducing the motive air to either above the diaphragm for a failed open requirement or below the diaphragm for a failed shut situation. The air failure to the valve above the diaphragm allows the spring to pull up the plugs from the valve seats. Air failure to valves below the diaphragm forces the spring to seat the valves in the closed position. It is also possible to fail a valve in place by blocking in the air to both the top and bottom of the valve, but this option is only used selectively.

Sizing a Control Valve

The sizing procedure for sizing control valves is described in the Appendix of this chapter.

Variable-Speed Control

Of increasing importance in flow control are variable-speed controllers. By controlling the speed of a compressor or pump, the delivered flow rate can be changed directly. The flow delivered will depend on the flow curve and characteristics of the specific device as speed changes.

In a simple example, a reciprocating pump, which delivers a fixed volume for each stroke, can vary flow by changing the number of strokes per minute. This type of pump is used for controlling the injection rate of sulfiding chemicals into a hydrotreating unit during catalyst activation.

In a centrifugal compressor application, varying the speed of a large compressor can be used to reduce power requirements and keep the compressor away from its surge point and the potential for damage to the machine.

If we look around for potential uses of variable-speed drives, there are many possibilities.

There are four main types of variable-speed drives you will find in refineries:

- Turbines
- Engines
- Electronic
- Mechanical

Turbines

One of the oldest and most common variable drives is the steam turbine. Speed of the turbine is controlled by a governor valve that admits a variable steam flow rate to the turbine steam chest. More steam results in higher turbine speed. The upper speed on the turbine is limited by the overspeed trip. Larger turbines incorporate more sophisticated controls for the governor but essentially operate the same way.

Turbines are normally used for their high reliability, but their variable speed and high-power output capabilities recommend them especially for large compressors.

Engines

The internal combustion engine is another traditional, variable-speed driver. Environmental regulations and economics are slowly phasing out engine drivers, but they are still used in remote locations.

Jet engine-derivative drives (really turbojets) are also variable-speed devices that are considered here in the same category as internal combustion engines. These are not common in refineries outside of cogeneration units, which make both power and steam.

Electronic Speed Controls

Electronic speed controllers or variable-speed drives have been steadily increasing in capability over the past few decades. Controllers capable of supplying over 5,000 hp are available now, where as they were limited to 1,000 hp only a few years ago.

Variable-speed drives normally control the frequency of electrical power to an AC motor to generate a variable speed. Higher frequency increases the speed. There are also variable voltage, DC drives.

An important advantage of variable electronic drives are in power (and operating cost) savings. You only use as much power as you need, plus a small loss as heat. The drives have become very reliable and efficient compared to early variable-speed drives. A few decades ago, a 5,000 hp variable-speed drive was the size of a semitrailer and needed an almost equally large cooling system to dissipate the heat. New drives are much smaller and do not generate nearly as much heat.

Mechanical Speed Control

Speed for smaller pumps and drivers can also be controlled mechanically. This is common on many reciprocating and progressing cavity pumps, for instance. A crank is turned to change the speed of the controller. Various mechanisms are used for these controllers, including belts and gears. Essentially the drive is akin to an automotive transmission.

Variable Volume Control

The final common method for flow control in a refinery is variable volume control. In this approach the volume displaced by a positive displacement device is changed mechanically to regulate the flow rate. The mechanism usually changes the stroke length. Variable volume devices encompass both piston and diaphragm types.

Variable volume devices are used extensively in metering pumps. The unloaders on reciprocating compressors are also variable volume devices, which change the effective compressor displacement to reduce the net flow and power required.

Flow Measurement and Control Conclusion

Flow metering and control is the most fundamental operation conducted by a control system. It is critical to modern, continuous operations when controlling pressure, level, and temperature, in addition to direct flow rates. There are many options when choosing the primary flow sensing elements, final control elements, and actuators. These must all be coordinated to produce the necessary control in the refinery processes.

Temperature Measurement and Control

Temperature measurement and control of refinery processes is a second key consideration. There are fewer methods for measuring temperature than flow, but these are no less important. In fact, from a safety standpoint, temperature is one of the most critical factors in avoiding loss of containment.

In the following discussion:

- The primary temperature sensing elements will be reviewed, along with their characteristics and limitations.
- The most common installation arrangements will be described, along with specific considerations.
- Implementation of various temperature controls will be discussed.
- Some special temperature monitoring and control cases will be reviewed, including reactor temperatures, skin and surface temperatures, and furnace tube wall temperatures.

Temperature Measurement Elements

Table 5 provides a survey of the most common temperature measurement elements in refineries and petrochemical facilities.

The most common elements and their measurement principles are:

Thermocouples

These devices make use of the fact that, when heated, a solid-state junction of two dissimilar metals generates a small voltage relative to a fixed reference junction. The voltage is linear over a wide temperature range. The most common thermocouples used in petroleum refining are J and K types.

Table 5 Range of common refinery temperature measurement elements

			Operating range				
Property change with temperature (range)	Reading method	Element	English, °F	Metric, °C	Accuracy	Annual drift	Additional notes
Voltage between dissimilar metals (−330 to +4,000 °F, −200 to +1,700 °C)	High-impedance volt meter with cold reference junction	Thermocouple, J	Continuous: +32 to +1,382 Short term: −350 to +1,472	Continuous: 0 to +750 Short term: −210 to +800	±4 °F at 32 °F, ±17 °F at 2,300 °F	<±9 °F	Iron-Constantan. More sensitive than type K
		Thermocouple, K	Continuous: +32 to +2,012 Short term: −450 to +2,500	Continuous: 0 to +1,100 Short term: −270 to +1,372			Chromel-Alumel. General use inexpensive
		Thermocouple, N	Continuous: +32 to +2,012 Short term: −454 to +2,372	Continuous: 0 to +1,100 Short term: −270 to +1,300			Nicrosil-Nisil. Stable and oxidation resistant
		Thermocouple, R	Continuous: +32 to +2,912 Short term: −58 to +3,210	Continuous: 0 to +1,600 Short term: −50 to +1,768			Pt/Rh 87/13 % – Pt
		Thermocouple, S	Continuous: +32 to +2,912 Short term: −58 to +3,210	Continuous: 0 to +1,600 Short term: −50 to +1,768			Pt/Rh 90/10 % – Pt
		Thermocouple, T	Continuous: −301 to +572 Short term: −450 to +752	Continuous: −185 to +300 Short term: −270 to +400			Copper-Constantan
		Thermocouple, E	Continuous: +32 to +1,472 Short term: −450 to +1,830	Continuous: 0 to +800 Short term: −270 to +1,000			Chromel-Constantan. Cryogenic uses
	Many other options are available						

Resistance (**−420 to +1,200 °F, −250 to +650 °C**)	Wheatstone bridge	Platinum resistance temperature detector (RTD)	to +1,764 depending on type of element	to +962 depending on type of element	±0.2 °F at 32 °F, ±2 °F at 1,200 °F	<±0.2 °F	Available in various coiled or wound-wire forms: strain free, thin film, wire-wound, and coiled. High accuracy and repeatability below 600 °C (1,112 °F)
		Other detector material options are available					
Expansion – filled systems (**−320 to +1,400 °F, −195 to +760°C**)	Direct	Bulb thermometer	Typical: +5 to +248; Available up to 930 °F	Typical: −15 to +138; Available to 500 °C	±5 °F	None	Expansion of a liquid in a sealed tube creates a force that drives a mechanical indicator or controller. Highest cost, lowest accuracy
	Direct	Bimetal strip	Linear: −4 to +392 Maximum: ~842	Linear: −20 to +200 Maximum: ~450			Difference in expansion between two dissimilar metal strips bonded together bends the strips one direction, creating a force that drives a mechanical indicator or controller, e.g., home thermostat and overtemperature protection of circuits

(*continued*)

Table 5 (continued)

			Operating range				
Property change with temperature (range)	Reading method	Element	English, °F	Metric, °C	Accuracy	Annual drift	Additional notes
Infrared radiation (−40 to 5,400 °F, −40 to 3,000 °C)	Direct or image enhanced	Infrared thermometer	−76 to +5,432	−60 to +3,000	±0.5–1.0 % of reading		Good range. Works for heater tubes. Requires corrections for reflection and hot gas luminosity. Requires correct emissivity
		Infrared camera	32–1,832	0 to 1,000+			Portable and fixed available. Good for more comprehensive furnace tube monitoring

A J-type thermocouple has a junction between iron and Constantan. Constantan is an alloy of about 55 % copper and 45 % nickel. The normal, stable operating temperature range for this type of thermocouple is about 32–1,382 °F (0–750 °C).

The most common, general purpose thermocouple is K-type. This has a junction between Chromel (90 % Ni, 10 % Cr) and Alumel (95 % Ni, 2 % Mn, 2 % Al, and 1 % Si). Stable operating range is 32–2,012 °F (0–1,100 °C).

There are many other types of thermocouples available in varying temperature ranges.

Thermocouples are the workhorses of temperature measurement in a refinery. They are located throughout the process systems and supply the bulk of the temperature data to the control systems.

Thermocouples have three issues that may affect their accuracy and repeatability:

1. Gradual, cumulative drift on long exposure to elevated temperatures. This is mostly seen in base-metal thermocouples (like J and K). It is due to oxidation, carburization, or metallurgy changes within the metals in contact.
2. Short-term cyclic change when heated into the 500–1,200 °F (250–650 °C) range. Notable in types J, K, T, and E. Again this is due to metallurgical changes.
3. Time-temperature changes due to magnetic transformations. For K couples this occurs in the 77–437 °F (25–225 °C) range and for J couples above 1,350 °F (730 °C).

The issues may dictate the preference for one thermocouple type over another for certain applications. Noble metal thermocouples (like R and S) and some nonmagnetic types of couples help mitigate these issues.

Resistance Temperature Detectors (RTDs)

When very accurate, repeatable temperatures are needed, you look to RTDs. This type of temperature element consists of a length of very fine (usually platinum) wire wound around a core. The wound element is surrounded by a sheath to protect it from direct exposure.

There are also carbon film RTDs that can be used at temperatures down to absolute zero, but these are not common in refineries.

The usual platinum RTDs are limited to applications below about 1,100 °F (600 °C). Above this temperature, the platinum can become contaminated by metal from the RTD sheath and lose accuracy.

There are six factors to consider in comparing RTDs with thermocouples for an application:

1. *Temperature range*: An RTD upper temperature is limited as noted above, but below that temperature, the RTD will be more accurate than a thermocouple. Above 932 °F (500 °C), a thermocouple is the only option for contact temperature measurement.

2. *Response time*: Thermocouples are better for fast temperature response times of fractions of a second. RTDs are slower.
3. *Size*: RTDs, including their sheaths, are usually two to four times larger in diameter than thermocouples (1/8–¼ in. or 3.2–6.4 mm).
4. *Accuracy*: Thermocouple accuracy is limited to about ±3–4 °F (±2 °C). This is normally good enough for most applications. RTDs are more accurate; so if an exact temperature is required, an RTD is indicated.
5. *Stability*: A thermocouple will drift some for the first few hours of use and will age at high temperatures. An RTD is stable for many years within its operating limits.
6. *Cost*: A thermocouple installation is less expensive than an RTD.

Normally, a thermocouple will be used in a refinery, but RTDs will be used in specific applications.

Thermal Expansion Devices

Bulb Thermometers

An industrial bulb thermometer is a metal tube with a fluid trapped inside. This is similar to the classic bulb thermometers we all have at home in our water heaters. The fluid may be volatile.

When heated, the trapped fluid expands or vaporizes, increasing the internal pressure and moving a connected sensing tube, producing a mechanical force which can cause a control action or just be connected to an indicator. This type of element is often seen in low-cost temperature control systems. The bulb of the thermometer is immersed in the material being measured. The long coil of attached tubing is connected to the controller or indicator.

A typical application for this type of thermometer would be in a temperature-controlled cooling water (or tempered water) system to control the amount of water bypassing the cooler. Some dial thermometers for local indication may have bulb sensors.

The biggest argument in favor of these devices is that they are cheap and adequate for many applications. They have limited temperature range, however.

Bimetal Strip Temperature Measurement

A bimetal strip is made from two thin strips of different metals with different coefficients of expansion that are brazed or otherwise attached side by side over their length. When heated, this “bimetal strip” bends as the metal on one side expands more than the other. The phenomenon is repeatable.

The device is almost always local to the temperature measurement point.

The bimetal strip can be connected to an indicator for temperature or to a control means, usually a pair of on/off electrical contacts. The bimetal strip may actually be one of the contacts. This type of instrument can be used in heating system thermostats and in electrical circuit breakers. Dial thermometers for local temperature indication may be bimetal.

Infrared Radiation

Any material emits infrared radiation that is related to the temperature of the material. Infrared thermometers make use of this phenomenon to determine the temperature without having to physically contact the material. The temperatures determined by infrared devices are not as accurate as contact methods, but they can measure the temperatures of materials that are far hotter than anything a contact thermometer can manage.

The high temperature limits for IR devices make them ideal for monitoring furnaces and furnace tube temperatures. Handheld IR “guns” are used to “shoot the tubes” in a furnace to determine the tube wall temperature. IR cameras are used to provide an overall survey of furnace tubes for hot spots, scan for overloaded circuits, look for insulation failures, and many other tasks. The IR images from a camera are translated into a false-color image to accentuate temperature differences.

Because of the cost, IR devices are not normally permanently installed in a refinery, but are instead used on an as needed basis.

The accuracy of measurements from IR devices is limited by several factors, among these are:

- Difficulty in determining the correct emissivity for the material being measured.
- Reflections from the surroundings, like other tubes and refractory walls in a furnace.
- Temperature is most accurate if the view angle is straight on or 0 degrees.
- When measuring furnace temperatures, you are looking through the firebox gases, which are emitting their own radiation. A narrow measurement frequency of IR helps reduce this impact, but it still influences the measurement.

The limitations in IR devices means that the accuracy is normally limited to about ±4 °F (±2 °C) in low range with good calibration. In a furnace at 2,000 F and several interferences, the accuracy is closer to ±25–50 °F (±15–30 °C).

Additional Temperature Measurement Options

There are a few additional temperature measurement options coming onto the scene in recent years, although these are not widely used in refineries to date.

One of the most interesting options uses the light reflecting properties of fiber optics. These new temperature detectors enable many temperature points to be incorporated into one fiber-optic cable, which can be very long. One possible use of such a system would be to provide an indication of the hottest wall temperature on a reactor shell with much greater resolution than other methods. The upper temperature limit for this technology so far is only about 500 °F (260 °C), but it does offer another possible measurement development to watch.

Typical Temperature Measurement Arrangements

Here we will focus on the application of thermocouples and RTDs in refinery process temperature measurement. There are four types of applications discussed, which cover the most commonly encountered situations.

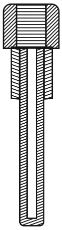
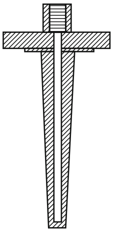
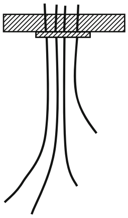
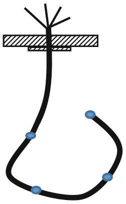
Thermowells

A thermocouple or RTD is seldom inserted into process fluids directly. They are inserted into the fluid housed within a thermowell. This is essentially a small, capped pipe designed for the process pressure, temperature, and chemical environment. The pipe is essentially open to atmosphere at the end opposite the cap. The temperature measuring element is inserted into the open end with the thermocouple junction or RTD positioned inside the thermowell at the desired location. The thermowells may be threaded or flanged, as dictated by the piping design conditions and specifications.

There are different types of thermowells, as illustrated in Table 6. The main types are as follows:

- *Straight thermowells* are commonly used where vibration is not a potential problem. Straight thermowells may contain more than one thermocouple, as in reactor thermowells. Each thermocouple can be independently positioned in the thermowell. Clips may be used to hold the thermocouple points against the thermowell wall and position them.
- *Tapered thermowells* are like straight thermowells but taper toward a smaller diameter toward the capped end. This helps them resist vortex-shedding-induced vibration damage. These are common in many fast-flowing process lines.
- *Flexible thermowells* are becoming the preferred type of thermowell in fixed bed reactors. These thermowells are small diameter and can be bent to place the

Table 6 Common thermowell types

Type of thermowell	Straight	Tapered	Flexible	Flexible multipoint
Picture	 Threaded style	 Flanged style	 Individual small tube for each TC	 4 TC points in same thermowell tube
Applications	General use	Flowing streams where flow-induced vibration could be a problem	Normally reactors	Normally reactors

thermocouple points in specific locations, not limited by the normal straight thermowells. There are multi-tube versions, where each thermocouple has its own tube, and multipoint versions, where all the thermocouples are packed in a small flexible tube with the thermocouple junction locations marked. These thermowells must have a support system installed to prevent damage or movement in service.

Furnace Tubeskin Temperatures

Infrared temperature measurement of furnace tubes and other similar services is fine for general temperature trending, but for more accurate temperatures, direct contact measurement is required. This is a challenge because the furnace firebox environment is very hostile toward materials when they are not cooled by external means, such as flow. It is also necessary to install the skin TIs on the side of the tube facing the flame, which is much hotter. Successful placement of the skin TI at the hottest point on the tube wall is also problematical. This can be calculated, but changes in fouling and firing tend to move the hottest point in the tube wall around. At best a tubeskin TI is just an indication.

While tubeskin TIs have a hard time with reliability in the firebox, they work fine in the convection section, where the environment is less rigorous.

Systems have been developed to attach thermocouples to furnace tubes that overcome many of the obstacles of the furnace environment. They can’t help the location limitations. The two most common installations for skin TIs are direct welded pads and refractory-shielded pads:

Welded Pads

In a welded pad installation, the thermocouple is routed through a flexible stainless steel sheath with MgO insulation to a high-alloy (like Hastelloy-X) weld pad and peened into the pad. The pad is then welded to the tube on the side of the tube facing the fire. There is adequate length and flexibility designed into the sheath for differential thermal expansion.

This type of installation has been somewhat successful, but the welds of the pad to the tube can break, the thermocouple can break off the pad, or the sheath and thermocouple may burn up. Variations of this installation have also been used, with similar issues.

The welded pads work well in the furnace convection section.

Refractory-Shielded Pads

This approach overcomes some of the issues of a welded pad. The thermocouple is routed through a stainless steel sheath insulated with MgO to a weld pad where it is attached. The pad is welded to the tube wall on the side pointing toward the tube. So far it looks just like a pad installation.

Now a 310 stainless steel shield is wrapped over the shielded TC and welded to the tube wall. The shield is packed with refractory and extends to cover the sheathed TC over the whole length exposed directly to the radiant heat.

This type of installation, and similar approaches available from manufacturers, has been somewhat more successful in improving skin TI reliability. They are still limited by the fixed location.

Reactor and Vessel Wall Temperatures

It is often necessary to attach skin temperature instruments directly to the wall of a reactor or other hot vessel. These are most often used to ensure minimum pressurization temperature requirements are met and to detect possible hot spots or maldistribution inside the vessel near the wall. The situation is somewhat parallel to the furnace piping, but welding onto the pressure vessel after fabrication and stress relief is a problem.

Note that this is one case where a thermocouple is not used in a thermowell.

One might ask why a magnetic thermocouple holder isn't used. The difficulty with the magnetic holders is that they become demagnetized at reactor operating conditions and then fall off. They are satisfactory for short-term measurements, however.

A number of approaches have been used for installing these skin thermocouples. A couple of them are described below, but each refiner has preferences.

Welded and Threaded Stud

During vessel fabrication, a threaded stainless steel stud can be welded to the vessel at the desired location. The thermocouple is then clamped down to wall using an appropriate washer and nut on the stud. This approach works somewhat but requires preplanning. The studs sometimes break off or the thermocouple comes loose in service. Since the location is usually heavily insulated, it is hard to detect the failure. Backup temperature measurements may be needed if a skin TI does not change along with the other skins.

Drilled Well

Another method used by some refiners is to carefully drill a hole into the vessel shell a specific distance, with a special taper to receive the thermocouple. The thermocouple is inserted and retained in the hole with the TC located at approximately the middle of the vessel wall. Many refiners are unwilling to drill into the vessel walls, but this method does appear to work.

Peened Thermocouple

In this approach, a smaller, shorter hole is drilled into the reactor wall and the thermocouple junction is peened into the vessel wall. These have a tendency to pop off from thermal expansion and contraction, so are have limited reliability.

Temperature Mixing Distances

In many cases, the objective is to measure the temperature of a combined stream that includes both hot and cold fluids. If you measure the temperature just downstream of the mix point, assuming flow is turbulent, you will find the temperature varies significantly.

Just as with flow metering, the location for temperature measurement of a stream when two fluids are mixed must be measured at a point far enough downstream that the fluids are again at a steady state. If the mixing involves reaching a new phase equilibrium, the problem is further complicated.

As a rule of thumb, a temperature measurement for the combination of two streams should be made at least 10–20 pipe diameters downstream of the mix point for turbulent flow. If flow is laminar or stratified, the measurement point may need to be much further downstream. The addition of an in-line static mixer can significantly shorten this distance. Manufacturers can help with the design and computerized fluid dynamic (CFD) modeling of the flow resulting from a static mixer and enable you to place the downstream TI at the best location.

Control Elements

Temperatures in refining processes are controlled by heat exchange, furnace firing, and flow of the reactants for the most part. Temperature control is thus reduced essentially to flow control of feeds, internal fluid flow, or fuels – all flow control issues.

Hence, the control of temperatures mimics the flow control discussion. A typical temperature control scheme for the inlet to a reactor using a fired heater might look like Fig. 10.

In this scheme, there are three TIs at the top of the reactor plus an inlet TI. All the reactor influent passes through the fired heater. The inlet TI can control the reactor inlet temperature by controlling the fuel gas pressure to the heater (providing a set point to the fuel pressure controller). The center TI at the top of the reactor bed acts as a backup controller through a selector switch on the DCS. The other two bed TIs are for calculation and indication.

TIs that will be used only for indication (TI 3 and TI 4) are sent directly to a thermocouple input unit that is part of the distributed control system (DCS). The TIs that may be used for control (TC 1 and TC 2) are transmitted to the DCS using smart, digital transmitters to improve accuracy and provide diagnostics. The cost of a smart or transmitted TI loop is higher than a simpler TI loop, so instruments do not always use a transmitter.

Overall, temperature cascades to fuel gas pressure control and the fuel gas flow is available for monitoring and alarming. As an aside, some people like to cascade temperature control to fuel gas flow control and then to fuel gas pressure control. This does produce smoother control, but response is slow if there is a major temperature change needed.

Concluding Comments

There are several options for temperature measurement, but the most common elements for temperature are thermocouples, with other instruments a remote second. The temperature instruments are usually installed in thermowells inserted

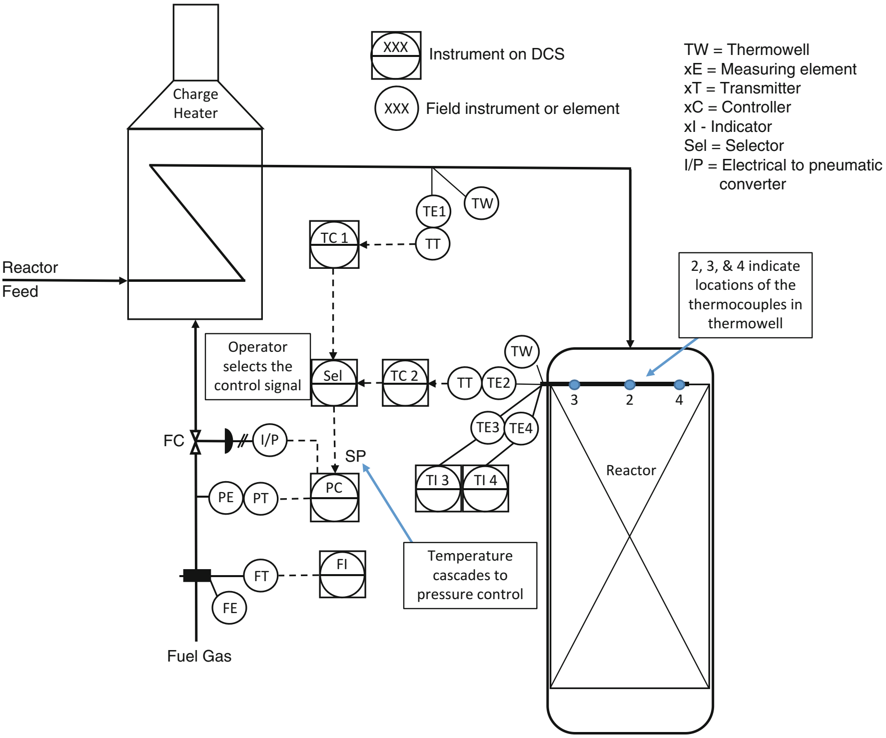


Fig. 10 Reactor inlet temperature control scheme

into the process fluids, although some types of temperature measurement (like infrared) do not require direct contact and some are inserted directly into the material being measured.

When mixing two fluids, be sure to allow adequate mixing distance and time or provide devices to accelerate mixing so the resulting temperature correctly represents the combined fluid conditions.

Remember that temperature control frequently translates into flow control to effect action.

This has only been a superficial treatment of temperature control. Working with your instrument supplier and experts within a facility can clarify the options and allow you to make better decisions on specific applications.

Pressure Measurement and Control

The third parameter that must be regularly measured and controlled in refinery processing is pressure. Aside from the process implications of having the wrong pressure for the physical and chemical processes in the units, pressure control is critical to safety.

Pressure Measurement Elements and Characteristics

Table 7 provides a survey of the general range of commonly applied pressure instruments in petroleum processing.

The most common pressure indicators in processing are the Bourdon tube gauges you will see throughout a facility. These are classically what we think of as a pressure gauge. They usually provide only local indication, although the principles can be adapted for local pressure control or the pressure can be transmitted to a remote control system.

More common for control systems today are electromechanical pressure sensors. These readily provide data to a remote control system as an electrical signal. The electronics for the sensor can be packaged with the sensor housing, so no separate transmitter is needed. The most common remote pressure sensors are normally capacitive.

There are three types of pressures that are measured in general:

- *Gauge pressure* – This is the pressure of the process compared to atmospheric pressure. A positive gauge pressure means pressure is above atmospheric. A negative gauge pressure indicates vacuum.
- *Absolute pressure* – This is the total pressure of the process compared to total vacuum. It is always positive and equals the gauge pressure plus atmospheric pressure. We are normally only concerned about measuring absolute pressures in vacuum systems.
- *Differential pressure* – Sometimes we are looking for small differences in pressure between two streams. In this case we do not want to compare against atmospheric pressure, but want to compare the two pressures directly. This is done in a dP or differential pressure cell. Essentially this is similar to other pressure sensors, except that the two sides of the sensor can be connected to the two pressures of interest in the dP rather than having one side connected to atmosphere. As an alternative, modern, high accuracy electronic pressure sensors can also be used for this service by taking the difference between two gauge pressures, if the difference is large enough.

Typical Installations

Some typical instrument installations, in simplified P&ID format, are in Fig. 11.

Pressure sensors are normally tapped directly into the process at the point being measured.

For simple, local Bourdon tube pressure gauges, there would be a root valve meeting the piping line class at the location point and a bleeder valve to allow servicing of the gauge. If the gauge is close enough to the tap or the pressure is low, the bleed valve may be omitted.

For a control pressure installation, there is normally a piping-class root valve installed for maintenance followed by tubing impulse lines leading to the pressure

Table 7 Pressure sensing instruments

Element type	Sub-categories	Pressure range, psia	Typical accuracy	Advantages	Limitations
Mechanical	Bellows elements	0–30	±0.5 %	Moderate cost. High force output. Absolute or differential pressures. Low-pressure capable	Require spring characterization. Need temperature compensation. Low ranges only. Work hardening of bellows
	Diaphragms and capsules	0–200	±0.5 %	Moderate cost. Close-couple to process. Small. Capable of high overpressures. Linear response	Limited range. Hard to repair. Susceptible to shock and vibration. More complex output transmission
	General purpose Bourdon tube gauge	15–10,000	±2 %	Low cost. Simple. Extensively used. High pressures. Good accuracy versus cost. Adaptable to transducers	Poor below 50 psig. Mechanical movement. Susceptible to shock. Hysteresis effects over range
	High accuracy test gauge	Vac to 3,000	±0.25 %	Similar to general purpose gauge, but higher accuracy	Similar to general purpose gauge and higher cost
Electromechanical	Strain gauge transducers	0–200,000	±0.25 %	Good accuracy. Range to 200,000 psig. Stable. High output signal. Small. No moving parts. Overload capacity	Need power supply. Electrical only. Ambient temps below 600 °F. Limited corrosion-resistant materials. Cost
	Piezoresistive sensors	0–6,000	±0.1–0.5 %	High accuracy. Linear. Repeatable. Smart sensors available. Small size	Higher cost. Electrical systems only. Temperature compensation. For dP, also compensate pressure
	Capacitive sensors	1 in.Wtr to 6,000	±0.2 %	Good accuracy and linearity. Easy to adapt to digital. Moderate cost	Temperature compensation preferred. Limited corrosion resistance

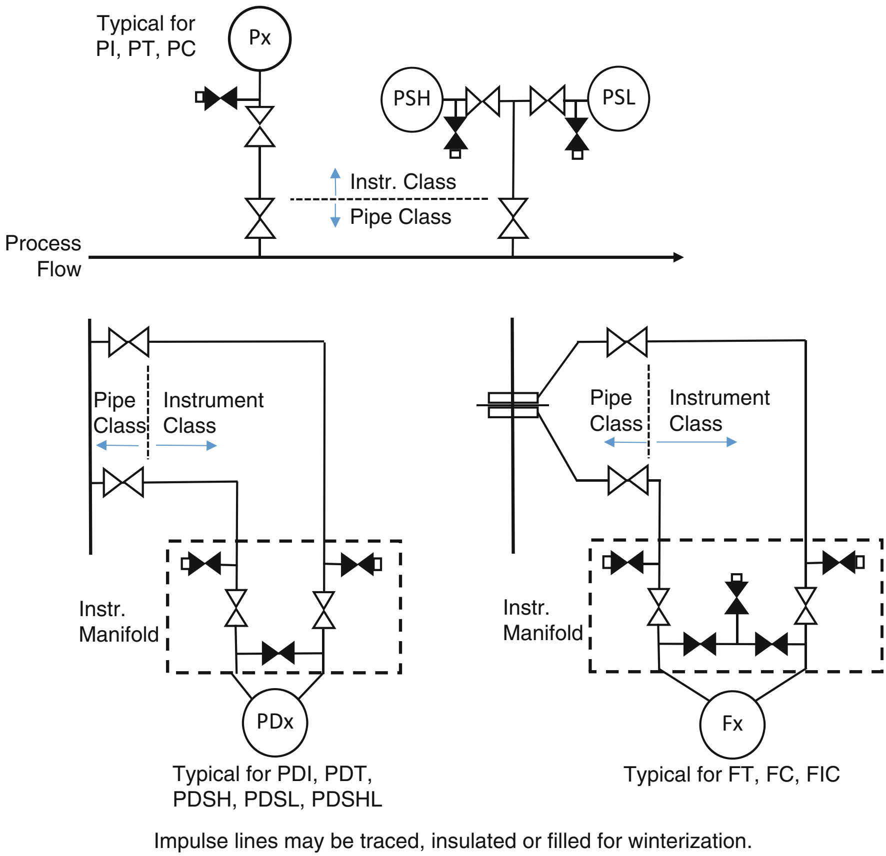


Fig. 11 Some typical pressure instrument installations

instrument manifold. The manifold on the pressure instrument is pretty much the same as those used for flow instruments. It allows for calibration of the sensor and bleeding the sensor impulse lines.

It is preferred that the impulse lines free drain to the sensor for liquids. If the impulse lines are very short, the liquid pressure instrument may be on the top half of the line also. A sensor has to be calibrated with the impulse line(s) full of liquid if this will be the normal condition.

For vapors, the pressure instrument should be located above the tap and the impulse lines should free drain into the process. These instruments can be located below the line but must then be calibrated with the lines full of liquid.

Many fluids can damage or corrode the sensitive parts of the pressure sensor. In these cases, isolation is provided between the process and the instrument. Isolation can take the form of filled taps (with an isolation fluid like glycol) or by installation of a high alloy or gold diaphragm seal at the pressure sensing point with a filled tube connecting the seal to the instrument. The pressure instrument must be calibrated with whatever sealing device is used. Care must be taken to avoid breaking or losing a seal fluid. Also, if a seal diaphragm is used against a hot hydrogen stream, the diaphragm must be gold plated to avoid intrusion of hydrogen and subsequent rupture of the diaphragm seals.

Steam pressure measurement presents a special case for installation. In steam lines, the impulse lines will often have a coil (or pigtail or siphon) in them which sets up a liquid condensate seal between the steam and the pressure sensor. This acts as an isolator between steam and instrument. The same approach can also be used for other condensing vapors, if desired.

Often pressure must be measured on pulsating flows. The shock created by each pulsation will damage pressure sensors if they are not protected. There are several devices available to dampen the pulses. Options include throttle screws, pulsation dampeners, snubbers, needle valves, and other devices. These slow down response to pressure but avoid damage.

Some process fluids can freeze, resulting in plugged or even ruptured impulse lines. This is particularly an issue with water or steam. In these cases, the lines must be "winterized." This can be accomplished by sealing the impulse lines with glycol solution or another, nonfreezing fluid, or by heat tracing the impulse line with steam or electric tracing. The pressure sensor also has to be winterized if it sees process fluid, although care has to be taken to avoid damaging the sensor with heat.

The same precautions listed above apply regardless of the pressure sensor service: indicating, controlling, differential, or flow metering.

Pressure Control Elements

As with flow and temperature, the primary pressure control elements are essentially controlling flows using control valves or one of the other control mechanisms discussed under flow.

The devices controlling pressures receive their signals from pressure controllers that are either field mounted or remote (in a control room or DCS), so the pressure control loops look like other loops.

We will, however, examine a few special cases where pressure control entails specific requirements.

Pressure Regulators

A pressure regulator is a self-contained pressure sensor/controller combination that maintains a fixed pressure. The set pressure can usually be changed manually by adjusting tension in a spring.

Tank Blanket Gas Control

Because of their large size, most storage tanks are not designed for pressures above a few inches of water. In many cases, tanks have to be blanketed with inert gases to avoid undesired reactions. At other times, they may have to vent vaporized gases to avoid overpressure. Special pressure control valves are used to accomplish these tasks. The valves can maintain a tank gas blanket pressure at a set point within a couple of inches of water. These valves use large diaphragms that are controlled by spring, pilot, or weights to achieve the fineness of control necessary.

Heater Draft

As with tanks, heater draft requires very tight control to within a few inches of water pressure. This is accomplished by using a narrow-range pressure transmitter that feeds a draft pressure controller which sends its output to a damper at the base of the heater stack or an induced draft fan to manage the pressure in the firebox. The control system is often redundant and has checks on its operation, such as excess oxygen monitoring and unburned hydrocarbons. These checks can override the controls and shut the heater down.

Most heaters do not have a draft control system, but have local draft meters or gauges instead. Sometimes these are actually water manometers but they can be special Bourdon tube draft gauges. The damper is manually controlled. The draft gauge taps are located at several points in the heater, including:

- At the burner level
- At the arch or convection inlet
- Ahead of the damper
- Above the damper

The normal point at which draft is controlled is the arch or convection inlet. A slightly negative pressure is required at this point to ensure air flow into the heater at the burners.

Distillation Column Pressure

The old adage that “there is more than one way to skin a cat” certainly applies to distillation column pressure control. Many ways of controlling the tower pressure at the overhead have been developed. One of the best summaries and discussions available is probably that by A.W. Sloley of The Distillation Group, Inc., published in Chemical Engineering Progress, January 2001 (see references). Table 8 provides a summary of the 19 methods described in that article.

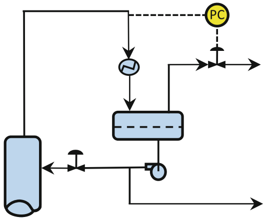
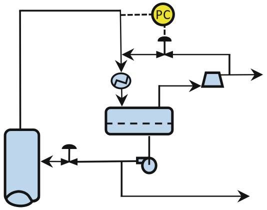
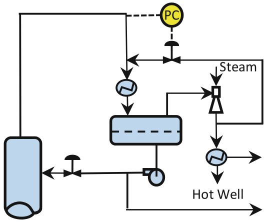
Some techniques work better than others. Simplicity works much better than elegance. Operators must be able to understand and control a tower using whatever method is chosen or the control will be unsuccessful.

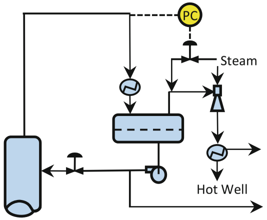
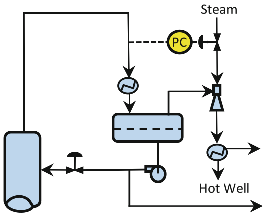
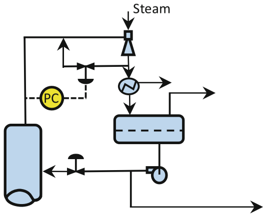
Concluding Comments on Pressure

Several pressure measurement options are available, with the most common being Bourdon tube gauges, pressure transducers, piezoresistive sensors, and capacitive sensors.

Installation of these sensors requires care to protect the sensor from damage due to freezing process fluids, corrosives, pulsations, high temperatures, and fouling.

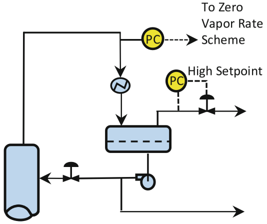
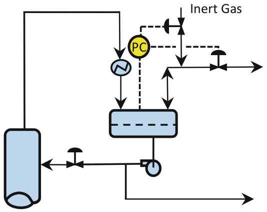
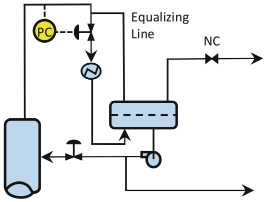
Table 8 Distillation column pressure control options

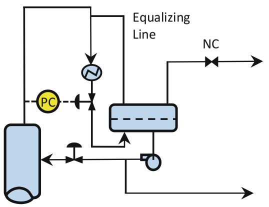
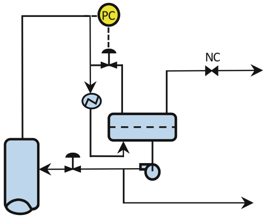
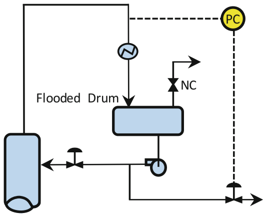
Method	Description	Sketch	Advantages	Disadvantages	Applications	Variants	Configuration	Concept	Precautions
Tower net vapor rate always > zero									
1	Direct control of product vapor rate from OH accumulator		Simple and direct	Generally none. May be slow with low vapor rate	Usually best choice for positive vapor rates	Condenser outlet to bottom of drum, but adds dP	Works best with condenser above drum. Gravity flow to drum from condenser. Free drain two-phase exchanger outlet	Controller directly affects column vapor inventory and pressure	
2	Control recycle vapor rate to compressor (spill back)		Simple and rapid control	May need to oversize compressor to add control margin. Not particularly energy efficient	When vapor goes to higher pressure equipment	Vapor may return upstream of condenser, to drum, or to compressor suction	Bypass to flare can be added to operate when compressor is down	Material is recycled to maintain constant suction pressure	
3	Control recycle vapor rate to ejector – ejector discharge recycle; ejector pulls vapor from OH accumulator		Ejector discharge available for recycle. Stable	Difficult to implement with ejector close-coupled to condenser. Large recycle line (low pressure) and control valve	Vacuum systems. Best for ejectors that don't like zero load. Often most economical	Recycle upstream of condenser. Recycle condenser vent upstream of ejector	Vapor may be a product or just noncondensables. In multistage ejectors, recycle loops around first stage (unstable otherwise)	Recycle gas loads up the ejector. More recycle means higher suction pressure	

4	Control makeup ejector load; ejector pulls vapor from OH accumulator, load control using steam injection to process		Easy to retrofit steam injection. Small flows needed	Lower energy efficiency. More steam and cooling water loads	Add on after the fact. Improves control. Useful in batch systems	Inert, noncondensable gas can also be used instead of steam	Inert gas use loads up condenser and any subsequent ejectors	Added load moves ejector along operating curves. Higher load = higher suction pressure	Injected steam should be dry to avoid erosion
5	Control ejector motive steam pressure; ejector pulls vapor from OH accumulator		Minimizes steam demand and condensate	Not normally a good choice. May only have a small control range	Added on after the fact. Poor choice			Lower pressure steam supply reduces ejector flow rate, reducing pressure ratio across ejector	Sometimes does not work. Narrow control range
6	Control recycle vapor rate to ejector – ejector discharge recycle; ejector pulls vapor from tower OH		All ejector discharge available for recycle. Often most stable	Hard to do with ejector close-coupled to condenser. Large recycle line (low pressure) and control valve. OH must be compatible with water	Best scheme for ejectors connected to tower that are unstable at zero load. Often most economical for stability	Can be used without overhead reflux (external reflux supply)	In multistage ejectors, recycle loops around first stage (unstable otherwise)	Recycle loads up ejector, increasing suction pressure	

(continued)

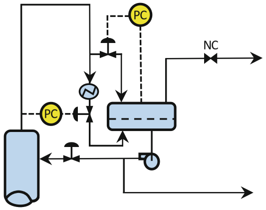
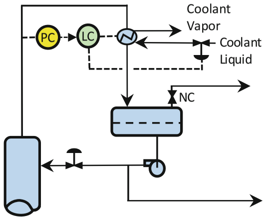
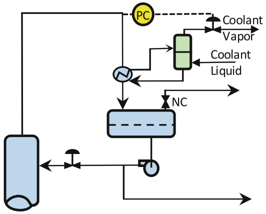
Table 8 (continued)

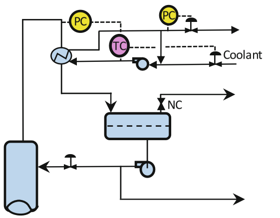
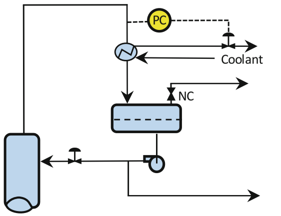
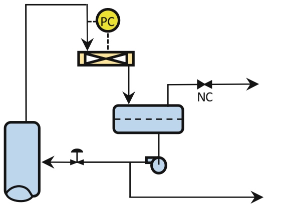
Method	Description	Sketch	Advantages	Disadvantages	Applications	Variants	Configuration	Concept	Precautions
Tower net vapor rate > or = zero									
7	Control vapor product rate in conjunction with a secondary method				Good for systems requiring inert gas venting	Numerous	Can be used with other methods that vary condenser duty, except for flooded drum (12)	Direct overhead pressure control. Changes heat transfer conditions in condenser	
8	Control makeup vapor supply (inert gas)		Simple. Fast response	Pressurizing gas make/vent arrangement more complex. Tuning issues	Pressure towers	Can add the inert upstream of condenser, but slower response	Pressurizing gas must be compatible. Does not require equalizing line. Small overlap where makeup and vent are both active works best	Gas addition or venting directly controls vapor inventory	
Tower net vapor rate zero (total condensing)									
9	Control flow to condenser with condenser at lower pressure		Simple	Drum level affects pressure. Need large control valves and extra exchanger capacity	Stable and effective for many applications		Need equalizing line for stability. Condensed liquid must enter below liquid in drum. If use air cooler, slope to drain. Cool to lowest temp	dP from control valve creates semi-flooded condition in condenser. Effectively variable area	

10	Control flow to condenser with condenser at higher pressure		Simple. Smaller control valve	Gravity drain required from condenser to drum. Extra exchanger area needed. Careful design of elevations	Stable and effective for many applications	Liquid may enter top of drum	Need equalizing line for stability. Condensed liquid must enter below liquid in drum. If use air cooler, slope to drain	Control valve causes liquid backup into condenser. Variable condensing area	
11	Control bypass flow to condenser receiver – hot vapor bypass scheme		Condenser may be mounted below drum	Complex concept – hard to understand. Condenser must be able to subcool	Used with large, heavy condensers at grade	Can use drum pressure instead of tower pressure. Condenser does not count as a stage	Must have liquid level in condenser at all times. Liquid must enter drum subsurface. Need adequate bypass size to make it work	Varies surface area in condenser. Drum has superheated gas over subcooled liquid. L and V not in equilibrium in drum	Sometimes does not work. Largely empirical design. Problem with high-purity products, self-refluxing condensers, corrosion of internal pipe
12	Direct control of liquid product rate		Liquid control of drum level not required	Changing exchanger area varies distillate product rate. May cause upsets downstream. Hard to reject noncondensables from upsets	Used with large, heavy condensers at grade	No condensate drum. Control of reflux rate instead of product rate	Must have liquid level in condenser at all times. Drum sometimes used to decant immiscible liquids. Sometimes no drum	Varies condenser surface area	If condenser is below the drum, subcooling is required for stability

(*continued*)

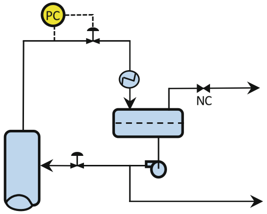
Table 8 (continued)

Method	Description	Sketch	Advantages	Disadvantages	Applications	Variants	Configuration	Concept	Precautions
13	Dual pressure control of bypass and condensate		Condenser may be below drum	Requires more control valves and subcooling area in condenser	Used with large, heavy condensers at grade. Used if condenser capacity cannot be easily varied (e.g., water boxes)		Must have liquid in condenser at all times	Varies condenser surface area	
14	Control vaporizing coolant level			Hard to blow down the vaporizing coolant if required	Heat recovery where one tower reboils another or for steam generators	Direct flow control of coolant, without level controller	Common in cryogenic plants	Varies level of coolant in the condenser to change heat transfer	
15	Control condenser inlet coolant pressure		Easier to blow down vaporizing coolant if required	More equipment	Heat recovery. Works with multiple shells in parallel		Unusual	Changes LMTD on coolant side of the condenser, changing capacity	

16	Control condenser inlet coolant temperature – tempered water concept		Gets the most out of coolant stream	More equipment. Slow response	Heat recovery. Helps control potential for overcooling of products and freezing	Pump in exchanger outlet instead of inlet	Called a tempered water system when used with cooling water. Common in steam generation heat recovery arrangements	Cooling stream temperature varies, changing LMTD	
17	Control coolant rate		Simple	May overheat coolant. Promotes cooling water fouling	Not common in new plants	Can pinch the outlet valve from exchanger and do this manually. Generally not a good idea	Need an override or limits to avoid fouling	Cooling stream temperature varies, changing LMTD	Causes exchanger fouling on coolant side
18	Control air cooler coolant rate (fans)		Simple	Mechanical issues with air cooler controls. Variable speed not used often due to cost	Most common method with air coolers	Can use blade pitch, louvers, or fan speed to control	Can combine types of control (pitch, speed, louvers) for fine-tuning. Slope to drain to drum	Varies air (coolant) flow rate to change LMTD and exchanger capacity	

(*continued*)

Table 8 (continued)

Method	Description	Sketch	Advantages	Disadvantages	Applications	Variants	Configuration	Concept	Precautions
19	Control condensation temperature or pressure		Simple, fast response	Big control valve. Condenser and drum pressure vary, causing problems for reflux pump	Pressure towers		Cooling is done to lowest temperature (i.e., overhead pressure is lower)	Direct overhead pressure control	Hard to do in vacuum systems, unless system has vacuum pump downstream. Variable reflux pump suction pressure

Pressure control ultimately boils down to flow control and management of fluids entering and leaving the process system. Pressure control for gases is similar to level control for liquids in that it is really a material balance control. If gas production rate varies, which is the usual case, a pressure controller will relieve the system of gas by holding a given pressure in a drum or tower. In this case the entire space above the liquid level actually constitutes a surge volume.

Level Measurement and Control

Level instrumentation is the next type we will explore.

Level monitoring and control is critical to avoid overflow or overfilling equipment. The principle applications of level control cover many key areas, including:

- Crude, intermediate, and production tank level and inventory change monitoring
- Custody transfer
- Management of process surge drum and tower levels and inventories
- Avoiding liquid carryover into rotating equipment resulting in damage
- Avoiding level carryover from vaporizing liquids
- Managing fluidized catalyst levels and densities
- Avoiding damaging pumps from running dry
- Avoiding spills and loss of containment from tanks, vessels, flares, and other equipment

We will start this examination by looking at the types of level-sensing instruments available and their characteristics. Then some common installation details and critical factors will be described. The discussion will move on to control elements and considerations for level, which will look a lot like flow control. This section will conclude with discussion, in some detail, of specific level control application issues, like minimum recommended surge times for various services.

Level Measurement Elements and Characteristics

Table 9 provides a survey of most of the types of level instruments found in petroleum processing today. The list is divided into three primary types of services:

- Continuous measurement – usually for control or monitoring
- Point measurement – usually for alarming and safety actions
- Liquid inventory gauging – tank levels

The most common level instruments in refineries depend on pressure differences, floats/displacers, or gauge glasses. These cover the majority of the continuous services and point applications in process systems. In tank farms, float and tape or head gauges dominate the applications.

Table 9 Range of level-sensing instrument types

Technology	Application phases	Operating conditions limits	Advantages	Disadvantages
Continuous level				
Pressure, differential pressure	Liquid	6,000 psig, 200 ft	Reliable. Simple. Easy to use. Flexible. Optional diaphragm seals. Unaffected by foam. Tolerable of agitation	Problems with high temp or vacuum. Affected by density. Can plug. Process corrosion. Hydrogen infiltration. Requires two process taps
Capacitance	Liquid, solid	1,000 psig, 500 °F, 100 ft	High temps and pressures. Good for interfaces. Unaffected by density, moderate foam, agitation, vapors	Affected by dielectric constant variation. Not good for high visc. Individual calibration. Fouling of probe. Error in emulsion layers
Ultrasonic	Liquid, solid	3,000 psig, −100 to +300 °F	Noncontact. Easy installation. Unaffected by density, dielectric constant, sludge, contamination, and fouling	Affected by changes in vapor. Temp and press limited. Poor in foam, high agitation, temperature changes
Radar, guided wave	Liquid, some solids		Different options. Unaffected by density, dielectric constant, visc, sludge. Low maintenance	Poor with agitation and foams or start-up. Larger process connections. Complex to configure. Antenna fouling
Displacer	Liquid	10,000 psig, 500 °F, 30 ft	Unaffected by agitation. Small spans possible. Measures interface. Can measure density. Low maintenance. High T and P	Not as good in high visc. Density affects. Sticky materials. Smaller spans (<32 in)
Nuclear	Liquid, solid	Not limited except by wall thickness	Noninvasive. Noncontact. High T and P. Aggressive materials. Does not clog. Unaffected by agitation	Negative perception. Requires licensing. Leak checks required. Expensive
Armored, magnetic	Liquid	to 10,000 psig, 600 °F	Simple. Direct visual reading. High metallurgy possible. Good for hazardous materials. Long ranges available	Float may stick. Fouling services. Mechanical indicators
Gauge glass	Liquid	1,450 psig, 750 °F	Direct reading. Simple	Risk of breakage. Limited height per gauge. Primarily local manual reading. Glass fouling or etching

Point level				
Capacitance	Liquid, solid	1,000 psig, 500 °F, 100 ft	Conductive or nonconductive materials. Interface measurement. Good for slurries. Easy installation. Wide temperature range. High pressures	Time-consuming calibration. Coating on probe
Floats	Liquid	2,000 psig, 750 °F, to 132 in	Unaffected by density changes. High temperatures and pressures. Low cost. Simple	Affected by density. Not for high visc. May stick. Corrosive or turbulent fluid protection. Hard to change set point. Physically large. Damage to float
Ultrasonic	Liquid	3,000 psig, −100 to +300 °F	Reliable. Easy to use. Self-testing. Unaffected by visc, density, dielectric, agitation	Affected by foam. Cannot handle temp extremes well. Not for high vacuum
Microwave (radar)	Liquid, solid		Noncontact. Nonintrusive. Unaffected by sludge, contamination, vapors	High cost
Vibration/tuning fork	Liquid, solid		Slurries. Interface. No moving parts. Unaffected by fouling. Good for low-density materials	No vibrating services. Need significant differences in specific gravity for liquid/vapor interfaces
Conductivity	Liquid	500 psig, 600 °F, 60 in.	Slurries. Interfaces. Low cost. Simple. No moving parts. Easy to install	Conductive fluids only. Fouling. May accelerate corrosion
Nuclear	Liquid, solid	Not limited except by wall thickness	Slurries. Noncontact. Nonintrusive. No moving parts. Unaffected by most factors	Negative perception. Requires licensing. Leak checks required. Expensive. Hard to calibrate

(continued)

Table 9 (continued)

Technology	Application phases	Operating conditions limits	Advantages	Disadvantages
Liquid inventory				
Hydrostatic tank gauging	Liquid	Ambient tanks, normal liquid temperatures for tankage	Mass measurement. Density correction. Install in service. Low maintenance. Very simple	Stratification and agitation affects reading
Float and tape	Liquid		Inexpensive. Many applications. Good accuracy	Intrusive. Mechanical. Reference point movement. Corrections for temp and specific gravity. High maintenance
Servo	Liquid		High accuracy. Can measure density	Intrusive. Reference point movement. Stilling well needed. Mechanical design. More complicated installation. Temperature corrections
Radar, guided wave	Liquid		High accuracy. Noncontact. Nonintrusive. Relatively insensitive to product type. Low maintenance. High reliability. Install in service	Reference point movement. Temperature compensation. Manual density required. Antenna fouling
Magnetostrictive	Liquid		High accuracy	Intrusive. Sensitive to shock, vibration. Moving parts may stick
Weight and cable	Liquid		High accuracy. Interface measurements. Deep tanks. Short contact	Intrusive. Mechanical. Must be manually activated. High maintenance
Hybrid systems	Liquid		High accuracy for level and mass. Direct density. Install in service	Very expensive. Need average tank temperature

Sources: "Selecting a level device based on application needs," Parker (Fisher-Rosemount Inc.) (1998) and "Sighting in on level instruments," Wallace (Fluor E&C) (1976)

Operation of float-type gauges (float chambers, displacers, and magnetic gauges) at high pressures requires special precautions because the floats can be damaged or collapsed by sudden venting or drain flows or sudden changes in pressure. Specific procedures are needed to flush the taps or level bridles around these types of instruments. The procedures are not difficult, but need to be followed. The level instrument supplier can advise on the proper procedures.

Some of the newer types of level gauges, such as guided wave radar (GWR), are becoming more common due to their lower installation costs and relatively low maintenance. Some of these technologies require backup systems for start-up as they are not suitable for the transitional conditions that accompany start-up.

One special application that warrants some discussion is interface gauging among oil/emulsion/water. If the density difference between the oil and water is sufficient and the elevation difference is adequate, then a traditional dP level instrument or displacer with the right specific gravity float works fine. For more difficult emulsions or where gravities are closer, the most reliable probes reported employ microwave (agar or equal) or radio frequency. Sensing by conductivity changes is also feasible as an on/off control. There are other approaches, but these seem to be the most reliable.

Level Instrument Installations

Figure 12 illustrates some of the more common level instrument installations for process systems and tanks.

Process Levels

In process systems, the level instruments may be connected directly to the process vessel or, commonly, they are connected to one or more level bridles that are connected to the vessel. There is normally a root valve between the process and the instrument system that meets the piping specification to allow isolation. A double block and bleed arrangement with blinding capability may be used in high-pressure services.

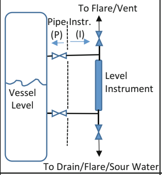
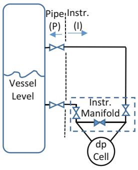
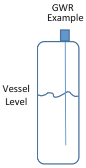
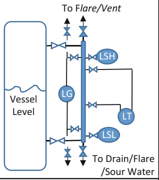
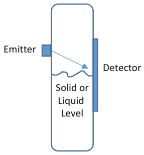
Outside the root valve, the class changes to instrument line class. If the instruments are hung off a level bridle, each instrument will have its own piping-class root valve and then instrument valves.

Direct connections to the process, without a level bridle, are simple, but if the root valve leaks or can’t be moved, the level instrument may end up out of service. This arrangement also exposes the level instrument to risk of fouling, high temperatures, and process corrosion. In some cases, the risks are managed by using sealed diaphragms or glycol-filled impulse lines for dP instruments.

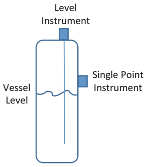
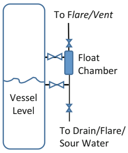
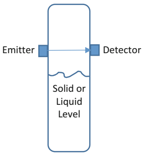
For safety instruments, like high-high level shutdowns, the normal preference is for these to connect directly to the vessel to reduce some of the risks of plugging if a bridle is used.

A level bridle is a vertical section of pipe that is connected to the process with root valves. The bridle normally has vent and drain valves connected to a safe location (like flare) to enable the bridle to be blown free of foulants periodically and to be depressured. The level instruments are then hung off the bridle.

Continuous Levels

Type of Instrument	Gauge Glass, Magnetic Float, Displacer	Differential Pressure	Microwave, GWR, Ultrasonic, Capacitance	Level Bridle Arrangement	Nuclear
Installation Sketch					
Notes	For non-hazardous services, vent and drain to atmosphere. Additional valves at instrument may be supplied. Winterization may be required. Level bridle may be used. Vents & drains are piping class.	Impulse lines may be filled to avoid freezing. Seal diaphragms may be installed on root valves and instrument manifold eliminated. Level bridle may be used.	Ultrasonic and mucrowave may differ. Level bridle may also be used.	All kinds of instruments can be connected to the bridle. Root valves for each instrument and the bridle are piping class. Vents & drains are piping class. Winterizing may be required. For emulsions, a third tap into the vessel is needed at approximately the mid point of the bridle.	

Point Level

Type of Instrument	Capacitance, Vibration, Conductivity	Float	Ultrasonic, Microwave, Radar	Nuclear
Installation Sketch			Similar options to Capacitance, Vibration, Conductivity	
Notes	May also be located on level bridle.	May also be located on level bridle. Winterizing may be required.		

Liquid Inventory

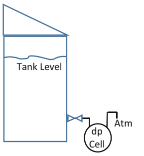
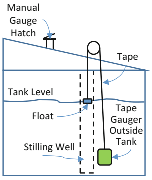
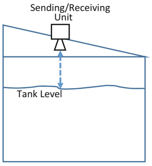
Type of Instrument	Hydrostatic	Float & Tape, Manual	Radar, Guided Wave
Installation Sketch			
Notes	Density compensation needed for best readings.	Manual gauging also allows determination of water cut in tank.	Non-contact measurement.

Fig. 12 Some typical level sensor installations

This arrangement has the advantages of (1) acting as a stilling well, dampening out the normal turbulence present in an active process vessel; (2) ability to blow out potential foulants; and (3) lower operating temperature than the process. Conversely, a bridle (1) introduces additional possible leak points, (2) can plug, (3) removes the attached instruments when taken out of service, and (4) readings must be compensated for density differences (especially on steam drums).

Note that a level bridle used for 3-phase separation needs three connections to the process. This is sometimes missed, resulting in poor level indication.

Level instruments, including any bridles, will require steam or electric tracing if the process fluids can freeze. Care must be used, however, to avoid tracing that causes the fluids in the bridle to boil.

Some refiners chose to purge the taps with inert gas or oil to keep them clear instead of periodically blowing down.

Level gauges or sight gauges can be a concern for leakage or failure. The gauge glasses can crack and fail if not correctly assembled and torqued. Steam sight gauges operating above about 500 °F require mica shields to avoid etching of the glass. In higher pressure or hazardous services, traditional gauge glasses are often being replaced by magnetic floats inside stainless or alloy tubes. These magnetic gauges have indicators for level that may consist of a single mag-follower or a section of many flip indicators that change color as the magnetic float passes by them. Magnetic gauges can be fooled by rapid level changes or by damaged floats, so redundant level indicators are a good idea.

Figure 12 does not address some of the level sensor installations, like nuclear. For these installations, the refiner needs to depend on their experience and the instrument vendor for installation details.

Tank Levels

Figure 12 shows a few of the more common tank gauging installations. These are fairly straightforward. If a liquid head-type gauge is used, the level reading will have to be compensated for density differences. Floats and other internal tank level devices, including manual tape gauging, are normally installed in stilling wells. These are just slotted tubes which protect the level devices from the liquid current moving around in the tank as it is filled or drained.

The water/oil interface in a tank is normally determined manually using a gauging tape coated with water indicator paste (water cutting).

Level Control

It is no surprise that the primary elements that control level in process systems and tankage are the same elements used to control flow. Levels that are used for control are connected to their respective level instrument, and the instrument output can be routed directly to the final level control element, a flow controller, or advanced process control. Ultimately, control all comes down to field manipulation of a flow control device as discussed under flow control.

We will not reiterate considerations in flow control here.

Specific Level Considerations

In this section, we will discuss a number of specific level control considerations that affect system design. The primary focus is on surge volumes, which is why we inventory fluids to begin with.

Surge volume is the volume retained in a vessel during operation at a set level. It is used for:

- Protecting equipment from damage caused by flow failures
- Protecting downstream processes from fluctuating flows which could cause poor process performance
- Protecting downstream processing from fluctuations in feed composition or temperature
- Protecting equipment from damage due to coolant failure

Types of Surge Volumes

There are primarily two types of surge volumes. These are:

1. *Upstream protection surge*. This is a surge volume provided to protect the upstream equipment and its associated pump from feed failure.
2. *Downstream flow surge*. This is surge volume provided to protect downstream equipment from feed failures or fluctuations.

Examples of Surge Types

Process Feed

Feed to process units is almost invariably on flow control. Many units also have a feed surge drum, particularly those units that are sensitive to flow fluctuations or where complete flow failure can cause equipment damage. This is an example of "downstream flow surge." The surge volume of the drum will depend on

- Source and reliability of source
- Type of control at source
- Variations and fluctuations in source rate

Column Feed from an Upstream Column

This feed stream will usually be controlled by the level in the source column, hence it will be fluctuating. If surge volume is provided only in the source column, it must be sufficient to cater for "upstream protection" and "downstream protection." The use of a surge vessel would be recommended for this case.

Feed to Fired Heaters or Boilers

The failure of flow through the tubes of fired heaters or steam boilers can cause serious damage through overheating of the tubes. Consequently "downstream protection" is required in this case. Invariably flows to heaters are on flow control.

Reflux Drum Considerations

- When the drum only furnishes reflux or reflux and product to storage, all that is needed in terms of surge volume is sufficient to provide "upstream protection." That is, the surge volume required is only to protect the reflux pump from losing suction in the case of column feed failure. The pump will be required to circulate reflux and cool the column down during an orderly shutdown period.

- When the reflux drum furnishes reflux and the feed stream to another unit, then the drum must furnish “upstream protection” surge and “downstream protection” surge.
- If there is a vapor product from the drum, additional volume must be provided in the drum to allow vapor/liquid disengaging. This will be such as to retain the same liquid surge capacity as described above.
- Should the vapor phase from the reflux drum be routed to the suction of a compressor, an even larger volume reflux drum will be required. This is to ensure complete disengaging of the vapor/liquid. Internal baffles or screens are also used in the drums vapor outlet section to ensure complete phase separation.

Quantity of Surge Volume

The amount of surge volume will vary with the various types given above and with the specific case in question. Sometimes this amount is set by company specifications or, in the case of engineering contractors, by the client. Generally however the process engineer will be responsible for setting a safe and economic surge volume. In doing this the engineer needs to analyze each case in terms of why the surge volume is being provided, then deciding how much based on this answer. Figure 13 provides some guidelines to the amount of surge that should be applied.

Some useful equations used in setting and handling surge volumes are.

For surge volume:

$$\text{Vol cuft} = (GPM)\ (\text{minutes})/7.48 \tag{6}$$

For vessel size:

$$\text{Diam, } D = \sqrt[3]{(\text{cuft}/2.35)@\text{L/D} = 3} \tag{7}$$

$$\text{Diam, } D = \sqrt[3]{(\text{cuft}/1.96)@\text{L/D} = 2.5} \tag{8}$$

$$\text{Diam, } D = \sqrt[3]{(\text{cuft}/1.57)@\text{L/D} = 2.0} \tag{9}$$

For line size:

$$\text{Diam, } D = \sqrt[3]{(\text{GPM}/25)@\text{velocity} = 10\,\text{ft/sec.}} \tag{10}$$

$$\text{Diam, } D = \sqrt[3]{(\text{GPM}/17)@\text{velocity} = 7\,\text{ft/sec.}} \tag{11}$$

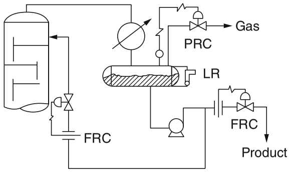
$$\text{Diam, } D = \sqrt[3]{(\text{GPM}/12)@\text{velocity} = 5\,\text{ft/sec.}} \tag{12}$$

For flow rate:

$$\text{ft/sec} = \text{GPM}/450 \tag{13}$$

a

TOWER OVERHEAD CONTROL 1



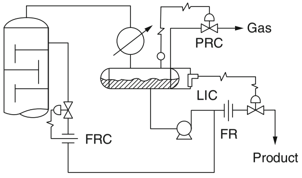
LIQUID OVERHEAD PRODUCT TO SUBSEQUENT PROCESSING*

15 minutes on product or 5 minutes on reflux, whichever is larger.

Note:

Similar surge requirements for:
- Reflux on temperature control
- No distillate drum gas make.

TOWER OVERHEAD CONTROL 2



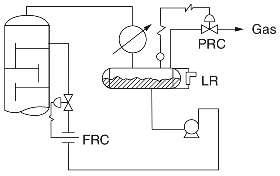
LIQUID OVERHEAD PRODUCT TO TANKAGE

2 minutes on product or 5 minutes on reflux, whichever is larger.

Note:

Similar surge requirements for:
- Reflux on temperature control
- No distillate drum gas make.

TOWER OVERHEAD CONTROL 3



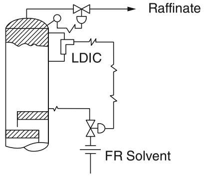
REFLUX CONDENSED • GAS PRODUCT

5 minutes on reflux.

Note:

Similar surge requirements for:
- Reflux on temperature control
- Level control on cooling water.

TOWER OVERHEAD CONTROL 4



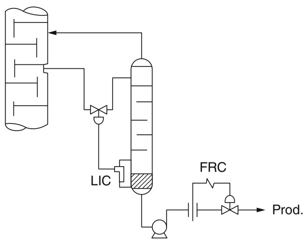
LIQUID - LIQUID EXTRACTION TOWER SOLVENT PHASE CONTINUOUS RAFFINATE ACCUMILATES IN TOWER TOP

Caustic towers - set by 14” displacer.
DEA towers - 5 minutes on DEA.
Phenol treaters - 10 minutes on phenol.

Note:

Feed and spent solvent streams are on flow control.

SIDESTREAM DRAWOFF CONTROL 5



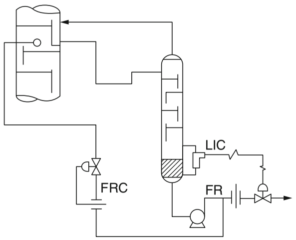
SIDESTREAM PARTIAL DRAWOFF

2 minutes on product through cooler or heat exchanger.

Note:

Same requirement when FRC is on drawoff and LIC is on product.

SIDESTREAM DRAWOFF CONTROL 6



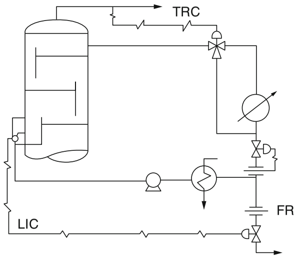
SIDESTREAM TOTAL DRAWOFF

2 minutes on product or 5 minutes on reflux. whichever is larger

Note:

Same requirement when pumpback reflux is on TRC.

SIDESTREAM DRAWOFF CONTROL 7



PUNPAROUND PRODUCT CIRCUIT

5 seconds or more on product.

Note:

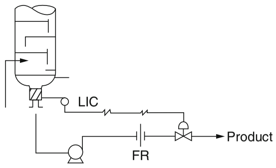
When product goes to subsequent processing* and when holdup feeding above tower is less than 15 minutes then pan must be installed with 15 minutes hold-up on product or 5 minutes on pumparound whichever is larger

- Where constant inflow rate is required.

(continued)

b

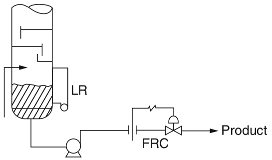
TOWER BOTTOMS CONTROL 1



MINIMUM BOTTOMS HOLDUP
TAR POT INSTALLATIONS

5-10 seconds on product

TOWER BOTTOMS CONTROL 2

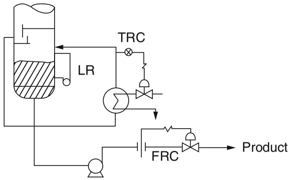


BOTTOMS TO SUBSEQUENT PROCESSING*

15 minutes on prodcut, or: 5 minutes on product (with LIC and FR, instead of LR and FRC) if holdup feeding tower is 15 minutes.

Note:
When product goes to tankage use: 5 minutes or more if product exchanger heat with process fluid, or 2 minutes or more if product is cooled.

TOWER BOTTOMS CONTROL 3

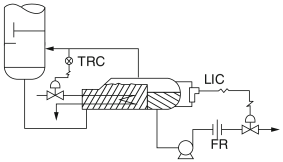


THERMO - SYPHON REBOILER
BOTTOMS TO SUBSEQUENT PROCESSING*

15 minutes on prodcut, or: 5 minutes on product (with LIC and FR, instead of LR and FRC) if holdup feeding tower is 15 minutes.

Note:
When product goes to tankage use: 5 minutes or more if product exchanger heat with process fluid, or 2 minutes or more if product is cooled.

TOWER BOTTOMS CONTROL 4

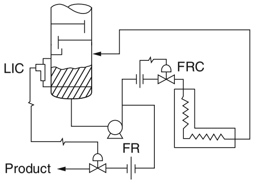


KETYLE - TYPE REBOILER
BOTTOMS TO TANKAGE OR SUBSEQUENT PROCESSING

5-10 seconds on product

Note:
Separate surge capacity with 15 minutes holdup is required if product is fed to subsequent processing* and when holdup feeding tower is less than 15 minutes.

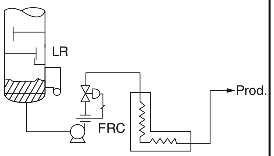
FURNACE FEED CONTROL 5



FIRED COIL REBOILER - PRODCUT DRAWOFF

Between NLL and LLL use either:
5 min. on product (if holdup feeding tower is 15 min,) or else 15 min.** on prod.
or:
10 min. on vapour plus 5 min. on liquid portions of furnace feed
whichever is greater plus:
3 min. on vapor portion of furnace feed below alarm level for safety (alarm level is set at 10% of the process instrument range).

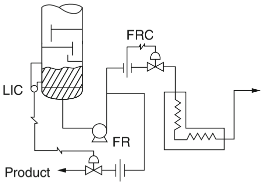
FURNACE FEED CONTROL 6



FIRED COIL PREHEATER FED FROM TOWER BOTTOM

Between NLL and LLL use:
5 min. on product for pipertille
15 min. on product for other towers.
Plus:
3 min. on furnace feed below alarm level for saftety (alarm level is set at 10% of the process instrument range).

FURNACE FEED CONTROL 7



FIRED COIL PREHEATER - PRODUCT DRAWOFF

Between NLL and LLL use either:
5 min. on product (if holdupfeeding tower is 15 min.) or else 15 minutes on product.
or:
5 minutes on furnace feed
Whichever is greater, plus:
3 min. on furnace feed below alarm level for safety (alarm level is set at 10% of the process instrument range).

- Where constant inflow rate is required.

** When 15 minutes on product is used provide FRC and LR instead of LIC and FR
HLL - High Liquid Level
LLL - Low Liquid Level

Fig. 13 (**a, b**) Typical surge requirements

For approximate control valve size:
One size smaller than line size. Thus:

Line	CV
4″	3″
6″	4″
8″	6″
10″	8″

Level Control

Surge volumes are maintained by controlling the amount of liquid entering or leaving the vessel in question. There are several means of accomplishing this and these are described and discussed in the following paragraphs:

- *Control the surge liquid outlet on level control*. This will give a close level control but a fluctuating outlet flow. The level control valve (LCV) will close completely at LLL. Thus, flow through the outlet line will be completely shut off at LLL.
- *Control the surge liquid outlet on flow control and provide a low level alarm*. This will give a fluctuating level but will eliminate flow fluctuations. As there is no LCV to restrict flow at LLL, then operators must physically reset the flow controller to maintain the surge volume. This has the disadvantage that the alarm condition could be missed or even ignored, resulting in possible damage to downstream equipment, and, in extreme cases, result in a fire or explosion hazard.
- *Control the surge liquid outlet on flow control reset by a level control*. This will give a wandering level but a smooth outlet flow. The LCV reset can still however cut off the flow completely on LLL.
- *Control the outlet flow by flow control and the system feed by surge volume level*. This will give close level control and also close outlet flow control. The outlet flow also will not be closed off by a LLL of the surge. In the case of feed to a fractionating tower, level control on the feed stream could cause tower upset conditions. This would be particularly undesirable on fractionators that operate close to critical conditions such as deethanizer.
- *Control the surge liquid on level control to an intermediate surge vessel*. The liquid from the surge vessel may then be flow controlled. This is the ideal method for controlling feed to a fired heater. The only question in this case is one of economics.

Level Control Range

Should the decision now be to use an LC on the surge outlet, the range of the instrument needs to be determined. The range is the vertical distance between the HLL and the LLL. Now if the liquid outlet is feeding another unit which requires a smooth flow, it is possible to achieve this by using a wide proportional band and a large range. The larger the instrument range and the wider the proportional band, the less sensitive is the level controller. Consequently the flow becomes smoother. However, the larger the range, the more expensive is the controller and of course the larger is the tower or vessel in order to accommodate the greater distance between HLL and LLL.

The selection of level control system and the level control range depends therefore on:

- How many outlet streams are there from the surge vessel?
- Which streams cannot tolerate complete shutoff before all the available surge is used?
- The degree to which the outlet stream requires smooth flow.

Surge and Level Control Summary

There are two very general rules to follow in selecting a control system for process inventory control. These are:

- If it is permissible for the product outflow rate to vary, use level control and a relatively small amount of surge capacity.
- If the product goes to a subsequent process where feed rate must be held constant, use flow control and considerably more surge.

Concluding Comments on Level Measurement and Control

There are numerous options for level sensing and control available. Each method has limitations. When selecting a means of measuring level, consider the entire range of operation over which the level instrument is expected to function from start-up, through operation, and to shutdown. How easy is it to maintain? What conditions will fool the level sensor?

Installation of level instruments must consider the process conditions, fluid, and phases to ensure reliable level indication. Maintenance of the level instruments is an important consideration also as they tend to require more attention than some other types of instruments.

Careful attention to the requirements and objectives for surge and level control actions is required. Think about how the level you are controlling fits into the process scheme and what the process needs for good management.

Composition Measurement and Control

Many processes require measurement and control of specific compositions or properties. Most often this is accomplished by periodic sampling of the process fluids followed by laboratory analyses. The lab results are then used to guide changes to the operation.

There are also a number of analyzers that can be installed online to measure specific properties. The online analyzer results can be used immediately for control.

New techniques have arisen in recent years that use calibrated correlations using normal operating parameters to infer properties for streams. We will touch on these, too.

Composition Measurement Elements

A large variety of online analyzers are available for measuring streams common in refineries and petrochemical plants. Table 10 provides a list of many of these options and where they can be applied. The following discussion will highlight a few of the more common online analyzer types.

- *Boiling point analyzer* – This analyzer can be used to determine the 5 % or 95 % points of products for fractionation control purposes, for instance. In this type of analyzer, a fixed, metered flow rate of stock is passed over a heater with vaporizes the sample. The surplus sample is then discharged at a rate appropriate to the desired % recovery. The heat input is varied to balance the target % vaporized. The balanced temperature of the vaporizer determines the boiling point at the desired % recovery.
- *Cloud point*, *pour point*, *or freeze point analyzer* – In these types of analyzers, a sample is introduced into the analyzer cell and cooled. The presence of crystals or complete solidification is determined optically by reflection or other means.
- *Distillation analyzer* – This can be an automated batch analyzer that essentially duplicates the ASTM distillation methods. These analyzers are expensive and maintenance intensive.
- *Chemiluminescence analyzer* – This type of analyzer works for compounds like NO, NO_2, NO_x, and O2. The analyzer makes use of the luminescence when the compounds are reacted with ozone. These analyzers are often found in emissions monitoring. They are often automatically calibrated on a set timing using calibration gas.
- *Flash point* – An example of this type of analyzer mixes air and sample together. Then sends them through a heater followed by a flash chamber where the mixture is subjected to a spark. The temperature at the flash chamber inlet is recorded when a pressure sensor sees evidence of a detonation.
- *Gas chromatograph* – This type of analyzer can be applied for many purposes, including tracking of separation quality in distillation columns. An online GC operates much like a lab GC. The preheated sample is periodically introduced into the column and the sample compounds are detected as they leave the column. The results are translated into the analysis. These analyzers tend to be expensive and require a great deal of maintenance.
- *Infrared and near-infrared* – There are several options available in the IR and NIR range. These look at IR transmittance through a sample compared to a reference stream at a specific wavelength (or wavelengths). Many properties can

be inferred from this analysis once calibrated, including octane and cetane. These can be used for continuous blending analysis, for instance. The analyzers are moderately expensive and require good calibration.

- *Ion-specific and pH electrodes* – These electrodes enable online analysis of several aqueous components continuously. The sample flows through where the electrode is immersed in the stream. The result is compared to a reference electrode. The electrodes must be replaced periodically. These systems are not overly expensive, but require regular maintenance and recalibration. The cells themselves are glass, so subject to breakage.
- *Mass spectrometer* – These analyzers are not common in refineries, but have been used to monitor fugitive emissions and gas analyses. The analyzer essentially rips the sample apart into ions and then passes the ions through a strong magnetic field where their deflection is a function of their mass and charge. The different ion concentrations are detected. The matrix of ion concentrations can be translated into composition. These instruments require regular calibration, specific to the service. They tend to be expensive and maintenance intensive.
- *Knock or cetane engine* – The normal laboratory knock or cetane engines can be adapted for online service, such as blending. These tend to be mechanically complex and require a lot of maintenance. They are also expensive. Some refiners have replaced the engines with NIR analyzers, although the final blends still require engine testing for certification.
- *Thermal conductivity* – These are very simple, inexpensive analyzers that use the heat transfer properties of the fluids being measured to infer compositions. They work well for gases like hydrogen in hydrocarbon gases. The analyzers are similar to the corresponding flow meters of the same types.
- *Ultraviolet spectrometer* – UV spectrometers are similar in principle to IR spectrometers using different light wavelengths. They may use absorption or transmittance.
- *X-ray fluorescence or absorption* – In these analyzers, a sample is excited by X-rays which cause it to fluoresce or absorb in specific wavelengths that depend on composition. The fluorescence or absorption is detected and translated to composition. These instruments require calibration and maintenance.

You can see that many of the methods employed in online analyzers are really just versions of laboratory instruments that have been adapted to field use and hardened to prevent damage. Most online instruments require regular calibration and maintenance to keep them running.

Online Analyzer Installations

Analyzers for online applications require appropriate sample taps and conditioning systems to ensure reliability and accuracy. This is critical in capturing the value that an analyzer can help create. If the analyzer is not available and reliable, the operators soon ignore it and all value is lost.

Table 10 A sampling of petroleum processing online analyzer applications

	Phase			Online analysis methods available															
Property	Solid	Liquid	Gas	Alumina capacitance/conductance	Boiling point analyzer	Calorimetry	Chemiluminescence	Cloud point analyzer	Colorimetry	Conductivity analyzer	Capacitance	Density (several options)	Distillation analyzer	Flame photometry	Flash point	Gas chromatography	Hardness	Infrared (various)	Ion – specific electrode or cell
Alkalinity		X																	
Ammonia			X				X											X	
Antimony	X	X																	
Aromatics		X	X																
Benzene		X	X																
Bromine	X	X																	
Cetane		X																X	
Chloride		X																	
Chlorine		X																	X
CO			X															X	
CO_2			X															X	
Combustibles			X			X													
Conductivity		X								X									
Dissolved oxygen		X																	X
Dissolved solids		X								X									
Distillation		X											X			X			
Emissions			X															X	
Gas composition			X													X			
H_2S		X	X				X												
Hardness		X																	X
HCl			X															X	
Heating value		X	X			X										X			
HF			X															X	X
Hydrocarbons		X	X													X		X	
Hydrogen			X																
Leak detection			X															X	
Metals (general)	X	X																	
Methane																		X	
NH_4HS		X																	X
Nitrates, Nitrites		X					X												
Nitrogen purity		X	X																
NO, NOx			X				X											X	

Light transmission	Mass spectrometer	Near – infrared spectrometer	Optical dew point	Oxidation cell	Phosphorous oxide electrolytic cell	Lead sulfide	Engine (knock or cetane)	pH electrolytic cell	Pour point analyzer	Parametric susceptibility	Resistance	Refractometry	Thermal conductivity	Thermal dispersion	Titration	Ultraviolet spectrometer	Viscometer (several kinds)	Vapor pressure analyzer	X – Ray fluorescence/absorption	Zirconium oxide fuelcell	Notes
								X							X						
													X								
																			X		
		X														X					
																X					
																			X		
		X					X														
																			X		
																X			X		Aqueous
													X								
				X							X		X								
																					Aqueous
																					Aqueous
																X					Air, CEMS
	X																				
						X					X					X					
																					Aqueous
	X												X								
													X	X							
	X																				
																			X		
																					Aqueous
													X								
																X					

(*continued*)

Table 10 (continued)

	Phase			Online analysis methods available															
Property	Solid	Liquid	Gas	Alumina capacitance/conductance	Boiling point analyzer	Calorimetry	Chemiluminescence	Cloud point analyzer	Colorimetry	Conductivity analyzer	Capacitance	Density (several options)	Distillation analyzer	Flame photometry	Flash point	Gas chromatography	Hardness	Infrared (various)	Ion – specific electrode or cell
Octane		X														X			
Oil in water		X																X	
Opacity			X																
Oxygen			X																X
Oxygen purity		X	X																
Petroleum products		X			X			X	X			X	X		X				
PH		X																	
Phosphate		X							X										
Phosphorous	X	X																	
Red-Ox potential		X																	X
Silica		X							X										
SO_2			X											X					
Sodium		X							X										X
Sulfur		X																	
Sulfuric acid		X										X							
Suspended solids		X																	
Toluene		X	X																
Toxic gases			X																X
Viscosity		X																	
Waste water		X																	
Water content	X									X	X						X	X	
Water content		X		X							X		X					X	
Water content			X	X						X								X	
Xylene		X	X																

Light transmission	Mass spectrometer	Near – infrared spectrometer	Optical dew point	Oxidation cell	Phosphorous oxide electrolytic cell	Lead sulfide	Engine (knock or cetane)	pH electrolytic cell	Pour point analyzer	Parametric susceptibility	Resistance	Refractometry	Thermal conductivity	Thermal dispersion	Titration	Ultraviolet spectrometer	Viscometer (several kinds)	Vapor pressure analyzer	X – Ray fluorescence/absorption	Zirconium oxide fuelcell	Notes
		X					X														
																X					Aqueous
										X										X	Excess 0_2
													X								
									X									X			
								X													
																					Aqueous
																			X		
																					Bleach
																					Aqueous
																X					
																					Aqueous
																			X		Oil
												X									
X																					
																X					
													X								
																	X				
																X					Aqueous
															X						
			X		X																
																X					

Sample Location and Lag Time

Analyzer samples may be drawn directly from the main process line and routed to the sample system through tubing. The tubing may be electrically or steam traced, depending on the fluid properties.

Ideally, the distance from the sample point to the analyzer should be as short as possible if tubing is used. Otherwise, the stream the analyzer is sampling has long since left the process and the sample data is meaningless.

To reduce the time lag between sampling and the analysis, it is common to establish a fast loop that has a much higher flow rate than a small sample tube. The fast loop starts at a high-pressure location and returns to a low-pressure location in the same process stream or another safe location. For instance, if the process has a level control valve on the stream, the fast loop flow could be pulled ahead of the valve and the fast loop return would be downstream of the valve. The fast loop line is routed to a location near the analyzer. A smaller sample line goes from the fast loop line to the analyzer, thus shortening the time from sample to analysis. The return sample can go back to a low-pressure point in the process, to slops or recovered oil, or to flare.

When a fast loop is incorporated into the design, care must be used to ensure the loop does not defeat the purpose of the control system or create unsafe conditions. If the fast loops work around a level control valve and if that valve closes due to a low-low level, the fast loop needs to stop also.

The sample point design needs to consider the flow conditions within the line being sampled:

- For a single-phase liquid or vapor, pull the sample from the top half of the line.
- For two-phase liquid and vapor, pull the sample from a section of line where the flow is turbulent and well mixed. Otherwise, attempts to get a good sample in two-phase lines are problematical.
- For large lines or ducts, it may be necessary to use an isokinetic line to get a representative sample.
- If there are foulants in the line, avoid any samples from the bottom of the line and it may be necessary to install a small extension of the sample tube into the line to avoid catching foulants running along the wall.
- In the case of flue gas excess oxygen analysis with ZrO_2 fuel cells, the probe must be inserted into the flue at high temperature. This is an exception to most sampling.

Obtaining a valid sample is the first critical step in getting a good analytical result. This applies to intermittent samples as well as continuous.

Sample Conditioning

A raw process sample needs to be “conditioned” in many cases to prepare it for analysis. A few of the situations frequently encountered in this regard are:

- *Cooling* – A hot sample will generally have to be cooled. There are high-pressure, high-alloy exchangers available for this purpose. Having to cool a sample is common for steam and condensate, some hydrogen plant samples, inter-reactor samples, and many others. The sample may be totally condensed as in steam samples or may contain noncondensable gases. If there are noncondensibles, a flash pot downstream of the cooler may be needed. The cooling system needs to prevent damage to the analytical instruments.

- *Liquid knockout/coalescing* – Sometimes you are only interested in the vapor and liquid will damage the analytical instrument. In these cases, as with cooling, a separator is needed ahead of the instrument. You have to be very careful, however, that the liquid removed is not part of what you are trying to analyze. For example, if the stream being analyzed is feed to a hydrogen plant and it has some condensable hydrocarbons that get removed in sample conditioning, the feed will be incorrectly characterized, resulting in too little steam and coking.
- *Filtration* – Most analytical instruments cannot handle incidental incoming solids or fines. These normally are removed by fine ($\ll 1$ μm) filtration. The filters need to be changed out on a routine basis.
- *Sample flow* – Most online analyzers are designed and calibrated for a specific flow rate. Deviations from the design sample flow rate will produce errors. Where critical, the flow is usually metered by a tiny rotameter or other constant flow control device.
- *Pressure reduction* – Many samples are taken at elevated pressures, but most sample analyzers operate at low pressures. Regulators are available to letdown the pressure. These are generally stainless or alloy and have very small C_Vs. There should always be filters ahead of the pressure regulator.
- *Manual sample point* – It is normal practice to incorporate a manual sample point into the sample conditioning system. This may be a routine operator sample point or it may only be used as a check sample for the analyzer.

Analyzer Installation

Many online analyzers are designed to be field installed. This would include pH and thermal conductivity analyzers. These instruments are hardened sufficiently that they are simply installed in the field on the process line or a takeoff from the line.

The more sophisticated analyzers, such as NIR, GC, or UV, require a controlled environment. This is especially important for environmental monitoring using continuous emissions monitors (CEMs). These analyzers are normally housed in small buildings with environmental controls. The buildings have positive pressure to prevent possible explosions in the event of a nearby hydrocarbon or hydrogen leak. This also means the analyzer and its associated electronics don't have to be explosion proof. Calibration gases or fluids are housed next to the building. If there is a fast loop from which the sample is drawn, the fast loop runs near the building, with only the smaller sample tubing entering the building. The sample conditioning system and analyzer with its electronics are inside the building. The sample vent or outlet line leaves the enclosure immediately after the instrument.

Sample Disposal

Once a sample is analyzed, you have to do something with the remains. For many samples that undergo nondestructive procedures, the sample can be returned to the process at a lower pressure point. If there is insufficient pressure to get back into the process, flare or slops/recovered oil systems are options. The destination has to be consistent with the hazards of the sample.

Some online analyzers for liquids may discharge the spent samples into a drum where they accumulate for later recovery. Be sure any such drum is well labeled to avoid regulatory problems.

Spent aqueous samples can often be sent to process sewer. If the samples become contaminated during analysis, they may need to be accumulated as a hazardous waste and periodically sent to disposal.

Inferred Properties

The growth of advanced control has brought the need for more continuous process analysis to take advantage of the improved techniques. This has led to the increasing use of inferred analyses for streams.

An inferred analyzer uses normal process data, such as flows, temperatures, and pressures, to estimate the value of a specific stream property that you would normally measure by sampling and lab testing. This enables much of the value of having an online analyzer with the hassle of actually having to buy it, install it, and maintain it.

Inferred properties are really just complex correlations based on analysis of a lot of operating and analytical data collected specifically for this purpose.

Inferred analysis is most often used for distillation-based properties. These could include 5 %, 10 %, 90 %, 95 %, and flash point. Inferred properties have also been used for following the concentration of a heavy key in a tower overhead or a light key in a tower bottoms.

Inferred analyses are periodically checked against the actual analysis by samples sent to the lab. The inferred property estimates are corrected based on the actual sample results. When an inferred property correlation drifts too far (i.e., the corrections are significant), a new correlation will be developed to replace the old.

The use of this approach is expected to expand as control systems become more sophisticated.

Controllers

Regardless of the architecture or type of control system being used, the core of the control system is the controllers themselves. These take the data from the various sensors in the field, the analyzers, the operator, the APC modules, and a variety of other inputs and determine the control moves that need to be made for each stream to satisfy all the desired operating conditions. The controllers then output the conditions to the field instruments, which make the actual adjustments. This is feedback control.

Types of Control Actions

While this is not a treatise on control instruments, it is appropriate to talk about some of the basic types of simple controllers encountered in a refinery as we draw the controls discussion to a close:

On/Off-Discrete Control

For some control applications, the controlled variable only needs to be kept between limits. For this purpose, we can use on/off control. You may find this type of control on a knockout drum level, where a level sensor signal goes to a controller that monitors the level. When the level reaches a fixed point, the controller turns on a pump and pumps the level down until it reaches a set low level. The controller then shuts off the pump until it is needed again. In some applications, there are only level switches at the high and low points and the action is accomplished with relays only.

PID Control

The most common type of control found in a refinery is PID control or proportional-integral-derivative. There are various forms of this control logic:

- Proportional only
- Proportional-derivative
- Proportional-integral
- Full PID

The terminology comes from the form of the controller equation:

$$u(t) = K_p e(t) + K_i \int_0^t e(\tau)\mathrm{d}\tau + K_d(de(t)/dt) \tag{15}$$

where:

$u(t)$ = controller output
K_p = proportional gain, tuning parameter
K_i = integral gain, tuning parameter
K_d = derivative gain, tuning parameter
e = error or difference between set point and measured variable
t = time or instantaneous time
τ = variable of integration between time 0 and time t

In the equation, the first term $[K_p e(t)]$ is called the proportional term because the output from it is proportional to the error from set point.

The second term $[K_i \int_0^t e(\tau)d\tau]$ is called the integral term. The contribution of this term is determined by both the magnitude and the duration of the deviation. If the measured value is far from the set point, the integral term makes a bigger move on output.

The final term $[K_d(de(t)/dt)]$ is the derivative term. This term fine-tunes the output for how quickly and in what direction the actual measurement is changing relative to the set point.

In practice, you will normally find:

- *Proportional control* – where only the first term is used. In proportional control, the output only changes if there is a deviation. If the error is constant, the output is constant, but it may not be at the set point. There is generally an offset between the set point and the process variable to make it work. Proportional band and gain are the tuning parameters. Proportional band is the % change in error that causes a 100 % change in output. Gain or proportional gain is the % change in output divided by the % change in input.
- *PI control* – where proportional and integral are used. This eliminates the error in proportional control but may result in a “reset windup” that drives the process variable too far or overshoots the set point. Then it takes a long time to get back. This is driven by reset rate or the frequency with which the control loop takes action (in resets per minute or minutes per reset). You may get cycling if not properly tuned.
- *PD control* – where proportional and derivative are used. Improves the rate of response of the controller. The derivative acts to boost the proportional controller output based on the rate and direction that the error is changing. This helps in slow processes. Can cause cycling in fast processes. The rate setting for derivative is normally in minutes.
- *PID control* – where all the terms are used. When tuned properly this provides the best basic control for a process, but tuning can be difficult.

Control Loop Tuning

There is automatic control loop tuning software available, but it is helpful to understand how the different types of control terms can be tuned. This is a very simple approach but can be a start:

- *Proportional* – Reduce the proportional band (or increase the gain) until the process begins to swing after a disturbance. Then double the proportional band or cut the gain in half.

- *Integral* – Increase the repeats per minute (or reduce the reset) until the process begins to cycle following a disturbance. Then reduce the reset to about one third of the setting.
- *Derivative* – Increase the rate setting until the process cycles after a disturbance. Then reduce the rate to one third of the value.

Conclusion

This has just been a survey around the various aspects of control systems as applied in refining today. For additional information, consult the listed references of any of the myriad materials available online and in your technical library on the subject.

Appendix 1: Control Valve Sizing

Process Flow Coefficient (C_v) and Valve Sizing

Process flow coefficient C_V is defined as the water flow in GPM through a given restriction for 1 psi pressure drop. These C_Vs can be determined by the following equations:

$$C_v = Q_L \sqrt{\frac{G_L}{\Delta P}} \text{ for liquid} \tag{16}$$

$$C_v = \frac{Q_s}{82} \sqrt{\frac{T}{\Delta P - P_2}} \text{ for steam} \tag{17}$$

$$C_v = \frac{Q_G}{1360} \sqrt{\frac{\mu_2 ST}{\Delta P - P_2}} \text{ for gases} \tag{18}$$

where:

C_v = flow coefficient
Q_L = liquid flow in GPM at conditions
ΔP = pressure drop across valve, psi
G_L = specific gravity of liquid at conditions
Q_S = steam rate in lbs/h
P_2 = pressure downstream of valve psia
Q_G = gas flow in SCFH (60 °F, 14.7 psia)
T = temperature of gas °R(°F + 460)
S = mol weight of gas divided by 29
μ_2 = compressibility factor at downstream conditions

The following are some special considerations that may have to be made in determining process C_V values.

Pressure Drop

For compressible fluids the maximum usable pressure drop in equations (b) and (c) is the critical value. As a rule of thumb and for design purposes, this value is 50 % of the absolute upstream pressure. (The valve can take more than the critical pressure drop, but any pressure drop over the critical takes the form of exit losses.)

Flashing Liquids

In the absence of accurate information, it is recommended that for flashing service the valve body be specified as one nominal size larger than the valve port.

Two-Phase Flow

If two-phase flow exists upstream of the control valve, experience has shown that for fluids below their critical point, a sufficiently accurate process C_V value can be arrived at by adding the process C_V values for the gas and liquid portions of the stream. The calculation is based on the quantities of gas and liquid at upstream conditions. The valve body is specified to be one nominal size larger than the port to allow for expansion.

Valve Rangeability

The rangeability of a control valve is the ratio of the flow coefficient at the maximum flow rate to the flow coefficient at the minimum flow rate ($R = C_V$ Max/C_V Min). Valve rangeability is actually a criterion which is used to judge whether a given valve will be in a controlling position throughout its required range of operation (neither wide open nor fully closed). In practice the selection of the actual valve to be installed is the responsibility of the instrument engineer. As the process engineer is usually the person responsible for the correct operation of the process itself; however, he must be satisfied that the item selected meets the control criteria required. He must therefore satisfy himself that the valve will control over the range of the process flow.

Control valves are usually limited to a rangeability of 10:1. If R is greater than 10:1, then a dual-valve installation should be considered in order to assure good control at the maximum and minimum flow conditions.

In some applications, particularly on compressor or blower suction, butterfly valves have been specified to be line size without considering that as a result the valve may operate almost closed for long periods of time. Under this condition, there have been cases of erosion resulting from this. It is recommended therefore that butterfly valves be sized so that they will not operate below 10 % open for any appreciable period of time and not arbitrarily be made line size.

Valve Flow Coefficient ($C_{V'}$)

In order to ensure that the valve is in a controlling position at the maximum flow rate, the valve $C_{V'}$ is the maximum process C_V value determined above, divided by 0.8. The reasons for using this factor are that:

- It is not desirable to have the valve fully open at maximum flow since it is not then in a controlling position.
- The valves supplied by a single manufacturer often vary as much as 10–20 % in C_V.
- Allowance must be made for pressure drop, flow rate, etc., values which differ from design.

Control Valve Sizing

Control valve sizes are determined by the manufacturers from the process data submitted to them. However, there are available some simple equations to give a good estimate of the required valve sizes to meet a process duty. Three of these are given below: Single-seated control valve sizes may be estimated by:

$$S(\text{inches}) = \left[\frac{\text{Valve}\,C_V}{9}\right]^{1/2} \tag{19}$$

Double-seated control valve sizes may be estimated by:

$$S(\text{inches}) = \left[\frac{\text{Valve}\,C_V}{12}\right]^{1/2} \tag{20}$$

Butterfly valve sizes may be estimated by:

$$S(\text{inches}) = \left[\frac{\text{Valve}\,C_V}{20}\right]^{1/2} \tag{21}$$

The constants (9, 12, or 20) in the denominators of these equations can vary as much as 25 % depending on the valve manufacturer.

A control valve should be no larger than the line size. A control valve size that is calculated to be greater than line size should be carefully checked together with the calculation used for determining line size. Usually, a control valve size should be one size smaller than line size.

Once the valve size is estimated and the valve C_V known, then the percent opening of the valve at minimum flow and maximum flow can be obtained by dividing the respective process C_V values conditions by the selected valve C_V. This information is normally required to check the percent opening of a butterfly at minimum flow. It is not normally necessary to calculate it for any other type of valve.

Valve Action on Air Failure

In the analysis of the design and operation of any process or utility system, the question always arises on the action of control valves in the system on instrument air failure. Should the control valve fail open or closed is the judgment decision of the process engineer after evaluating all aspects of safety and damage in each event. For example, control valves on fired heater tube inlets should always fail open to prevent damage to the tubes through low or no flow through them when they are hot. On the other hand, control valves controlling fuel to the heaters should fail closed on air failure to avoid overheating of the heater during the air failure.

The failure action of the valve is established by introducing the motive air to either above the diaphragm for a failed open requirement or below the diaphragm for a failed shut situation. The air failure to the valve above the diaphragm allows the spring to pull up the plugs from the valve seats. Air failure to valves below the diaphragm forces the spring to seat the valves in the closed position. Failure of a valve in place or locked is also possible, but seldom used.

References

Flow Measurement and Control

Alicat.com, Types of gas mass flow meters (2005). Accessed Jan 2014

W. Chin, Magmeters: how they work and where to use them. Control Mag. 32–34 (Krohne America, 1990)

W.S. Corcoran, J. Honeywell, Practical methods for measuring flows. Chem. Eng. Mag. 86–92 (Fluor Engineers and Constructors, Inc., 1975)

DAC Electric, High voltage variable speed drives, www.dac-electric.com. Accessed 29 Jan 2014

J.W. Dolenc, Choose the right flow meter. Chem. Eng. Progress. 22–32 (Fisher-Rosemount, 1996)

D. Ginesi (Bristol Babcock Inc.), G. Grebe (Cincinnati Test Systems), Flow meters: a performance review. Chem. Eng. Mag. 100–118 (1987)

D. Ginesi, Choices abound in flow measurement. Chem. Eng. Mag. 88–100 (Foxboro Co., 1991)

D. Ginesi, A raft of flowmeters on tap. Chem. Eng. Mag. 146–155 (Foxboro, 1991)

Greyline, Two technologies for flow measurement from outside a pipe, www.greyline.com. Accessed 27 Jan 2014

R.C. Hunt, Oscillatory flowmeters: an effective solution for flow measurement (MycroSENSOR Technologies, 2002), www.fluidicflowmeters.com. Accessed Jan 2014
Instrumart.com, Vortex shedding flow meters, www.instrumart.com. Accessed 27 Jan 2014
R. Kern, How to size flow meters. Chem. Eng. Mag. 161–168 (Hoffmann-La Roche Inc., 1975)
P.K. Khandelwal (Uhde India), V. Gupta (Sycom Consultants Consortium), Make the most of orifice meters. Chem. Eng. Progress 32–37 (1993)
M.D. Kyser, Positive displacement flow measurement. Control Mag. 40–42 (Badger Meter, 1990)
G. Livelli, Selecting flowmeters to minimize energy costs. Chem. Eng. Prog. 34–39 (ABB, 2013)
C.J. O'Brien, Flowmeter terms, types, & successful selection. InTech Mag. 30–33 (Moore Products, 1989)
S. Peramanu, J.C. Wah, Improve material balance by using proper flowmeter corrections (Canadian Natural Resources, 2011), www.hydrocarbonprocessing.com. Accessed Jan 2014
Seekyouranswers.blogspot.com, Turbine flow meter (2013). Accessed Jan 2014
Siemens Moore Process Automation, Inc., Three element feed control system. Accessed 29 Jan 2014
Spirax Sarco, Types of steam flowmeters, Steam engineering tutorials, www.spiraxsarco.com. Accessed 29 Jan 2014
J. Taylor, Selecting the right flow meter for your hydronic system (Wood-Harbinger, 2013), www.woodharbinger.com. Accessed Jan 2014
P.C. Tung, M. Mikasinovic, Sizing orifices for flow of gases and vapors. Chem. Eng. Mag. 83–85 (Ontario Hydro, 1982)
Wikipedia, Mass flow meter. Accessed 27 Jan 2014

Temperature Measurement and Control

R.H. Kennedy, Selecting temperature sensors. Chem. Eng. Mag. 54–71 (The Foxboro Co., 1983)
J.G. Seebold, Tube skin thermocouples. Chem. Eng. Progress 57–59 (Chevron Corp., 1985)
Wikipedia, Resistance thermometer. Accessed 30 Jan 2014
Wikipedia, Thermocouple. Accessed 30 Jan 2014

Pressure Measurement and Control

Ashcroft Inc., Pressure gauge installation, operation, and maintenance, www.ashcroft.com. (2002). Accessed Jan 2014.
R.E. Bicking, Fundamentals of pressure sensor technology. Sens. Mag. (1998)
W.J. Demorest, Jr., Pressure measurement. Chem. Eng. 56–68 (Honeywell Inc., 1985)
K. Hamza, *Pressure Measurement*, http://science-hamza.blogspot.com/ (Cairo, 2011). Accessed Jan 2014.
Instrumentationtoolbox.com, Strain gauge substitute (2011), www.instrumentationtoolbox.com. Accessed Jan 2014
B.G. Liptak, Pressure regulators. Chem. Eng. 69–76 (Bela G. Liptak Assoc., 1987)
R. Repas (Machine Design), C. Dixon (Kavlico Corp.), ABCs of refrigeration pressure sensing (2008), machinedesign.com. Accessed Jan 2014
D.L. Roper, J.L. Ryans, Select the right vacuum gage. Chem. Eng. 125–144 (Tennesee Eastman Co., 1989)
A.W. Sloley of The Distillation Group, Inc. Chem. Eng. Progr., (Jan 2001)
Winters instruments website, http://winters.com/. Accessed Jan 2014

Level Measurement and Control

D. Anderson, Match fit radars. Hydrocarb. Process. 104–109 (Vega Controls Ltd., 2013)

Control, What's the best way to control an interface level when an emulsion tends to form between phases? Control 48–52 (1992)

P. Hagar, Avoid temperature differences when using external chambers. Control 71–73 (Syncrude Canada, 1995)

E.A. Knight, J.R. Pugh, Properly select level-measurement devices for bulk solids. Chem Eng Progress 50–55 (Glasgow Caledonian University, 1996)

B.G. Liptak, Level measurement with problem liquids. Chem Eng. 130–133 (Bela G. Liptak Assoc., 1993)

S. Parker, Selecting a level device based on application needs. Chem. Process., Fluid Flow Annual 75–80 (Fisher-Rosemount, 1998)

B.O. Paul, Seventeen level sensing methods. Chem. Proc. 63–72 (Editor, 1999)

L.M. Wallace, Sighting in on level instruments. Chem. Eng. 95–104 (Fluor E&C, 1976)

Composition Measurement and Control

Controls Wiki, Process control definitions and terminology (2013), https://controls.engin.umich.edu. Accessed Jan 2014

PAControl.com, Process control fundamentals (2006), www.PAControl.com (Excellent and clear). Accessed Jan 2014

F.G. Shinskey, Foxboro, *Process Control Systems: Application, Design, and Tuning* (McGraw Hill Publishing Company, New York, 1988)

Wikipedia, PID controller. Accessed 3 Feb 2014

Utilities in Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_17

Abstract

All oil refineries and other petroleum processing facilities need utilities in order to function. The common utility systems include steam, fuel, various waters, air, electrical power, and sewers, among others. This chapter explores the processes, design, reliability, and operation of these critical systems.

Keywords

Utilities • Refinery • Steam • Power • Water • Fuel

Introduction

All oil refining processes require utilities in order to function. The common utility systems are:

- Steam and condensate
- Fuel (gas and oil)

- Water systems (cooling, boiler feed, potable, fire)
- Compressed air (instrument, plant)
- Electrical power supply
- Nitrogen
- Sewers (oily water/plant, chemical, storm)
- Other utilities

The engineering and design of several of these systems is usually the responsibility of a chemical engineer. On operating plants and processes, the process engineer undertakes the responsibility for the correct and efficient operation of utility facilities. The duties associated with the power systems are usually left to the electrical engineer or department, although the process engineer does have an input in the sizing of the system by developing a list of power requirements for all electrical equipment. This includes all motors and electrically operated equipment such as: the desalter, product dehydrators, electrostatic precipitators, and the like.

Because utility systems are so critical to the operation of a processing facility, it is necessary to ensure the security of these systems. Redundancy and other methods are used to ensure reliable supplies. Anti-backflow and anti-cross-contamination provisions are required to ensure the utilities are not contaminated by process fluids or other utilities. Remarks on typical methods to maintain system reliability and potential traps are incorporated into the discussion of each utility.

The following paragraphs describe the typical utility systems found in the oil refining industry. The details of these systems may vary from facility to facility, but their format and general layout will be similar to that described here.

Steam and Condensate Systems

Steam is the most basic utility in a refinery. Many of the uses of steam have been around since ancient times. While it has largely been replaced by electrical power in driving machinery, it still maintains several roles, including process heating, process reactant, driving rotating equipment, and heat tracing/retention.

An important feature of steam for many uses is its extreme reliability. It is not unusual for steam systems to have been in service, without outage, for 40–50 years. No other utility can claim that level of reliability. Of course, the system has to be designed specifically for that sort of reliability and the associated maintenance. We will mention some of the techniques for maintaining steam availability at all times.

The Refinery Steam System

Figure 1 illustrates a configuration and integration of a typical steam system in a modern refinery. The system is centered on steam headers that run throughout the facility to distribute or accept steam at different pressure levels. The highest level (HP Superheated) is usually a high pressure, superheated steam at

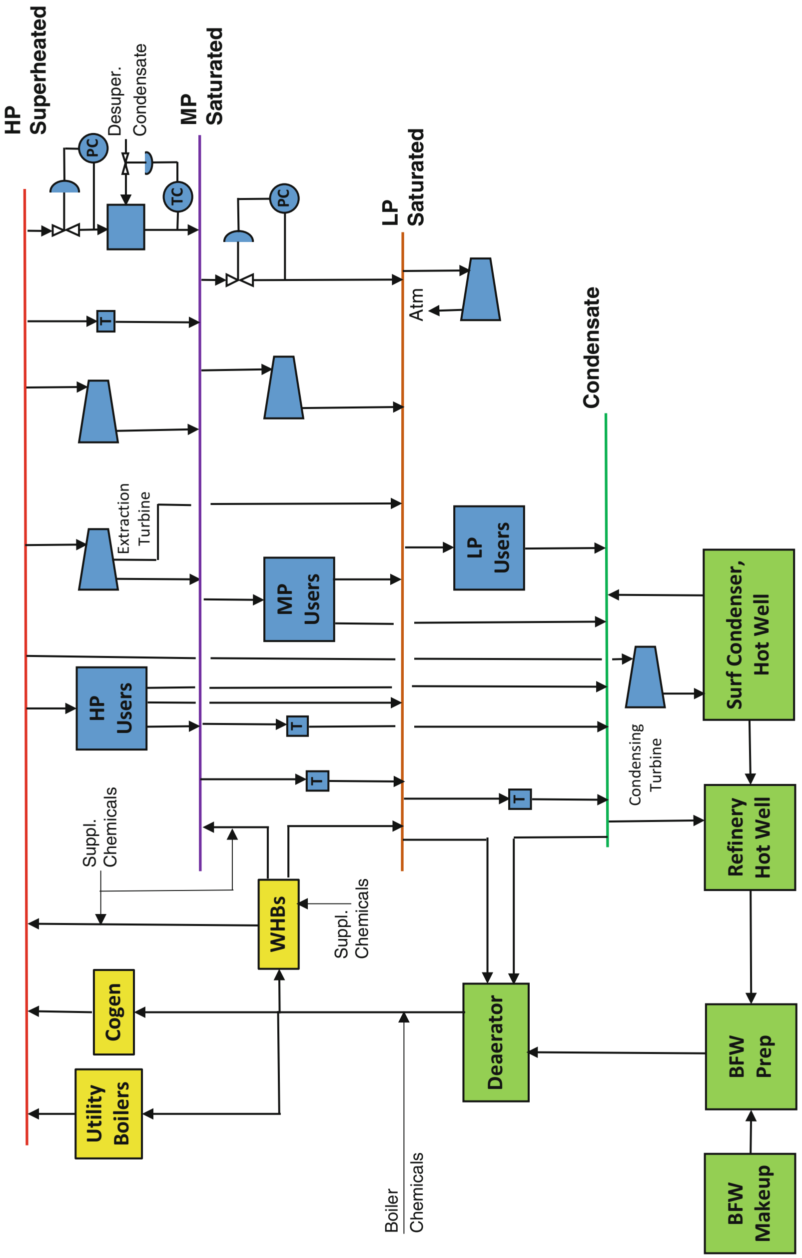


Fig. 1 Typical refinery steam system

about 600 psig (~40 barg) with, perhaps, 180 °F (100 °C) of superheat. This high-pressure steam supplies dry steam to turbines and other users. The high-pressure steam is letdown to lower-pressure levels through turbines and control valves with desuperheating.

The MP-saturated steam header may run about 150 psig (10 barg). It may also feed turbines and process heat users. Often, waste heat boilers supply this header.

The lowest steam pressure header (LP Saturated) usually runs around 50 psig (3–4 barg). It is primarily used for steam tracing, but can also supply heat for low-pressure reboilers, strippers, and the deaerator. There are sometimes emergency generator or compressor steam turbines tied to the LP header that exhaust to atmosphere. They are not normally in service.

All the steam headers cascade eventually to the condensate header(s) which operates at low pressure (5–10 psig or 0.3–0.7 barg). Higher pressure, intermediate condensate headers may also be present.

Some large turbine drivers may also contain surface condensers and operate with deep vacuums at the turbine final stage outlet. The surface condensate has to be pumped to the combined condensate systems for reuse. Because the surface condenser runs at vacuum, it often pulls air into the system, adding load to the boiler feed water deaerator and oxygen scavenger chemicals.

Boiler feed water makeup is very expensive, so most refineries try to maximize the reuse of condensate, adding only supplemental boiler feed water (BFW) makeup from softeners, demineralizers, or reverse osmosis units. We will discuss the production of BFW a little later in this chapter.

Steam generation is critical to the system. The traditional generator is the utility boiler. In addition, refineries today will generate steam from waste heat boilers (AKA heat recovery steam generators) tied to the process units and from cogeneration facilities, which make both steam and power. Another company may own and operate the cogeneration facility in an over-the-fence arrangement.

Of course not all facilities have all these headers, generators, and users, but this is a very common configuration in many refineries and petrochemical facilities.

Components of the Steam System

There are many components in a refinery or petrochemical plant steam system. This section will describe some of the key components.

- Boiler feed water manufacture
- Steam generation
- Waste heat boilers
- Pressure letdown and desuperheating
- Steam traps and condensate headers

Refer to Fig. 2 in the following discussion, which provides additional detail.

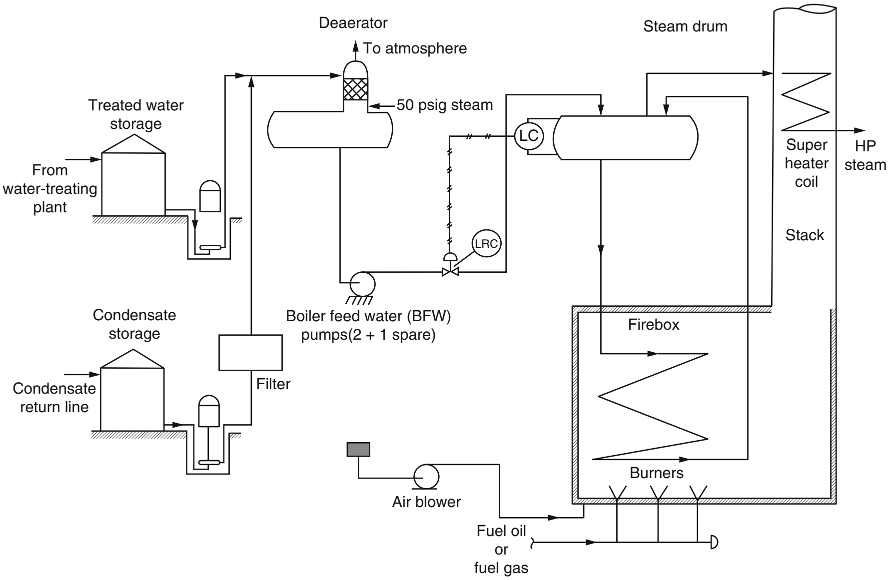


Fig. 2 A typical steam generation unit

Making Boiler Feed Water

In most plants steam condensate, accumulated in the various processes, is collected into a single header and returned to the steam-generating plant. It is stored separately from the treated raw water, because condensates may contain some oil contamination. There is additional discussion of condensate issues later in this section.

A stream of treated water and condensate are taken from the respective storage tanks and pumped to the deaerator drum.

The condensate stream passes through a simple filter en route to the deaerator to remove solid contamination. The combined water and condensate streams enter the top of a packed section of the deaerator called the "heater section." Low-pressure steam is introduced immediately below the packing in the drum to flow upward countercurrent to the liquid streams. Any air or CO_2 entrained in the water is removed by this countercurrent flow of steam to be vented to atmosphere. The combined, deaerated waters are the boiler feed water (BFW).

An oxygen-scavenging chemical is usually injected into the deaerator tank or drum to remove any residual, trace oxygen. The target oxygen is usually less than about 10 ppb. BFW leaving the deaerator tank is usually injected with the boiler chemicals.

Refer to section "Boiler Feed Water (BFW) Treating" for a more detailed discussion on making BFW.

Steam Generation

The deaerated BFW is pumped by the BFW pumps into the steam drum of the steam generator. There will normally be multiple pumps for this service (e.g., 3 × 60 % each).

Two will be operational and one will be on standby. Those pumps normally operating are usually motor driven, while the standby pump is very often driven by an automatically started steam turbine or diesel engine. These pumps are quite large in capacity, operating at high head and discharge pressure. The main steam lines in most plants are high pressure (at least 700 psig at the generator coil outlet), so the pump discharge pressure will be much greater than the HP steam outlet. These pumps are the most important in any refinery or chemical plant. If they fail, no steam can be generated, and the whole complex is in danger of total shutdown or worse. Therefore multiple separate pumps are used to cater for the normal high head and high capacity, and a separate pump driver operating on a completely different power source than electrical power or steam is mandatory to minimize the danger of complete shutdown.

The steam drum is located above the generator's firebox. The liquid in the drum flows through the generator's coils located in the firebox by gravity and thermosiphon. A mixture of steam and water is generated in the coils and flows back to the steam drum. Here the steam and water are separated from the stream. The saturated steam from the drum goes through a non-return (check) valve and flows to a superheater coil.

The steam is heated to the plant's HP steam main temperature in the superheater coil and enters the high-pressure steam header for distribution to the various users. The steam pressure is controlled by a pressure controller on the steam outlet to the header.

Waste Heat Boilers

Most refinery and petrochemical processes occur at greatly elevated temperatures. The process schemes usually preheat feedstocks for the process using heat in the process effluent. This works economically down to a point, but often there is more than enough process heat to supply the preheat needs. In those cases, waste heat boilers (WHBs) are often used. In a hydrogen plant, the waste heat boilers can actually be major sources of steam in a facility. Cogeneration is really just another form of waste heat boiler, where the surplus heat coming from the turbine or engine generator set can be used to raise and superheat steam.

WHBs take two common forms:

- For large heat sources, the WHB will have exchangers or coils in the process or flue gas along with a steam drum. These systems essentially operate like the utility-type boiler described above. They may deliver saturated or superheated steam to the steam headers.
- For many smaller heat sources, the WHB will take the form of a kettle with a steam separator (see Fig. 3). BFW brought into the kettle is boiled off, collected, runs through a steam separator, and then enters the steam header. These systems usually make only saturated steam. The kettle must be periodically blown down to maintain conductivity control.

Some WHBs have their own BFW systems, and it may be necessary to treat the steam from these generators separately for condensate corrosion control.

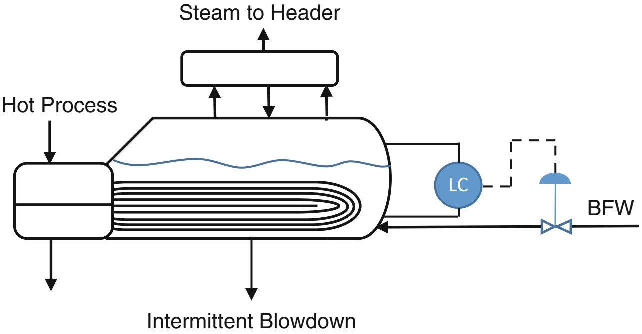


Fig. 3 Kettle-type waste heat boiler arrangement

Pressure Letdown and Desuperheating

Steam to the lower-pressure headers is generated through turbines where possible. Where lower-pressure steam is required and it is not possible to produce it through equipment, then letdown stations are located in suitable places in the system. When steam pressure is reduced to the lower-pressure headers, the associated increase of temperature above that specified for the lower-pressure steam may need to be reduced. Desuperheaters are used for this purpose.

A desuperheater consists of a chamber in the steam line into which cooler condensate is injected. These items are purchased equipment with specially designed injection nozzles for the condensate. The amount of condensate delivered is controlled by the downstream temperature of the steam. Desuperheaters are located at critical locations of the plant where relatively large quantities of high-pressure steam are reduced to low pressures such as the discharge from turbines.

Steam Traps and Condensate

There is continuous heat loss from the steam headers. This causes local condensation of the steam, especially in low flow regions. This condensate will collect at low points in the headers. With flow changes or even normally, the condensate can damage the headers through pipe hammer or the turbines and control valves through erosion. The condensate can also freeze in cold weather, rupturing the lines where it has collected. For these reasons, steam traps are installed on steam lines. The traps are located at low points in the lines and at each drop ahead of a steam turbine. The traps help insure the steam is dry, where required. They also protect the condensate header from overpressure by steam blow-through from the higher-pressure steam headers.

There are several types of condensate traps available from manufacturers. The most commonly found traps in refineries and petrochemical facilities are thermodynamic and bucket types, although others (like continuous drainer float types) are used in specific services.

Sizing of steam traps is an important consideration and is often overlooked. A trap that is too large and does not cycle frequently enough will fail, as will a trap that is too small and cycles all the time. A trap should open and close at least every few minutes. Monitoring and repairing failed traps can save a great deal of energy. Manufacturers have tools and techniques for monitoring trap operation.

Avoid trapping high-pressure steam directly to condensate. It is best to trap high-pressure steam to medium-pressure or low-pressure steam as shown in Fig. 1.

When most types of steam traps fail, they blow steam through into the lower-pressure header. This failure mode is somewhat by design as it continues to maintain dry steam at the expense of higher usage. But, this can overpressure the downstream header, especially if it is the condensate header, and prevent other traps from functioning properly. Monitoring of steam traps can be as simple as listening to them for how often they cycle or as complex as infrared monitoring. Manufacturers have simple tools and techniques for monitoring trap operation. There is a great deal of good training information about traps that is worth your review. Much is available on the Internet.

The traps ultimately cascade down to the condensate header(s). The main condensate return header is usually operated at a positive pressure of between 5 and 10 psig (0.3–0.7 barg). The collected condensate is stored at atmospheric pressure, and very often the small amount of steam flashed from the header pressure to the storage pressure is used in the deaerator instead of the low-pressure steam (the deaerator operates at or near atmospheric pressure).

Note that the recovered condensate will be reused as boiler feed water, hydroprocessing wash water, process makeup water, and so on. It can come from many places, some of which may contaminate the condensate. Ahead of the facilities depicted in Fig. 2, hot condensate should be collected in one or more “hot wells” and then forwarded by pump to the common storage tank(s) or header. The vapor space in the hot well should be monitored for hydrocarbons, which would indicate possible leaks into the condensate system. Small quantities of oils can usually be handled, but larger amounts of oil or oxygen are not allowed.

If a significant leak is identified, that condensate should be dumped to sewer (or a safe location) until the leak can be eliminated; otherwise, the steam system becomes contaminated with hydrocarbon or oxygen, which is not healthy in many of the steam uses. For instance, you cannot have hydrocarbon in your steam when you are trying to gas-free a fired heater before lighting it or when you are trying to gas-free a vessel for maintenance.

Utility Steam Stations

Most plants have utility steam stations that come off the medium- or low-pressure steam headers. These numerous “utility drops” are located strategically throughout the units. The stations have steam hoses for use in cleaning equipment, temporary heating, and many other uses. There is a steam trap located just upstream of the utility station.

Often these utility stations also have plant water and plant air connections. The steam and plant water systems are sometimes connected to allow direct injection heating of the plant water that can be controlled manually or with a self-contained steam valve. There is further discussion of these stations under the appropriate other utilities in this chapter.

Prevention of Steam System Contamination

As with most utilities, it is necessary to ensure that what comes out of the steam lines is steam *and only steam*. Wherever steam is connected to the process, there should be backflow prevention consisting of one or more check valves, one or more block valves, a bleeder, and an isolation point (blind) as a typical minimum.

Connections made for steaming process vessels and other cleanout purposes should be removed immediately after use and especially before pressuring the process system.

These are normally considered best practices, but often get overlooked.

Boiler Controls

Utility boiler systems, and some waste heat boiler services, are designed for reliable, nearly self-contained control of the boiler.

The primary control on the boiler is aimed at maintaining steam pressure at its set point. This is accomplished by controlling the fuel pressure/flow rate to make as much steam as is needed to hold the pressure. Air is normally supplied to the boiler firebox based on demand using a forced draft fan. The air may be preheated by flue gas. If there is a preheater, there will normally also be an induced draft fan that controls the heater draft (firebox pressure) and fine-tunes the draft based on excess oxygen and CO in the flue.

Because the boiler will attempt to make whatever steam is demanded, it could run dry unless the water supply is ensured. Water supply is ensured by use of a three-element control scheme in most systems. This is covered in the handbook chapter entitled "► Process Controls in Petroleum Processing" under the section on "Evolution of Control System Types". Using steam rate and steam drum level changes, a 3-element control brings in BFW on flow control so that the boiler has water under all conditions unless the water supply fails completely. This is a material balancing system.

Steam drum or kettle boiler level instrumentation has to be compensated for the difference in densities between the steam drum/kettle and the level bridle/instrument. This adjustment can be significant. Inside the drum/kettle, the water is much hotter than the level instrument, and there will likely be multiple phases present. The liquid is also turbulent, not a quiet level. In the level instrument, the fluid is cooler, more dense, and quieter. If you run the level instrument at the same level you want in the drum, the actual level in the drum will be much higher, leading to carryover. Be sure to properly account for the density differences and fluid dynamics involved.

Boiler and Condensate Chemical Treatment

We alluded to boiler chemicals earlier. There are four treatment objectives for boilers:

- Eliminate contaminants that can deposit downstream
- Prevent corrosion by dissolved oxygen and CO_2

- Prevent deposition and corrosion of the steam generation system
- Prevent corrosion of the condensate system

The elimination of contaminants from the BFW is accomplished by demineralization, softening, or reverse osmosis as noted earlier. These processes will be discussed in more detail later.

Oxygen and CO_2 are removed by steam stripping of the BFW in the deaerator as previously described. In a BFW system, either inorganic or organic oxygen scavengers can be used to eliminate any remaining, trace dissolved oxygen. The most common inorganic scavenger is sodium sulfite (Na_2SO_3). Organic scavengers often take the form of derivatives of erythorbic acid. The scavengers are injected into the deaerated water leaving the heater/stripper as it drops into the drum/storage section of the deaerator.

Corrosion and deposition in the boiler system are managed a couple of different ways. The buildup of dissolved solids and hardness in the boiler water is managed by purging or blowing down a small percentage of the water in the boiler. The lower the purity of the feed water, the more boiler water must be purged. In a large steam generator, there will usually be a small continuous blowdown pulled near the surface of the water level in the steam drum and an intermittent blowdown pulled through a pipe along the bottom of the steam drum and any mud drums (low points).

In addition to blowdown, a chemical mixture is used to manage deposits and corrosion in the boiler systems. These impacts come from accumulation of iron, calcium, and magnesium. Blowdown controls these somewhat, but chemicals help the blowdown to be effective. The common chemicals used are phosphates for precipitating solids, a chelant for complexing the potential foulants, and a polymer dispersant to keep foulants and corrosion products moving into blowdown. High purity caustic may also be injected for pH control. These chemicals are normally injected into the BFW as it heads to the users and may be supplemented at the users.

The condensate system ends up collecting all the CO_2 and other acidic compounds that may be in the steam system. The pH of the condensate system can be quite low. pHs as low as 3.0 have been reported in untreated condensate systems. To control condensate corrosion, amines and oxygen scavengers are normally injected into the steam header at the source leaving the boilers. One or more amines are selected so that they drop out into the steam and condensate headers at different temperatures. An incorrect amine selection will result in corrosion of one of the headers.

Chemical vendors are a valuable resource for understanding boiler treatment chemistry and solutions to corrosion or fouling problems.

More detail on boiler feed water chemistry is in section "Boiler Feed Water (BFW) Treating" of this chapter.

High Reliability Steam Supply

Reliability of steam supply is critical to plant operations. Many facilities depend on backup steam when the primary electrical system fails to supply the most sensitive operations.

Steam reliability starts at the BFW level. The purification equipment that supplies the BFW makeup should be redundant. Multiple trains are generally available to purify the water. A significant amount of purified water is normally held in a storage tank. The tanks should be sized to contain all the water needed by the plant steam system for several hours, typically 12–24 h. This means a big tank. If process water users pull off the tank, the suction lines to these users should be high in the tank so that there is sufficient water reserved below their connections for the boilers.

BFW from the tank is pulled by multiple, redundant transfer pumps (possibly separate connections to the tank) to the deaerator. The transfer pumps will usually be electrically driven with steam or diesel backup. The deaerated water is usually sent to the steam generators via multiple, redundant, high-pressure BFW pumps using at least two different types of drives.

In the most reliable configurations, there are at least two primary steam generators (sometimes several) that have priority over any other generators for BFW. The generators produce into a ring header that allows isolation of parts of the header for boiler turnarounds and maintenance, while the balance of the header remains in service. Hydrogen plants can also be designed to provide emergency steam.

For turbine-driven BFW pump standbys, the emergency steam supply is drawn from the ring header, as are the standby turbines for FD and ID fans. Instrument air compressors are also pulled off the ring header. Essentially, everything needed to run the steam system is internally supplied from the ring header in the event of outside or electrical failure. If necessary, the steam may be vented to atmosphere.

The integration of a cogeneration unit into the steam and electrical systems needs to be carefully considered. The connection of these two systems through the cogen puts both at risk. If the cogen provides too much of the steam in the plant, failure of the cogen will bring the plant down, because the boilers cannot fire up fast enough to cover a loss without tripping. Simultaneously, you have most likely also lost electrical power. The best practice is to ensure you have enough base load on the boilers that the plant can take a cogen trip combined with a steam and electrical load-shedding plan to be implemented immediately in the event of cogen loss. To prevent trips caused by outside electrical disturbances, it is also advisable to have protective relaying that will allow the facility to island or isolate itself if the outside electrical grid trips. Of course, this won’t always work, but it helps.

When designing a steam system, always think about achieving absolute reliability of supply. Know when you are accepting a compromise that could affect reliability and be sure you agree with taking that risk.

Steam and Condensate System Monitoring

The steam and condensate systems need to be sampled and monitored regularly to ensure a good, reliable performance. A water treatment chemical supplier can help with the analytical tests and their meaning.

Some recommended minimum periodic samples and tests, along with their frequencies, are:

- Boiler feed water makeup streams (daily to weekly): pH, conductivity, hardness, total dissolved solids, oil, and grease (condensates)
- Boiler feed water supply (daily to weekly): pH, conductivity, hardness, dissolved oxygen, total dissolved solids, and boiler treatment chemical concentrations
- Boiler water/blowdown (weekly): pH, conductivity (daily or continuous), hardness, total dissolved solids, boiler treatment chemical concentrations, and iron
- Steam from steam drum (condensed, weekly to monthly): pH and conductivity
- Condensate at various locations in the system (monthly): pH, conductivity, amine inhibitor concentration, and iron

Boilers should be monitored daily by tracking and trending:

- Net steam production per unit of heat fired (e.g., Mlbs/MMBtu)
- Stack excess oxygen
- Stack temperature
- Preheated air temperature
- Stack appearance (steam in the stack indicates a leak)
- Visual verification of steam drum or generator liquid levels
- Visual check of flame patterns and adjustment or cleaning if indicated

Analysis of the results and implementation of actions when results are heading in a bad direction are the keys to maintaining healthy steam and condensate systems.

Troubleshooting Steam Systems: A Few Common Issues

We will touch briefly here on a few common boiler or steam generation issues and provide some hints about where to start looking for problems. While these are couched in terms of boilers for convenience, they apply to all types of steam generators.

Boiler Carryover

Carryover occurs when the steam from the boiler contains entrained water or other material (even volatilized salts or silica) from the steam drum. Allowing carryover for any significant amount of time will foul and damage downstream equipment. Turbines and superheat coils are especially at risk from carryover.

Some places to look when investigating carryover include:

- *Variations in pressure*. Sudden reductions in drum pressure will cause the drum water contents to suddenly expand due to the release of steam bubbles. The level in the drum goes high and allows the carryover. This can be a problem with back pressure control, or one of the users may be pulling the steam header down.

This may also occur during an upset that suddenly increases steam demand, but those situations are usually short-lived. If pressure reductions are large enough, the boiler will shut down on high-high level.

- *Foaming*. Bubbles can build up on the surface of the water in the steam drum, effectively raising the drum level. The bubbles get carried out with the steam. If you have foaming, check your boiler chemistry. Be sure the BFW preparation, especially the demineralizers, softeners, or RO, is actually working. Be sure the drum is being blown down correctly. Increase blowdown frequency and amount to purge out whatever bad actors are present.
- *Drum level instrument problems*. As mentioned under controls, the steam drum level has to be compensated for density difference between the drum and the level instruments. Check the level taps. Ensure they are clear. Verify that the level gauge matches the instruments. Verify that all the instruments agree on the level. Correct level is absolutely critical to avoiding carryover.
- *Internal failure*. A steam drum is not just an empty space. There are baffles, steam purifiers, steam separators, belly plates, etc., that ensure controlled separation of the steam from water. Mechanical failure of any of these can result in carryover. These are hard to diagnose externally, but are easily spotted once the drum is opened. If you've tried everything else, then you need to physically inspect the drum.

Condensate Corrosion

Corrosion in the condensate systems will often show at remote, low-pressure locations. A pattern of corrosion in condensate systems should trigger an investigation. Common problem areas include:

- *Deaerator/degasifier operation*. Ensure the deaerator is stripping correctly. This can be done by testing the BFW at the deaerator for dissolved oxygen (DO). The DO test is very sensitive. Your chemical vendor may be able to help, or you can use an ampoule test tube immersed completely in water. Check the condensate pH and analyze it for CO_2 and other acids which can indicate poor deaerator performance.
- *Amine selection*. Review the condensate treatment program with your treatment chemical vendor. Condensate treatment is not a one-size-fits-all application. Amines of different boiling ranges need to be selected based on your steam and condensate system pressures.

Tube Failures

Boiler tube failures or leaks indicate that deaeration or chemical treatment is inadequate. However, they may also indicate firebox problems. A couple of things to check:

- *Verify deaerator is operating correctly*. Deaerator problems are often indicated by oxygen pitting of the steam drum or deaerator.
- *Verify the boiler chemicals are being applied correctly*. Waterside fouling will result in failures.

- *Verify adequate blowdown*. Again, this is part of waterside management.
- *Flame impingement*. Flames licking tubes may cause local overheating and failures. Look at the flame patterns for issues. Flame instability is another indication of a possible leak. The burner nozzles may need cleaning, or there may be a problem with the air registers.

Decreasing Steam Production Efficiency

Sometimes the steam production may begin decreasing, but the firing stays the same or increases. This can indicate a couple of things:

- *Fouling of the boiler tubes*. Check water chemistry, chemicals, blowdown, and the other related factors.
- *Tube leak*. Trend the steam production vs. makeup BFW or material balance the waterside of the boiler. If you can't account for all the incoming water, it is probably leaking out. Check the stack for steam on a cold morning.

Loud Boiler Hum or Vibration

This phenomenon can occur when the heating value of the fuel gas gets too low, usually because of excessive amounts of hydrogen. The gas is combusting by small explosions. If not corrected, the vibrations will ruin the heater refractory and cause more damage. This problem has to be corrected at the fuel supply source.

Condensate Header Banging

Loud banging of a condensate header is the result of steam collapsing in the header and creating shock waves. This normally means that one or more steam traps have failed or are not primed and steam is blowing through into the header. The failed trap(s) need to be located and repaired. Sometimes all this takes is blocking the trap in temporarily on the condensate side and then unblocking it after sufficient condensate has accumulated. Alternately, the trap can be immersed in cold water or ice to establish a condensate seal. This phenomenon may also occur during sudden rainstorms, but is normal in that case.

Fuel Systems

Oil refineries and petrochemical plants may have three separate fuel systems:

- Fuel gas
- Fuel oil
- Natural gas

Some burners in these plants may be designed to fire any of these fuels. Some normally fire either the fuel gas or the fuel oil stream and can be easily switched over from one to the other. Most modern refineries, limited by environmental regulations, only fire natural gas and fuel gas. In the USA, for instance, few refineries fire fuel oil.

The pilot burners however must be natural gas or fuel gas. Natural gas is preferred as it does not plug or coke the pilot gas tip. If fuel gas is used, the pilot tips require regular cleaning or replacement. The pilot burner fuel supply is kept separate from the main fuel gas supply.

Some systems are designed such that if the pilot flame is lost, the whole burner system is shut down. In other systems, like side wall fired furnaces, there are no pilots, but there are literally hundreds of burners. The furnace design and company safety philosophy dictate the options for a given furnace.

Generally the design of the burner systems in most plants has many safety and shutdown features. After all, in processes that handle flammable material, the heater burners are the one feature in the plant design that can be a major fire or explosion hazard if not properly operated and managed.

Common burner and heater shutdowns include:

- High-high and low-low fuel pressure
- High-high process outlet temperature
- Loss of pilot burner (depending on the design, may also be detected as HH or LL pilot gas pressure)
- Atomizing steam failure (oil burners)
- Low-low process flow to heater
- Low-low heater draft

There are exceptions to all these shutdowns. It is common practice to provide a pre-alarm on any shutdown, so all these parameters also have pre-alarms to allow time for operator action.

Fuel Gas System

This is the simpler of the two systems. A typical fuel gas system is illustrated in Fig. 4.

Waste gas streams from the process plants are gathered and scrubbed free of H_2S with amine solutions (MEA, DEA, DGA, MDEA). Streams that have already been scrubbed may bypass the columns. The rich amine solution is sent to the sulfur plant for regeneration and sulfur recovery. Generally, there will be two or more scrubbers which may handle saturated gases, unsaturated gas, or a mixture. The H_2S is normally reduced to less than 100 ppm by the scrubbers. Recent US regulations have reduced the allowable total sulfur to less than 30 ppm, including H_2S, COS, disulfides, mercaptans, and any other sulfur form. Additional treatment may be used to reach these new targets. Refer to the topic titled "▶ Refinery Gas Treating Processes" in this handbook for additional details on gas treating.

The low sulfur gases are then directed to the plant's fuel gas mix drum. This drum operates at 30–150 psig (2–10 barg) pressure (depending on the system design)

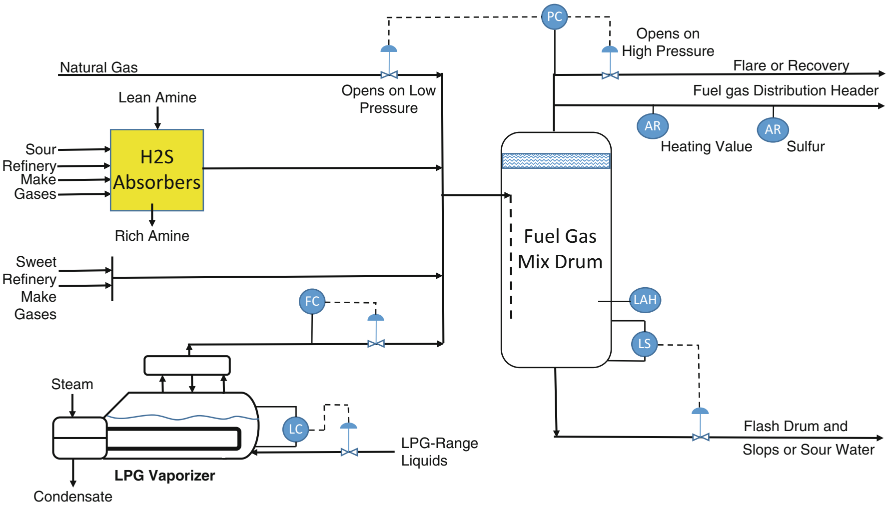


Fig. 4 A typical fuel gas mix system

and somewhat above ambient temperature. Collected hydrocarbons and moisture may be knocked out in this drum and drained to slops, or a small steam coil may be installed in the drum to gasify any “below dew point” material that may have condensed out.

The drum is held at the desired pressure by pressure control valves which allow surplus gas to flow to flare or bring in an external, clean source of gas, usually natural gas or clean LPG, on low pressure. If LPG is used as a secondary fuel source, it is routed to the fuel gas drum via a vaporizer. The vaporizer is usually a kettle-type boiler, heating and vaporizing the LPG at the drum pressure. Medium- or low-pressure steam is used as the heating medium for the vaporizer.

In practice, sending surplus fuel gas to the flare is the least preferable option. Environmental regulations prohibit this type of flaring in many areas. More commonly, the fuel gas pressure control system is operated so that there is always a small, positive makeup gas stream into the system to hold pressure.

Figure 5 depicts the key parts of a fuel gas system within a process unit. There will typically be a local fuel gas knockout drum, which may service several heaters. Any liquid that has condensed in the fuel gas distribution headers (and amine carryover from the scrubbers) is drained to slops/recovered oil from the knockout drum. From the knockout drum, the fuel gas is controlled into the local fuel gas ring header at each heater, and the burners pull their fuel off the heater fuel gas ring header. It is advisable to steam trace and insulate the fuel gas line after it leaves the knockout drum to prevent further condensation and corrosion. Corrosion products will plug the burners. Often, inline Y strainers are installed in each burner line to ensure clean gas to the burner. Some processors also use stainless steel pipe between the knockout drum and each heater.

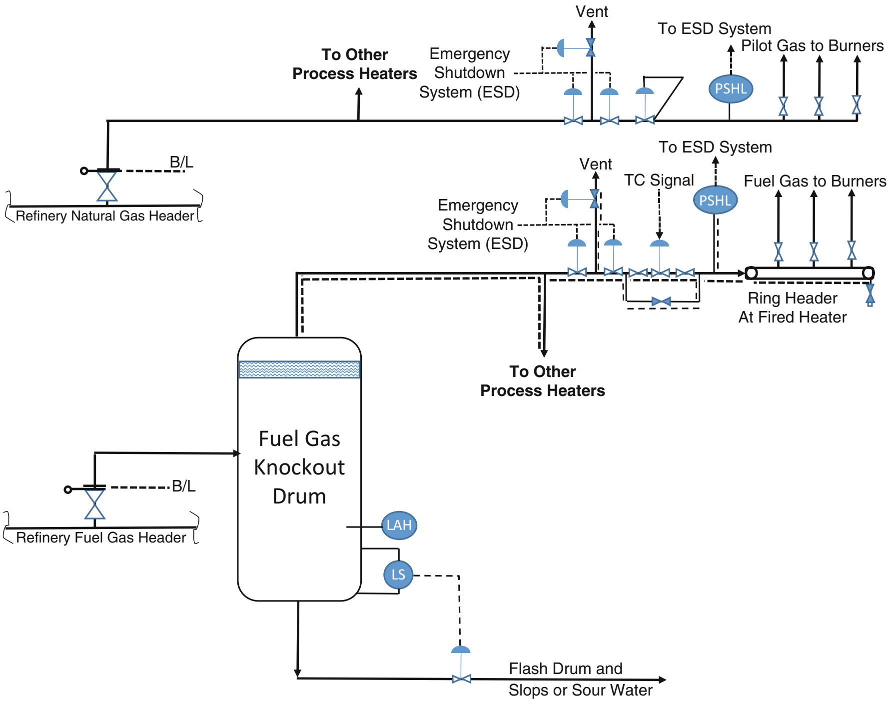


Fig. 5 Local fuel gas system

Parallel to the fuel gas header is the pilot gas header. This header has a simple pressure regulator controlling supply pressure at each heater to normally about 5 psig (0.3 barg). Pilot gas flow is either off or on, with the pilot orifice itself regulating the flow. The pilot gas is often filtered or strained. As noted above, natural gas is preferred for pilots to prevent plugging.

Some heaters contain an automatic switch over from gas firing to fuel oil firing on low gas flows or when manually selected. The fuel gas system is "dead ended." That is, there is no return system to the fuel gas drum, the gas header is pressured up, and gas flows to the burners by means of this differential pressure and intermediate control valves.

Fuel gas flow to the burners is controlled by heater outlet temperature or another temperature downstream of the heater coil process outlet line. Several control configurations may be used for fuel gas to the heater:

- Direct control with TC output
- TC cascade to fuel gas PC which controls the valve
- TC cascade to fuel gas FC which controls the valve
- TC cascade to FC cascade to PC which controls the valve

Each of these approaches has some merits and drawbacks. The control responses get slower, but smoother as you go down the list. We tend to like to have the fuel gas respond quickly, so the first couple of approaches tend to be used the most.

In a dual-fired furnace, the same controller may also regulate the oil firing arrangement when the heater is operated on fuel oil.

Fuel Oil System

Figure 6 is a schematic of a typical fuel oil system. Some plants use petroleum residues as fuel oil. These types of fuels are high in viscosity and very often have a high pour point. For these reasons the fuel oil is stored in insulated and heated cone-roofed tanks. Heating may be accomplished by steam coils located in the base of the tank or by external steam heat exchanger through which the fuel oil is continually circulated.

Positive displacement pumps (usually rotary type) are used to deliver the fuel oil from the tank, through the distribution system to the heater burners. These pumps are always spared, and the spare pump is driven by a steam turbine, while the operating pump is motor driven.

The fuel oil passes through a duplex filter before entering the suction of the pumps. This filter is included to remove any solid contaminants that may be in the oil such as fine coke particles which would foul the fuel oil burner. The discharge pressure of the pumps is controlled by a slipstream routed back to the storage tanks through a pressure control valve. This valve is activated by a pressure control element on the pump discharge header.

The pumps discharge the fuel oil via the pressure controller to a preheater. This preheater may be a simple double-pipe heat exchanger for relatively small units or a regular shell and tube exchanger for the larger systems. Double-pipe type exchangers are favored in this service when economical because they are easier to clean and maintain. The fuel oil leaves the preheater to enter the fuel oil distribution system hot enough to maintain a viscosity low enough for the oil to flow easily and to be easily atomized by steam at the fuel oil “gun” (or burner).

All the piping associated with residual fuel systems is heavily insulated and steam traced. The distribution systems for residual fuel oils are usually the recirculating type. That is, the fuel leaves the preheater to circulate to all the user plants in a loop where the quantity used is taken off the stream and the remainder allowed to return to the system. The return header is routed back to the storage tanks. The circulation system handles between one and three times the quantity of oil that is actually burned.

Fuel oils are introduced into the fire box and ignited through a fuel oil burner sometimes called a fuel oil gun. In order to ensure combustion in a manner suitable for a fire box operation, the fuel oil needs to be dispersed into small droplets or spray at the burner tip. In heavy residual oils this is almost always accomplished by steam. Alternately, compressed air is sometimes used for this purpose.

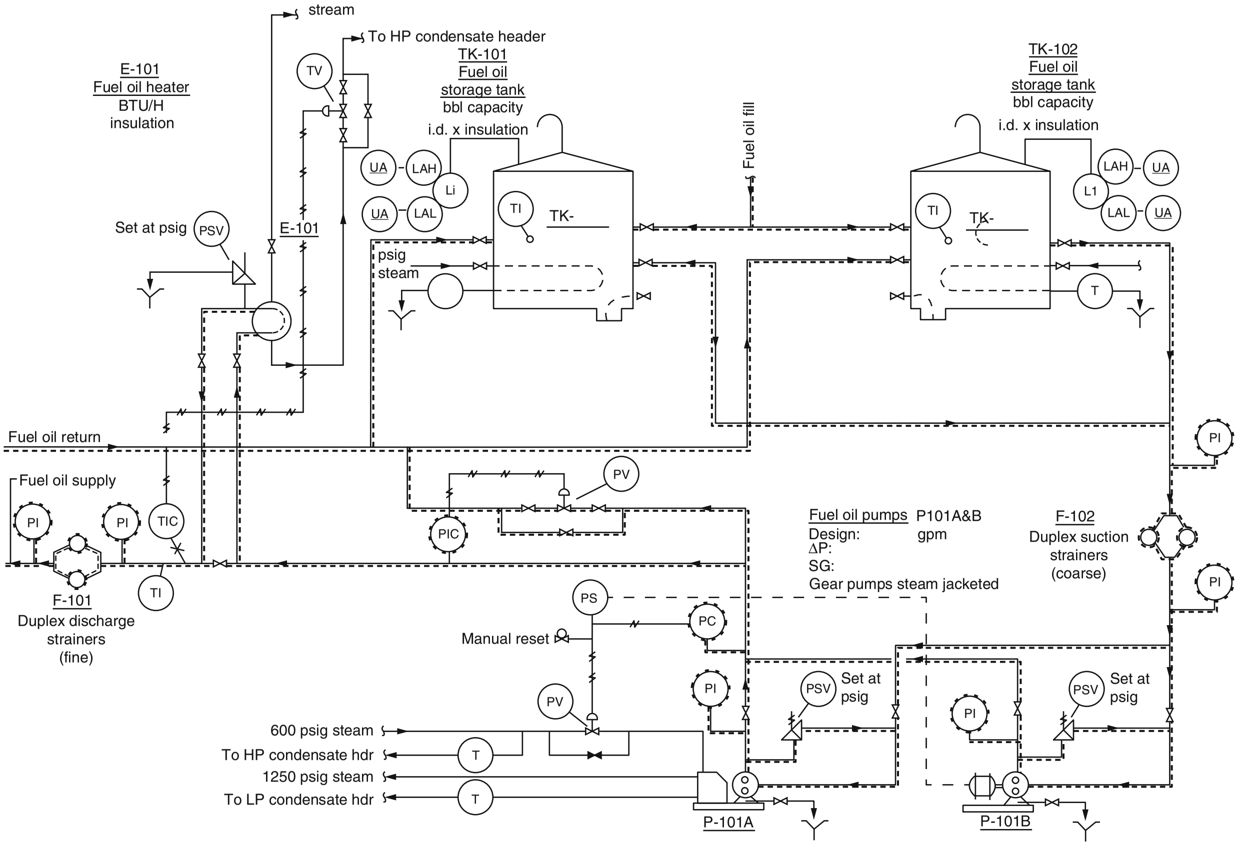


Fig. 6 A typical fuel oil system

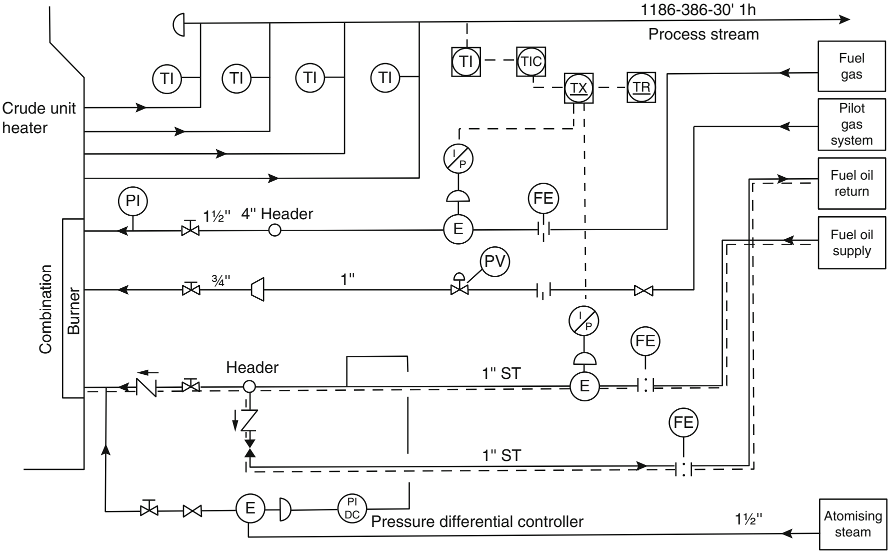


Fig. 7 A burner control system

This atomizing stream is introduced into the gun chamber and comes into contact with the oil stream just before the burner tip. The kinetic energy in the atomizing medium forces the oil into suitable droplets as it leaves the burner. Steam is normally used as the atomizing material because it is usually cheaper, more readily available, and has a more reliable source than air from a compressor.

The steam pressure for atomizing should be 15–25 psig higher than the fuel oil pressure. The quantity of steam will range from 1.5 to 5 lbs per gallon of oil. Dry steam with a superheat of about 50 °F is preferred for atomizing.

In order to control the process heater operation, oil burners require a turndown ability. That is, they must operate satisfactorily over a prescribed range of flow. In keeping with an operating range for oil flow, the atomizing medium must also have a similar operating range. Burner pressure is a critical requirement for turndown. The steam (or air) pressure at the burner should be 15 psi or 10 % (whichever is the greater) higher than oil pressure at the burner. The fuel oil supply system should be 100 psi higher than the burner requirement.

The oil burner operation, as with the fuel gas burner, is controlled by the heater's process stream outlet temperature. The temperature control valve activated by the coil outlet temperature increases or decreases the oil flow from the circulating oil stream to the burner. A proportional control valve on the atomizing steam line regulates the flow of steam to the burner in keeping with the oil flow. Figure 7 shows an example of a burner control system.

There are various methods for safety shutdown. The one shown here shuts down the oil flow on steam failure and on loss of the pilot burner. In some systems there is also an automatic changeover to gas firing on low oil pressure.

Burner Management Systems and Safe Firing of Heaters

We have already described the common shutdowns on fired heaters. Not all heaters or companies use the same matrix, but most are very similar. Some reasoning behind each of the shutdowns mentioned is worth reviewing:

- *High-high fuel gas pressure*. Fuel gas pressure that is too high causes the flame to lift off the burner tip and become unstable because the flame velocity leaving the tip exceeds the flame propagation velocity. This can result in the fuel essentially blowing the flame out. Without a shutdown, fuel would continue to enter the firebox until it found an ignition source and ignited, often explosively.
- *Low-low fuel pressure*. Similar to high-high fuel gas pressure, a low-low pressure can result in loss of flame and heat. The furnace could then fire harder to make up for the loss, introducing gas that can accumulate. While pilots help this by igniting unburned hydrocarbons continuously, flame loss is still a risk.
- *High-high process outlet temperature*. This is an indication that something has likely failed in the control system and the furnace is firing without feedback. Often high-high fuel gas pressure will shut down the furnace before high-high process outlet. HH outlet temperature may also indicate other problems, like low-low flow in the tubes. It really is a secondary monitoring for several parameters. Note that in a no-flow situation, the process outlet temperature will actually drift lower and call for more firing.
- *Loss of pilot burner* (depending on design; may also be detected as HH or LL pilot gas pressure). Pilots may have heated thermistors to tell when they are on or may use pressure sensors. Loss of pilots becomes a big problem if there is an additional loss of flame on the burner. Some people shut down a furnace on loss of pilots, while others alarm the situation. Loss of pilots is not always a problem. In a large furnace with many burners, loss of pilots may have no immediate impact, but they must be restored in short order. As noted above, some heaters do not have pilots, but have hundreds of burners that are not much larger than pilots. This shutdown would not apply to them.
- *Atomizing steam failure (oil burners)*. If atomizing steam (or air) fails in an oil-fired furnace, the fuel oil will not be properly burned. Unburned oil will collect in the heater floor and flow out onto the ground, creating a mess, if not a fire hazard. Hence, it is critical that an oil-fired furnace be shut down on loss of atomization.
- *Low-low process flow to heater*. In most heaters, process flow is required to ensure the heat being fired is removed safely. Loss of flow in the heater tubes will result in damage to the tubes and may cause tube ruptures. Some heaters are designed to go to a limited temperature without flow in the heater tubes, but, in general, flow is required to operate a heater.
- *Low-low heater draft*. Loss of draft in a heater means that the firebox pressure is high enough that combustion air cannot get into the burners. The flames will go out. This is a dangerous situation with a hot firebox, fuel, and no combustion. Often explosions result if the fuel finds some air; hence, the heater is best shut down on loss of draft.

Shutdown systems for heaters are normally separate, secure systems. As shown in Fig. 5, many refiners use automatic double block and bleed (DBB) to positively stop fuel flow to the furnace. The DBB is operated by the multiple-redundant safety integrity system (SIS), after pre-alarming. Some refiners will also drive the fuel control valves closed in addition to the DBB or in lieu of DBB.

Safe heater firing needs to be practiced whenever a heater must be lit. The key steps in safe heater firing are:

1. Shut off and isolate all fuel sources (including pilot gas). Block in all burners and pilots.
2. Purge the firebox free of combustibles using snuffing steam or FD/ID flow. Verify there are no combustibles in the firebox with an LEL meter or other analyzer.
3. Unblock pilot gas and set pilot gas supply pressure.
4. Ignite all pilots, one at a time.
5. Once pilots are lit, the fuel gas control valve should be completely closed and the fuel gas supply unblocked (the low-low-pressure fuel gas trip may have to be bypassed until a couple of burners are lit).
6. Crack the fuel gas to the burners manually and light each burner, one at a time, off the burning pilot gas tips.
7. Begin controlling the fuel gas pressure manually initially as burners are added. Once enough burners are lit, the fuel gas controller can begin working.
8. Keep burners dispersed evenly throughout the firebox as they are lit to avoid impingement.
9. Maintain a high initial heater draft and bring draft down as the heater approaches a normal operation.
10. The heater can then be switched to automatic firing and draft control.

There are some preferences in how this firing sequence is executed, but it will generally follow the above pattern.

Fuel Gas Cleanup and Burner Fouling

The fuel gas mix drum also acts as a knockout drum for potential amine liquids entering the fuel gas from the various absorbers throughout a typical system (Fig. 4). This is not 100 % effective, especially in a system where plant expansion may have increased rates substantially.

Expect the fuel gas header to contain water, amines and amine salts, traces of oxygen and CO_2, chlorides, tar-like hydrocarbons, and other undesirable materials. The biggest problem presented by these materials is fouling at the burner tips, which are very small and operate at high temperatures often. The amine salts and wet environment are particularly corrosive to the fuel gas header piping.

It is advisable to provide local fuel gas knockout drums at each process unit to remove condensed or accumulated liquids, solids, and corrosion products.

Such a drum is shown in Fig. 5. In some large furnaces, the furnace may even need to have its own knockout drum.

Once the fuel gas has been cleaned and separated in the unit knockout drum, keep it clean and dry by tracing the fuel gas piping to the users. Some refiners also use stainless steel piping between the knockout drum and the furnace(s).

Some types of furnaces and burner designs expose the burner tips to extremely high temperatures. An example would be a hydrogen plant where the tips see the firebox at about 2,800 °F (1,573 °C). At these temperatures, even natural gas will crack and foul the tips. These need to be watched closely for signs of fouling and cleaned before they become problems.

Troubleshooting

A few of the more common problems related to fuels are highlighted below, along with some possible causes and remedies:

- *Frequent burner tip fouling*. Verify the knockout drums are working properly and the design flow rates are not being exceeded. Verify the absorbers are not overloaded, not foaming, not operating at excessive temperatures, and have enough lean amine flow. If the final fuel lines are traced, verify the tracing is operating. Clean the tips as required using the correct drill size or replace the tips.
- *High fuel gas volume requirements, unusual flame patterns, or sounds*. Verify the heating value of the fuel. It may have too much hydrogen. Heating values below about 500 Btu/scf can be a problem.
- *Flame impingement*. Look for burner fouling, high fuel gas pressures, not enough burners in service, and problems with air registers or draft.
- *Liquid pooling below oil-fired heater*. Loss of atomizing steam/air, burner tip problems, and leak.
- *Pilot failure to light*. Check pilot gas pressure and lineup. Check pilot gas orifice to be sure it is clear. Adjust air intake orifice on pilot. Be sure heater draft is not excessive so that it is blowing the pilot out.
- *Burner failure to light*. Be sure the pilot is burning. Check fuel gas pressure and lineup. Check fuel oil pressure, lineup, tracing, and atomization medium. Check for burner or distribution header plugging. Be sure heater draft is not excessive and that the air registers are not too far open so the flame is being blown out.

Water Systems

The major water systems found in most refineries and chemical plants are:

- Cooling water
- Treated water for BFW and process uses

- Fire water
- Potable water

We will discuss each of these systems in turn.

Note that in this discussion and in water treatment literature, hardness, alkalinity, and even individual ions are often expressed as their $CaCO_3$ equivalent. Table 1 provides a handy conversion reference for converting from the water analysis to $CaCO_3$ equivalents.

Table 1 Calcium carbonate equivalents (The Nalco Water Handbook 1979)

Substance	Mol wt.	Equiv. wt.	To convert to $CaCO_3$, multiply by	To convert $CaCO_3$ to substance, multiply by
$Al_2(SO_4)_3$ (Anhyd)	342.1	57.0	0.88	1.14
$Al(OH)_3$	78.0	26.0	1.92	0.52
Al_2O_3	101.9	17.0	2.94	0.34
$BaSO_4$	233.4	116.7	0.43	2.33
$Ca(HCO_3)_2$	162.1	81.1	0.62	1.62
$CaCO_3$	100.1	50.0	1.00	1.00
$CaCl_2$	111.0	55.5	0.90	1.11
$Ca(OH)_2$	74.1	37.1	1.35	0.74
$CaSO_4$ (Anhyd)	136.1	68.1	0.74	1.36
$Ca_3(PO_4)_2$	310.3	51.7	0.97	1.03
$Fe_2(SO_4)_3$	399.9	66.7	0.75	1.33
MgO	40.3	20.2	2.48	0.40
$Mg(HCO_3)_2$	146.3	73.2	0.68	1.46
$MgCO_3$	84.3	42.2	1.19	0.84
$MgCl_2$	95.2	47.6	1.05	0.95
$Mg(OH)_2$	58.3	29.2	1.71	0.58
$Mg_3(PO_4)_2$	262.9	43.8	1.14	0.88
$Mg_3(SO_4)_2$ (anhyd)	120.4	60.2	0.83	1.20
SiO_2	60.1	30.0	1.67	0.60
$NaHCO_3$	84.0	84.0	0.60	1.68
Na_2CO_3	106.0	53.0	0.94	1.06
NaCl	58.5	58.5	0.85	1.17
NaOH	40.0	40.0	1.25	0.80
$NaNO_3$	85.0	85.0	0.59	1.70
Na_3PO_4 (anhyd)	164.0	54.7	0.91	1.09
NaH_2PO_4	120.0	40.0	1.25	0.80
Na_2SO_4	142.1	71.0	0.70	1.42
Na_2SO_2	126.1	63.0	0.79	1.26

(*continued*)

Table 1 (continued)

Substance	Mol wt.	Equiv. wt.	To convert to $CaCO_3$, multiply by	To convert $CaCO_3$ to substance, multiply by
Al^{+3}	27.0	9.0	5.56	0.18
NH_{4+}	18.0	18.0	2.78	0.36
Ba^{+2}	37.4	68.7	0.73	1.37
Ca^{+2}	40.1	20.0	2.50	0.40
Cu^{+2}	63.6	31.8	1.57	0.64
H^{+}	1.0	1.0	50.0	0.02
Fe^{+3}	55.8	18.6	2.69	0.37
Fe^{+2}	55.8	27.9	1.79	0.56
Mg^{+2}	24.3	12.2	4.10	0.24
Mn^{+2}	54.9	27.5	1.82	0.55
K^{+}	39.1	39.1	1.28	0.78
Na^{+}	23.0	23.0	2.18	0.46
Sr^{+2}	87.6	43.8	1.14	0.88
Zn^{+2}	65.4	32.7	1.53	0.65
HCO_3^-	61.0	61.0	0.82	1.22
CO_3^{-2}	60.0	30.0	0.67	0.60
Cl^-	35.5	35.5	1.41	0.71
CrO_4^{-2}	116.0	58.0	0.86	1.16
F^-	19.0	19.0	2.63	0.38
OH^-	17.0	17.0	2.94	0.34
NO_3^-	62.0	62.0	0.81	1.24
PO_4^{-3}	95.0	31.7	1.58	0.63
HPO_4^{-2}	96.0	48.0	1.04	0.96
$H_2PO_4^-$	97.0	97.0	0.52	1.94
SO_4^{-2}	96.1	48.0	1.04	0.96
HSO_4^-	97.1	97.1	0.52	1.94
SO_3^{-2}	80.1	40.0	1.25	0.80
HSO_3^-	81.1	81.1	0.62	1.62
S^{-2}	32.1	16.0	3.13	0.32

A substance's equivalent weight is the molecular weight of the substance or ion divided by, either, the valence of the positive ion (or total valence of negative ions). The $CaCO_3$ equivalent is $CaCO_3$'s equivalent weight of 50.0 divided by the substance's equivalent weight. Hence sodium with valence +1 and weight of 23.0 has an equivalent weight of $23.0/1 = 23.0$. The $CaCO_3$ equivalent is $50.0/23.0 = 2.18$. Multiplying ppm sodium by 2.18 would give the $CaCO_3$ equivalent concentration.

Cooling Water

We will focus here on the normal circulating cooling water systems that cool by evaporation in cooling towers. There are special circulating, tempered or attenuated, closed-loop cooling water systems in some services. These are not addressed here.

Cooling Water System Flow Sheet and Equipment

Figure 8 is a mechanical flow sheet section showing the arrangement around a cooling tower for the collection and supply of cooling water.

The cooling water system is a circulating one. That is, there is a cold supply line with an associated warmer return line from all its users. Figure 9 shows a section of this distribution system. The typical differential between the cold supply and the warm return is 15–20 °F (8–11 °C). Cooling water from a given exchanger should generally not exceed about 140 °F (60 °C). Beyond this, excessive fouling of cooling water is observed. Chemical treatments can help, but are not completely effective.

The water returned to the cooling tower by the return header enters the top of the tower and flows down across the tower internals countercurrent to an air flow, either induced or forced by fans, passing up through the tower. The return header for a counterflow tower normally has a full line-sized standpipe extending well above the top of the tower to allow any possible gases that leak into the cooling water system to vent. These inlet standpipes must be monitored for exhausting gases – usually visually. In extreme cases of sudden, large leaks, the standpipes can prevent damage to the distributors and the tower. The open top decks of crossflow towers do not require the standpipes.

There are two common types of cooling tower used in petroleum processing facilities, as illustrated in Fig. 10:

- *Crossflow*. In these towers, the tower fill or packing is located down the sides of the tower structure. Air flows roughly horizontally though the fill as the water flows from distributors downward through the fill. There are inlet air louvers around the outside of the fill and drift eliminators inside the thick walls of fill. In the center of the tower is a plenum that collects the moist air. An ID fan pulls the air out of the plenum and exhausts it to the atmosphere through a venturi stack. These towers tend to be shorter and cheaper than counterflow towers, at the expense of efficiency.
- *Counterflow*. In counterflow towers, the air intake is located at the bottom of the fill, and the fill nearly covers the whole tower footprint. Above the fill are the drift eliminators to intercept entrained water. Above the drift eliminators are the plenum chamber and an induced draft fan exhausting to the atmosphere. These towers tend to be more expensive, but more efficient. The hyperbolic cooling towers you see around power plants are often of this type, but the hyperbolic shape eliminates the need for the fans.

A continuous blowdown of cooling water return is normally maintained for the control of solids and dissolved solids in the system. This will be discussed further along with chemicals.

The water, cooled by the air flow and evaporation, is collected in the cooling tower basin (cold water basin in Fig. 10). Makeup water (usually potable water) is

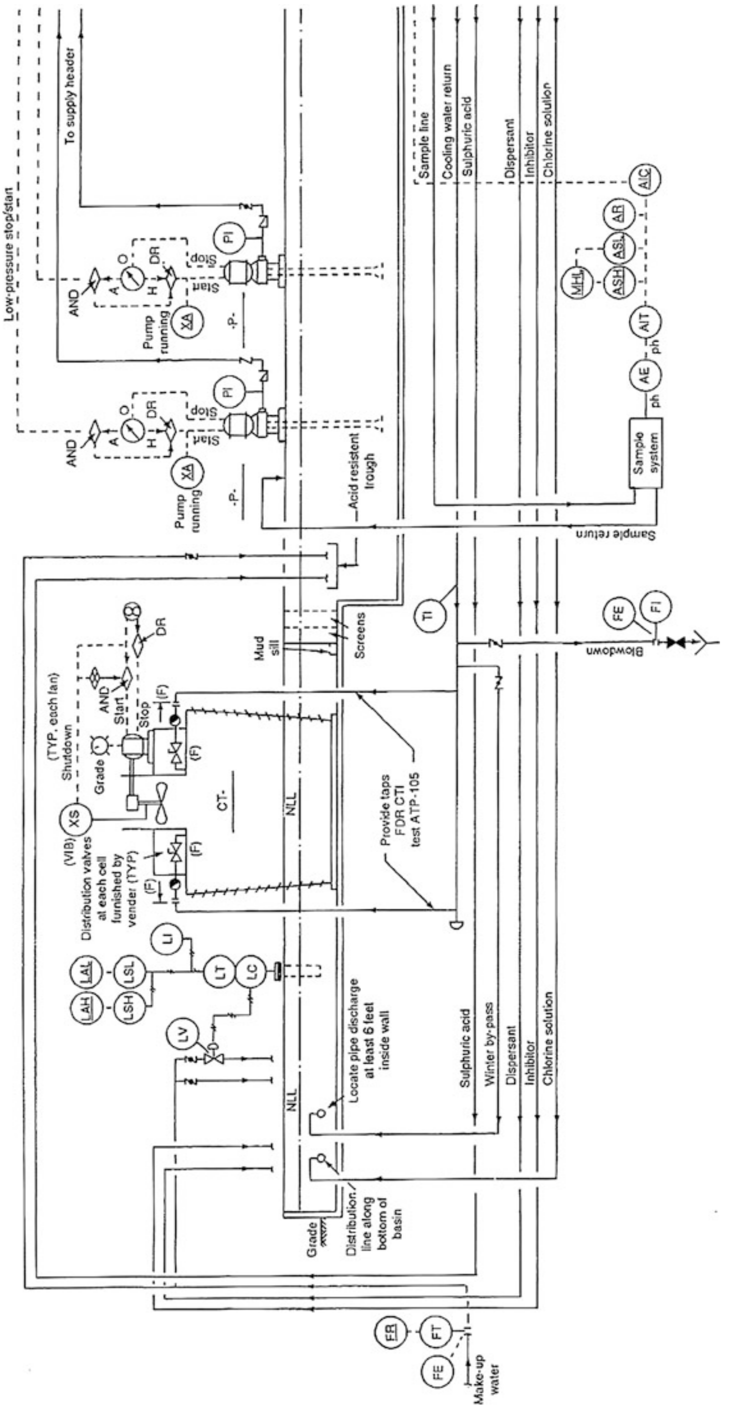


Fig. 8 Mechanical flow diagram of a water cooling system

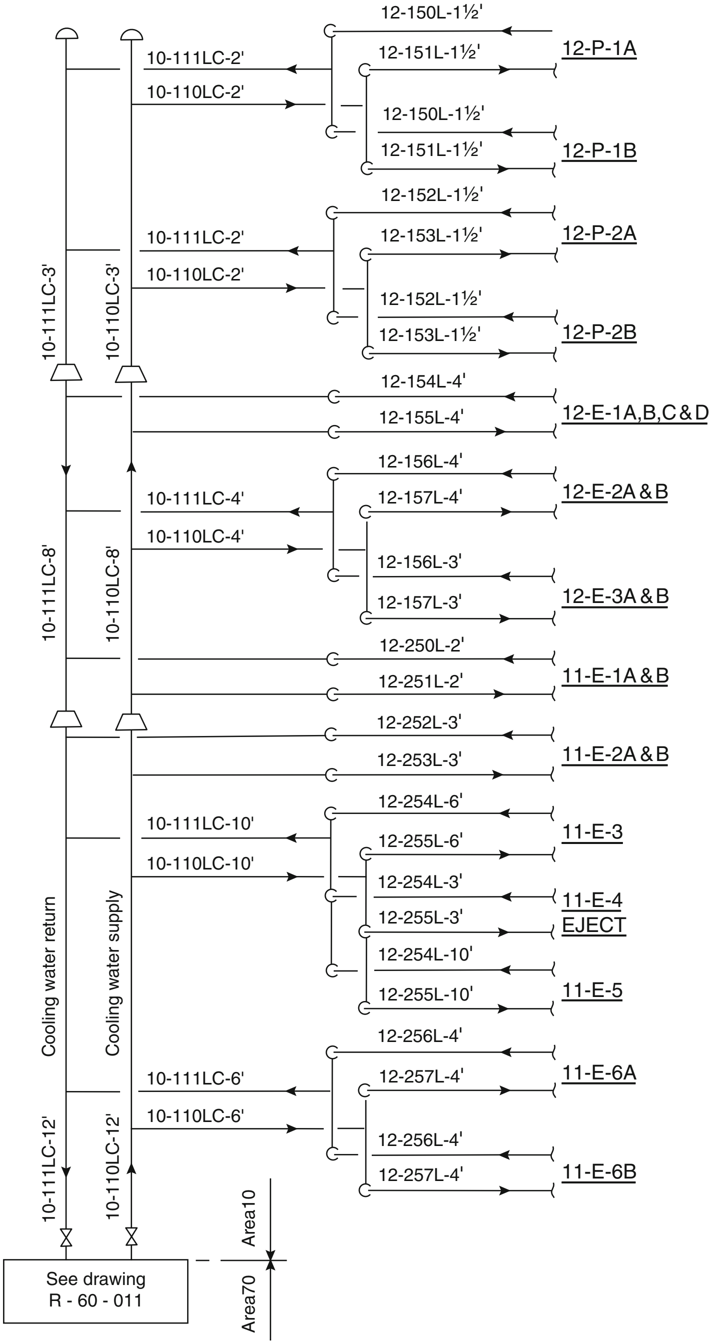


Fig. 9 A diagram of a cooling water distribution system

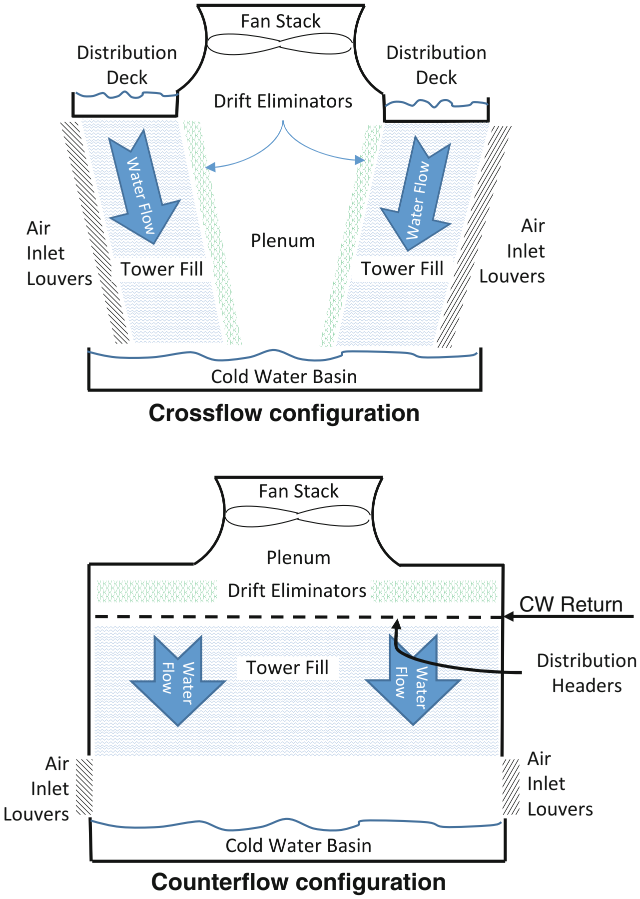


Fig. 10 Common cooling tower configurations (Puckorius 2013)

added to the basin under level control. The makeup water rate is equal to the evaporative load plus wind and drift losses plus blowdown plus leakage losses. The evaporative loss can be determined directly from the amount of heat rejected to the cooling water. Wind and drift losses are typically <0.1–0.3 % of the circulation. 0.1 % is usually a good number. Blowdown depends on makeup water quality and is discussed below. Leaks depend on the specific system and equipment condition, but should be almost negligible.

Vertical cooling water circulating pumps take suction from the cooling tower basin sump to deliver the water into the plant's distribution header. The sump design issues are discussed below. Cooling water pumps are usually high-capacity centrifugal pumps with a moderate differential head. Because of the critical nature of the water supply, the pumps are redundant. Spare pumps are commonly automatically started on low-low cooling water flow or pressure. There may be four or more pumps with each rated at around 60 % of design capacity – two in operation and two on standby. A mixture of motor and steam turbine drivers are quite common. Some facilities have two 100 % pumps with one electric and one steamer. For reliability, autostart turbine-driven pumps usually are kept with the turbine hot and may be on slow roll to ensure they can autostart when needed. The slow roll speed has to be sufficient to ensure the pump lubrication is adequate.

Cooling water pump sumps are located adjacent to the cooling tower. The entrance to each sump usually has two removable trash screens (about 0.5″ or 1.3 cm mesh) in series. There is a small sill or foot at the bottom of each screen to catch material that may fall off the screen when it is removed. The screens are removable for regular (weekly) cleaning – one at a time. After the screens, the pumps should be individually housed in bays. Design of the bays and the exact pump locations in the bays may require computerized fluid dynamic analysis (CFD) to ensure adequate pump suction. If the pumps are all in the same bay or sump or they are too close together, the flow into one pump's suction often interferes with flow into a neighboring pump. Separation of the individual pumps into bays prevents most interferences.

The cooling water supply and return lines may be quite large when central cooling water systems are employed. Lines over 5 ft. diameter (1.6 m.) are not unusual. The largest lines are often buried and are made from jointed, fiber-reinforced plastic.

The supply header pressure is kept at around 30–50 psig (2–3.5 barg), and, very often in large plants covering long distances, booster stations are installed at predetermined locations to maintain the supply header pressure. These booster stations consist of pump pits with high-capacity vertical pumps rated smaller, of course, than the main supply pumps. In some cases, inline pumps may also be used to boost pressure without a sump. The location of these booster stations is determined by a rigorous hydraulic analysis of the distribution system which also determines the header pipeline sizes. The return flow is collected from each user into the return header and flows back to the cooling tower under the users' outlet pressure.

The locations and orientations of towers can significantly affect performance. Towers are normally made from one or more cells, with each cell being like a smaller tower in itself. Every two cells share a common dividing wall. Each cell usually has its own fan. All the cells together share a common cold water basin. See Fig. 11. The orientation of the cells is normally perpendicular to the prevailing wind to avoid short-circuiting of air flow. When one or more cooling towers are present in an area, they are normally lined up end to end down the long axis and with the prevailing wind perpendicular to the long axis, again to avoid short-circuiting.

Operation of cooling towers in cold climates presents special challenges. The accumulation of ice on upper decks and air inlet louvers can result in collapse. The cold water is often too cold for many services. Approaches to dealing with these issues include reversing the cooling tower fans, installing temporary covers over top distribution decks (in crossflow towers), and shutting off fans as necessary. In extreme cases, the normal open cooling water system may be replaced by a closed-loop tempered water system with cooling supplied by air coolers instead of

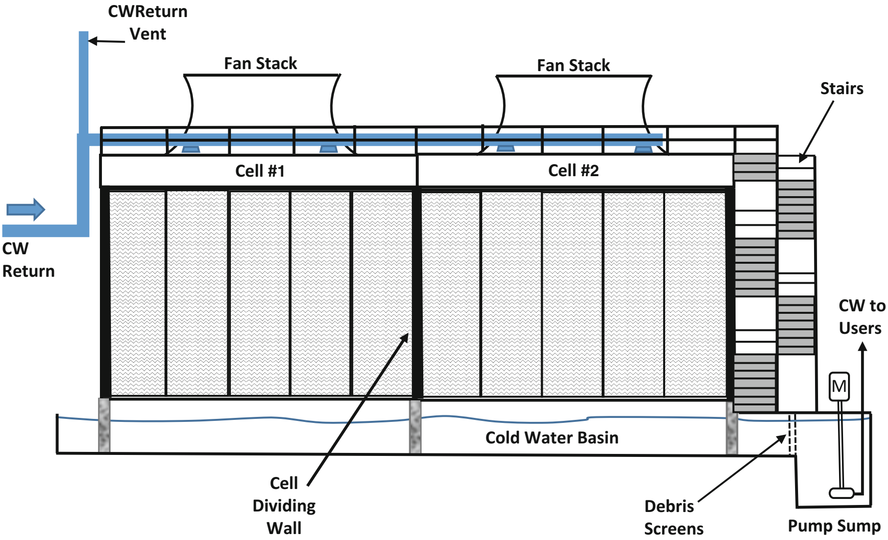


Fig. 11 A two-cell, crossflow cooling tower

evaporation. The closed-loop systems normally use glycol and different water treatments than open towers.

Cooling Water Chemistry and Treatment

The water in the cooling tower basin and in the cooling tower itself requires blowdown for hardness control and chemical treatment to prevent the buildup of algae and other undesirable contaminants. A separate small treatment plant may be used for mixing the inhibiting chemicals and injecting them into the critical sections of the system.

The blowdown rate required depends on the makeup water quality. A tower can usually operate at about 4–5 cycles of concentration. Cycles of concentration are roughly equal to ppm TDS/hardness of the circulating cooling water divided by ppm TDS/hardness of the makeup. Poor quality water with a lot of hardness will limit the cycles of concentration possible and increase the makeup requirement. High-quality water with low TDS and hardness can be cycled much higher.

The normal chemical treatments applied are:

- *Corrosion control*. At one time, chromate was the primary corrosion treatment, but environmental issues have eliminated chrome treatment programs. Today's options include orthophosphate, polyphosphates, zinc, and azole (if there are copper alloys in the system). The heavy metal treatments may be limited for environmental reasons.
- *Deposit control*. Phosphonate, carboxylate, and bio-dispersants.
- *Microbiological control*. Halogens (chlorine, bromine), sodium hypochlorite (bleach), chlorine dioxide, and organic biocides. Chlorine is by far the most

effective, but safety and environmental concerns are limiting its use. Bleach works very well. Bromine and organic biocides are fine in normal service, but have difficulty if there are any leaks into the system.

- *pH control*. To make many of the other chemicals work and to help control hardness deposits, sulfuric acid is normally injected to control pH in the required range, usually about 7.5–8.5 pH. The optimum range for pH, however, depends on the specific treatment chemicals used. The water treatment chemical supplier will set the range.

The chemicals should be injected into an actively flowing slipstream from the cooling water supply line. The stream should be reintroduced into the basin opposite the cooling water pump sumps so that the chemicals are carried across the basin and further distributed. Be careful, however, that the chemicals are not introduced into a dead area of the basin, or they will cause localized corrosion at the introduction point.

There are a number of fouling indices used to track cooling water treatment chemistry. The index definitions are presented below without much discussion or description about how to calculate them. There are several articles and a great deal of literature that explore these indices more completely.

- *Langelier Saturation Index (LSI)*. This is equal to the difference between the actual pH and the pH at saturation of calcium carbonate. An LSI below zero is a non-scaling condition. An LSI above 1.5–2.5 is a scaling condition. The pH at saturation is a function of the calcium hardness, alkalinity, and temperature. Correlations are available in the references.
- *Ryznar Stability Index (RSI)*. This index is given by

$$RSI = 2(pH_{\text{saturation}}) - pH^{3.5} \tag{1}$$

where:

$pH_{\text{saturation}}$ = pH at calcium carbonate saturation
pH = actual circulating water pH
An RSI below 6.0 indicates possible scaling and RSI above 6 is progressively non-scaling. An RSI above 8 may result in corrosion of carbon steel.

- *Stiff-Davis Index* (SDI). This index can be used for high concentration water. It is defined by

$$SDI = pH - \log_{10}(I/[\text{Ca}]) - \log_{10}(I/[\text{alkalinity}]) - K \tag{2}$$

where:

pH = actual circulating water pH
I = calculated ionic strength of the water (usually ~1)
[Ca] = calcium ion concentration, mg/l
[alkalinity] = alkalinity concentration, mg/l

$$= \left[\text{HCO}_3^-\right] + 2\left[\text{CO}_3^{2-}\right] + [\text{OH}-] \tag{3}$$

K = constant based on ionic strength and temperature

Similar to LSI, an SDI below zero is a non-scaling condition. An SDI above zero is a scaling condition.

- *Practical (or Puckorius) Scale Index (PSI)*. This index attempts to account for buffering. It is defined by

$$PSI = 2 \times pH_{\text{saturation}} - pH_{\text{equilibrium}} \tag{4}$$

where:

$$\begin{aligned} pH_{\text{saturation}} &= \text{defined above} \\ pH_{\text{equilibrium}} &= 1.465 \times \log_{10}[\text{alkalinity}] + 4.54 \end{aligned} \tag{5}$$

Interpretation of PSI values is similar to RSI.

Cooling Water System Monitoring

Monitoring a cooling water system includes both mechanical and chemistry tracking. There is no substitute for physical inspection of the tower, in addition to instrumentation and samples. Some of the factors to monitor include:

- *Mechanical*. Inspect tower visually.
  - Look at fans and drivers, condition of the fill, condition of the casing, cleanliness of the screens, corrosion, water flow patterns to the pumps, and anything else that looks unusual. Especially watch for fouling of the tower fill or packing. Plugged packing reduces the tower efficiency. Extremely plugged packings have resulted in physical collapse of towers.
  - Observe the return header standpipe for splashing or signs of leaks into the system.
  - Watch for algae buildup, as this indicates a leak. Address problems noted.
  - If the appearance of the circulating water becomes muddy or “chocolate brown,” you may have a low pH.
  - Look at the air exhausts for signs of excessive drift. This may indicate problems with the drift eliminators.
- *Thermal*. Look at the data.
  - Track the difference between supply and return temperatures.
  - Track cooling water flow rates and pressures.
  - Watch the cooling water return temperatures for values over 130 °F (55 °C) which could indicate overloaded conditions or insufficient flow.
- *Chemistry*. Review and act on sample results (your’s and your chemical supplier’s) for the cooling water and injection system operation. Periodic samples (appropriate frequencies) should include:
  - pH
  - Hardness
  - Alkalinity
  - Total dissolved solids
  - Total suspended solids

  - Scaling indices
  - Residual or available chlorine (or other biocide)
  - Water treatment chemical concentrations
  - Blowdown biochemical oxygen demand, total organic carbon, and volatile organic carbon

Troubleshooting

A few tips are offered here on problems commonly encountered in cooling water systems:

- *Increasing algae or slim accumulation – sudden or gradual*. This indicates undertreatment of biocide for the water conditions. Check the biocide dosing system and dosage (bleach, chlorine, etc.) to be sure it is working correctly. The tower may have to have a shock treatment with a heavy biocide dose to control some cases. If there is a step change in the bio-deposit accumulations, suspect a leak. You will have to sample to narrow down the source of the leak. Allowing a leak to continue will foul the system and cause corrosion of other exchangers. Maintain a high blowdown rate until the leak is resolved.
- *Carryover or overflow of return header vent*. Indicates a leak into the system or excessive plugging of the distributors. Identify and eliminate the leak. Caution should be exercised if the vented vapors can be encountered by personnel as the leak could contain H_2S.
- *Muddy appearance of cooling water*. This normally accompanies a low pH. A control problem with the acid injection pump or valve or an overflow of the acid storage tank into the basin will cause this. The corrosion rate within the cooling water circuit will rise dramatically. Maximize your blowdown and increase corrosion inhibitor injection until the problem is resolved. This may require a few days.
- *Low cooling water flow rate or pressure*. Check the cooling water pumps for proper operation. Switch to the standby pump(s), if necessary. Check the pump inlet screens for plugging. Clean the screens. Verify that the flow and pressure instruments are correct. Check tower water level control – low level will reduce flow.

Cooling Tower Safety

- *Chemicals*
  - If the tower uses chlorine gas for biocontrol, care needs to be taken in managing the gas cylinders. Some companies locate these in sumps and cover the cylinders with water. As a minimum, they need to be in a secondary containment area.
  - All chemicals used in cooling towers need to be provided with secondary containment (dikes or pits) to control spills. The drains on the containment should be kept closed until the containment is deliberately drained, such as after a storm.

  - The secondary containments must be designed to prevent contact between incompatible chemicals. For instance, acid must be separated from bleach tankage.
  - Brominators can present a problem with generation of gas sufficient to cause an explosion of the brominator vessel if the vessel is not properly managed.
  - All the chemicals used in cooling water treatment present some safety hazards. These need to be appropriately managed.
- *Legionella bacteria*
  - One safety issue that has come to light in recent years applies to tower maintenance. Cooling towers tend to grow *Legionella* bacteria in the packing and drift eliminators. *Legionella* can cause a fatal respiratory infection. Workers cleaning a tower should use air respirators suitable for this hazard until the tower is completely cleaned. No one else should enter the tower until it is cleaned.

Boiler Feed Water (BFW) Treating

All water contains impurities, no matter from what source the water originates. Sometimes, in a petroleum processing plant, water with most of these impurities can be used without treating of any kind. However, when it comes to generating steam, particularly high-pressure steam, and uses of water in the processes, these impurities become problematic. We will focus here on water for steam generation, but the discussion applies equally well to process uses.

To operate steam generators effectively, and to avoid serious damage to the unit, impurities in boiler feed water either have to be removed or be converted into compounds that can be tolerated in the system.

Types of Boiler Feed Water Impurities

In general there are three types of soluble impurities naturally present in water and which must be removed or converted in order to make the water suitable for boiler feed purposes. These are:

- *Scale-forming impurities*. These are salts of calcium, magnesium, silica, manganese, and iron.
- *Compounds that cause foaming*. These are usually soluble sodium salts.
- *Dissolved gases*. These are usually oxygen and carbon dioxide. The soluble gases must be removed to prevent corrosion.

Table 2 provides a more comprehensive listing of the various impurities, impacts, and treatment options.

Boiler Water Management

Buildup of solids in the boiler itself is managed or kept at a low level by blowdown. This is the mechanism of draining a prescribed amount of the boiling water from the

Table 2 Boiler impurity impacts and treatment options (http://energyconcepts.tripod.com/energyconcepts/water_treatment.htm)

Impurity type	Impacts	Control	Notes
Soluble gases			
H_2S	Odor, corrosion	Deaeration	From leaks or contaminated water
CO_2	Corrosion, esp. in condensate	Deaeration, neutralizing chemicals	Filming and neutralizing amines for condensate
Oxygen	Corrosion and pitting of boiler tubes	Deaeration, O_2 scavengers	
Suspended solids			
Sediment and turbidity	Sludge, scale, carryover	Clarification, filtration	5 ppm max in most applications
Organic matter	Carryover, foaming, deposits, corrosion	Clarification, filtration, chemicals	Surface and some well waters
Dissolved or colloidal solids			
Oil and grease	Foaming, boiler deposits	Coagulation, filtration	Condensate contamination
Hardness, Ca, Mg	Scale, loss of heat transfer/ efficiency, tube failures	Softening plus internal treatment	HCO_{3-}, $SO_4^{=}$, Cl^-, NO_3^- in order of increasing solubility
Sodium, alkalinity, NaOH, $NaHCO_3$, Na_2CO_3	Foaming, condensate corrosion, potential caustic embrittlement	Deaeration, ion exchange, RO	
Sulfates ($SO4^{=}$)	Hard scale if Ca present	Demineralization, RO	Max 100–300 ppm as $CaCO_3$
Chlorides	Uneven boiler operation (belching), lower efficiency, deposition on turbines and superheaters, foaming	Demineralization, RO	
Iron and manganese	Boiler deposits, erosion, inhibit heat transfer	Filtration, demineralization, RO	Most common form is ferrous bicarbonate
Silica	Hard boiler scale, turbine blade deposits	Lime softening, demineralization, RO	Very hard scale. Silica is volatile at higher temperatures with water present = turbine blade deposits

boiler steam drum or mud drums at regular intervals. This amount is calculated from the analysis of the solid content of the feed water and must equal the amount brought into the system by the feed water. Figure 12 gives an example of boiler blowdown.

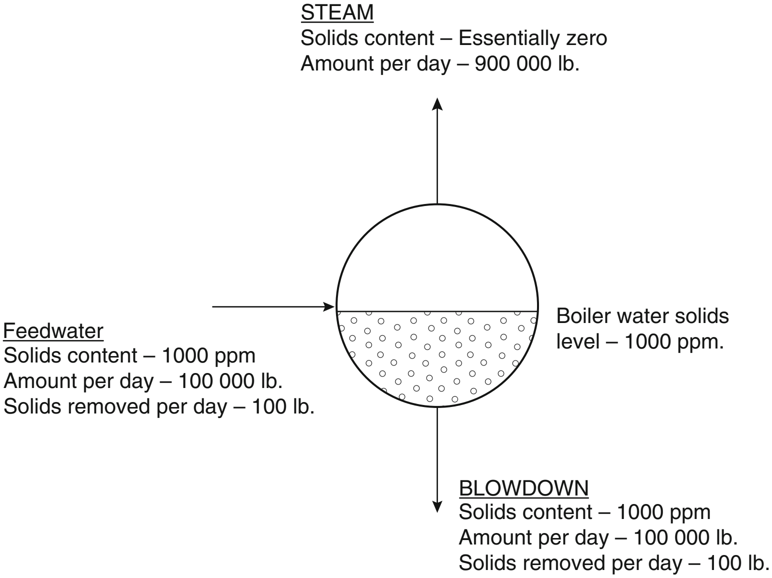


Fig. 12 How blowdown reduces the amount of solid buildup

Table 3 ABMA limits of various solids in boiler water

Boiler pressure (psig)	Total solids (ppm)	Alkalinity (ppm)	Suspended solids	Silica
0–300	3,500	700	300	125
301–450	3,000	600	250	90
451–600	2,500	500	150	50
601–750	2,000	400	100	35
751–900	1,500	300	60	20
901–1,000	1,250	250	40	8
1,001–1,500	1,000	200	20	2.5
1,501–2,000	750	150	10	1.0
Over 2,000	500	100	5	0.5

ASME has also provided some guidance for boiler feed water and boiler water along the same lines, as noted in Table 4 for BFW and boiler water. Although the table is stated for water-tube boilers, it is commonly also applied to waste heat boilers with the hot gas in the tubes (similar to a fire-tube boiler)

The American Boiler Manufacturers Association (ABMA) has developed limits for the control of various solids in boiler water. These are given in Table 3.

Other considerations regarding the limits of solids in BFW are:

- *Sludge*. This is a direct measurement of feed water hardness (calcium and magnesium salts) since virtually all hardness comes out of solution in a boiler.

- *Total dissolved solids*. These consist of sodium salts, soluble silica, and any chemicals added. Total solids do not contribute to scale formation, but excessive amounts can cause foaming.
- *Silica*. This may be the blowdown controlling factor in pre-softened water containing high silica. At elevated pressures high silica content can cause foaming and carryover.
- *Iron*. High concentration of iron in BFW can cause serious deposit problems. Where concentration is particularly high, blowdown may be based on reducing this concentration.

Preparation of Boiler Feed Water Makeup

There are three types of BFW treatment in use. There are the external type of treating and the internal processes. As the names suggest the external processes are those that treat the water before it enters the boiler. The internal treatments are those in the form of added chemicals that treat the water inside the boiler, and these were discussed under steam and condensate systems. Only the external processes are described here. A great deal of detailed information is available on each of these processes from vendors, treatment chemical suppliers, and in literature, so the descriptions here are only cursory.

The "Hot Lime" Process

This is a water softening process which uses hot lime contact to induce a precipitate of the compounds contributing to hardness (mostly Ca and Mg carbonates). The sludge formed is allowed to settle out. Very often coagulation chemicals such as alum or iron salts are used to enhance the settling and the removal of the sludge formed. In most plants that use the "lime" process, the reaction by the addition of lime and soda ash is carried out at elevated temperatures. However the reaction can be allowed to take place at ambient temperatures. The hardness of the water from the "cold" process will be about 17–35 ppm, while that from the "hot" process will be 8–17 ppm. Cleanup filters containing anthracite are often used to finish the treating process.

Ion Exchange Processes

As the name implies this process exchanges undesirable ions contained in the raw water with more desirable ones that produce acceptable BFW. For example, in the softening process, calcium and magnesium ions are exchanged for sodium ions. In dealkalization, the ions contributing to alkalinity (carbonates, bicarbonates, etc.) are removed and replaced with chloride ions. Demineralization in this process replaces all cations with hydrogen ions (H^+) and all anions with hydroxyl ions (OH^-) making pure water ($H^+ + OH^-$).

The ion exchange resins need to be regenerated after a period of operation. The operating period will differ from process to process and will depend to some extent on the amount of impurities in the water and the required purity of the treated water. Regeneration is accomplished in three steps:

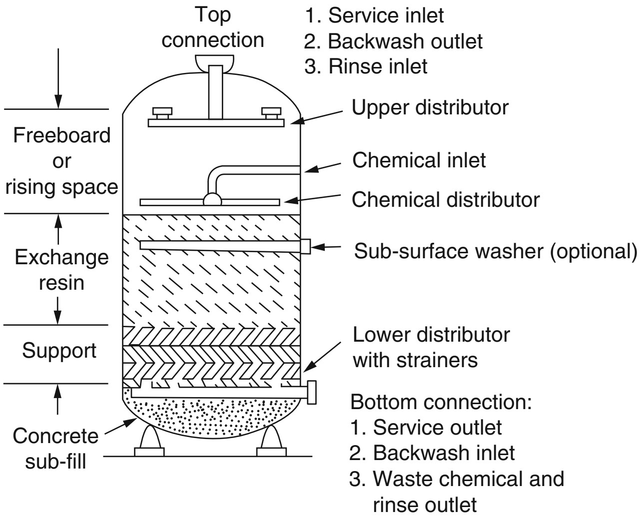


Fig. 13 A typical ion exchange vessel

- Backwashing
- Regenerating the resin bed with regenerating chemicals
- Rinsing

Figure 13 shows the internals of a typical ion exchange unit.

Under operating conditions the raw water is introduced through the top connection and distributor. The water flows through the resin bed where ion exchange takes place. The treated water is removed via the bottom connection. Under regeneration operation, raw water as backwash is introduced through the bottom connection and removed from the top connection. During its passage upward through the resin and support beds, it “fluffs” the beds and removes any waste material that has adhered to them. The backwash water is then sent to the plants wastewater disposal system.

Regenerating exchange chemical is introduced directly above the resin bed through a chemical distributor and allowed to flow downward to be removed at the bottom water outlet. The regenerating cycle is completed with the rinsing of the bed to remove any surplus regenerating chemicals. This is done by introducing a stream of raw water at the top connection and removing it from the bottom connection. This water is also disposed to waste.

Normally ion exchange units are installed in pairs (or more). When one is operating, the other is being regenerated. An automatic switch over of electronically controlled valves takes the pair of units through the correct cycles at the prescribed time intervals, without disrupting the treating process. Figure 14 shows a typical “hookup” of an ion exchange unit.

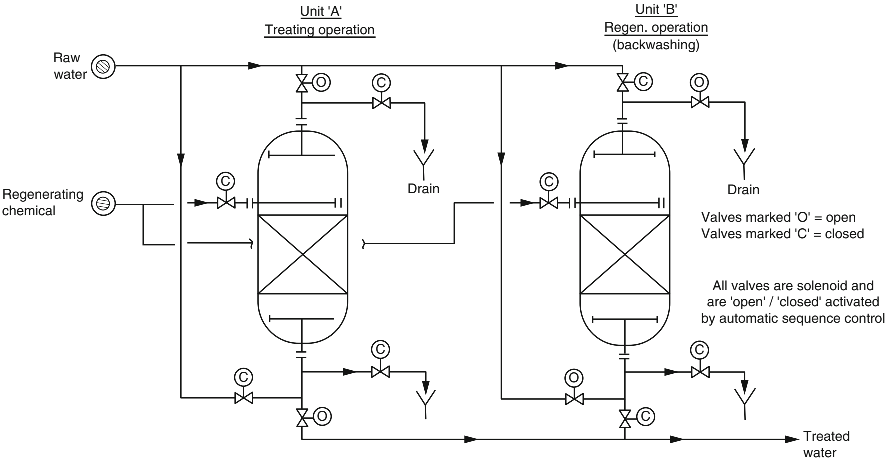


Fig. 14 An ion exchange unit hookup

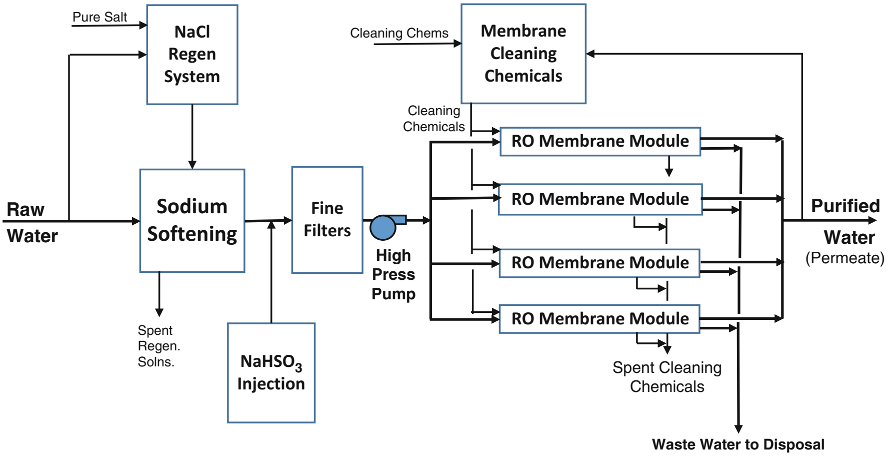


Fig. 15 Reverse osmosis system block flow diagram

Reverse Osmosis

Many newer facilities make boiler feed water by reverse osmosis (RO) using a selective membrane. The block flow diagram for an RO unit looks like Fig. 15.

In a reverse osmosis system, raw water, normally city water or other filtered and chlorinated water, is softened using sodium zeolite. Sodium replaces the calcium, magnesium, and other cations quantitatively. This is essentially the same as the first step in the other ion exchange processes. The softener resin is regenerated periodically by salt (sodium chloride) solutions. The spent regeneration solution is rejected to the sewer normally, although the final fast rinse can be used as cooling tower makeup, since it is essentially clean water. At least two 100 % softener vessels are used so one can be regenerating while the other is in service.

The softened water is filtered through a fine (micron-range) filter. Sodium bisulfite solution is injected to scavenge any residual chlorine in the softened water which can damage the RO membranes.

The water is pumped to fairly high pressure and sent to the RO membrane skids. The pumps for this use are often seal-less. The pumps may actually be integrated into and controlled by the RO skids as a self-contained unit with its own PLC.

The RO skids consist of several pressure tubes about 8–12″ diameter (0.2–0.3 m) and around 20 ft. (~6 m) long. Inside the tubes normally are wound membranes packaged in smaller modules. The softened water enters one side of the membrane. The smaller water molecules preferentially diffuse through the membrane under pressure, leaving the impurities behind. The clean water permeate leaves the modules, headed to the users, usually through a large storage tank.

The remaining water, which contains the impurities, is sent to sewer or can be used as cooling tower makeup (since it is soft).

The RO membranes must be chemically cleaned regularly (every few months) as they build up foulants, micro bio growth, and slight bits of hardness that get through. The timing for cleaning is normally determined by the increase in pressure drop through the modules and the loss of clean water recovery as a percentage of feed water. A connected, packaged cleaning system may be used, or the membrane modules can be removed from the tubes fairly quickly and sent off-site for thorough cleaning.

Modules will last several years if properly maintained. Some types are damaged by chlorine and may require replacement if the sodium bisulfite injection is not reliable. The modules also lose a little capacity each time they are cleaned because not all contaminants are normally removed. This impact can be minimized by attention to the cleaning process.

The RO modules are usually spared because of the maintenance requirements. Three 60 % modules or two 100 % modules are common configurations. Often, the RO system is owned and operated by a water treatment company, who will ensure good reliability.

Note that one thing RO systems do not like is low rates or no flow. If water is allowed to sit in the modules without movement, the membranes tend to foul. Attention to sizing of the system is necessary.

Monitoring an RO system requires watching:

- Softened water hardness (for regeneration needs)
- Sulfite injection rate
- Pre-filter pressure drop (for changeout)
- Membrane pressure drop for each skid
- Product water conductivity, pH, and hardness from each skid
- Wastewater conductivity from each skid

- Product water recovery vs. feed water rate from each skid
- Required cleaning frequency for each skid

A couple of RO system trouble indicators are:

- *Sudden increase in RO membrane pressure drop*. If all the skids are affected, check the softeners and the pre-filters. It is likely that the softeners have failed. If only one membrane skid is affected, it is possible that the membranes have collapsed because the pressure supplied from the pumps was too high or there may be a valve problem.
- *High pressure drop through the membranes building over time*. Indicates membrane fouling. Time to clean the membranes.
- *Sudden loss of flow*. Check the pressure pumps and lineups. The pumps sometimes fail without warning.
- *Increasing product water conductivity or TDS trend after cleaning*. Membrane damage is possible. Check the dechlorination sodium bisulfite flow for problems. It may be necessary to replace the membrane modules.

Rely on the RO system or membrane manufacturer and your water treatment chemical vendor for troubleshooting help. These systems work great normally, but troubleshooting can be difficult.

Pretreatment Process Comparison

The quality of water provided by softening, ion exchange, and reverse osmosis systems needs to be capable of meeting the requirements for the boiler feed water and drum water in Tables 3 and 4. In general, softening would apply to lower-pressure steam generation. RO systems cover the medium pressures, but can be augmented by polishing, additional stages, and ultrafiltration to supply high-pressure systems. Demineralization is for the medium- to higher-pressure generators.

Deaeration and Degasification

The deaeration and degasification process is used in almost all BFW treatment to remove dissolved gases from the water. Usually, this is just referred to generically as deaeration and we will use that convention here.

Normally treated water and returned condensate are routed to a deaerator immediately prior to entering the boiler steam drum. Figure 16 is a sketch of a typical deaerator drum layout.

The drum consists of a retention vessel surmounted by a degassing tower section (also referred to as the “stripper” or “heater” section). The degassing section contains a packed or trayed volume over which the treated water (and condensate) stream is passed. If this section is trayed, the trays are of special design with a spacing of about 2–3″ (~50–75 cm), and there may be 30–40 trays packed into the stripper section. Metallurgy is stainless steel.

Table 4 Water quality guidelines for reliable, continuous operation of water-tube boilers (ASME)

Boiler feed water limits			
Drum pressure, psig	Iron, wppm	Copper, wppm	Total hardness, wppm $CaCO_3$
0–300	0.100	0.050	0.300
301–450	0.050	0.025	0.300
451–600	0.030	0.020	0.200
601–750	0.025	0.020	0.200
751–900	0.020	0.015	0.100
901–1,000	0.020	0.015	0.050
1,001–1,500	0.010	0.010	ND
1,501–2,000	0.010	0.010	ND
Boiler water limits			
Drum pressure, psig	Silica, wppm SiO_2	Total alkalinity, wppm $CaCO_3$	Specific conductance, μmho/cm
0–300	150	350	3,500
301–450	90	300	3,000
451–600	40	250	2,500
601–750	30	200	2,000
751–900	20	150	1,500
901–1,000	8	100	1,000
1,001–1,500	2	NS	150
1,501–2,000	1	NS	100

Low-pressure steam, usually letdown saturated 50 psig (~3.4 barg) steam or 5 psig (0.3 barg) steam from condensate flash, is introduced to the bottom of the degassing section. The steam flows upward through the packed section and countercurrent to the water. This action removes or strips the dissolved gases from the water. These gases then leave with the steam from the top of the degassing section to be vented to atmosphere. In some uses, like hydrogen plants, the stripped gases may contain traces of hydrocarbons, other organic compounds, and ammonia. In these cases, the vented gas may be routed to a heater or back into the process under pressure to prevent emissions. The gas-free water free flows into the main retaining section or “tank” of the deaerator.

The treated water feed is introduced to the degassing section of the deaerator through atomizing spray/distributor. This reduces the water stream to fine droplets prior to entering the packed/trayed section. This enhances the removal of the gases in the water. Deaerators operate. Preferably, at about 2–3 psig (0.1–0.2 barg) and at this pressure, all of the CO_2 contained in the water and most of the oxygen are removed.

The BFW pumps draw suction directly from the deaerator storage section. To ensure that there is available sufficient NPSH for the pumps to operate properly, deaerator drums are installed on a structure at least 15 ft. (~5 m) above the center

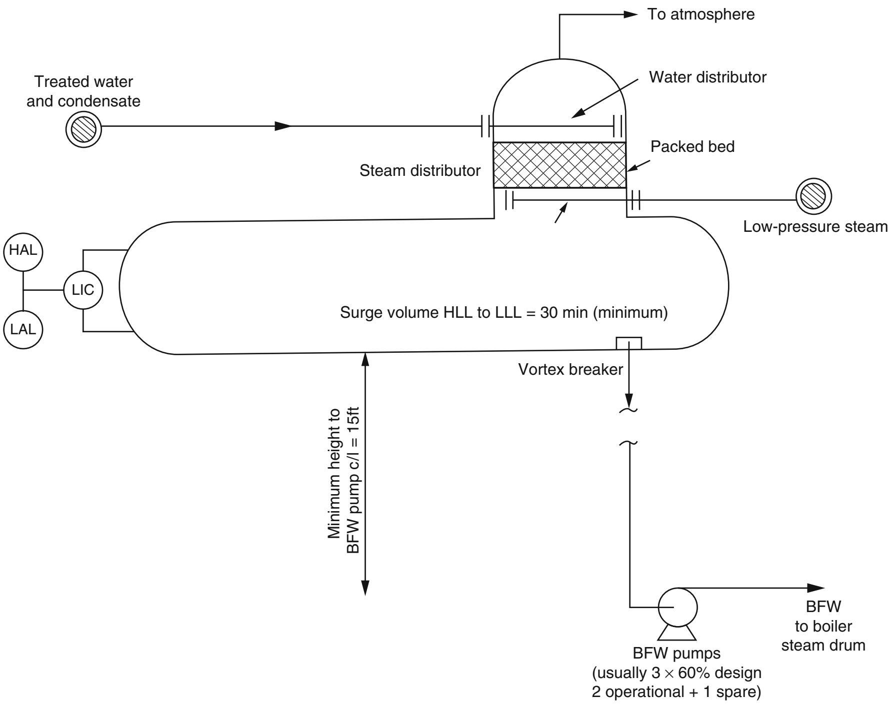


Fig. 16 A deaerator drum

line of the pump suction. Most large pumps (as BFW pumps are) usually require a relatively high NPSH when handling hot water.

The retention section of the deaerator should have as a minimum 30 min of surge between HLL and LLL. The water feed to the deaerator is normally on retention section level control. The boiler feed water from the BFW pumps will be on flow control with steam drum level or 3-element controller reset. Very often boiler feed flow has low flow alarm and at very low flow has automatic boiler shutdown device.

Chemical Treatment and Other Considerations

Boiler feed water may be treated at the point it is generated or may be treated locally in a process unit for specific situations and stresses. The chemicals needed for boiler feed water treatment are described in detail in the section "Boiler and Condensate Chemical Treatment" of this chapter. Summarizing the treatment requirements, the water needs to be treated to:

- Eliminate any traces of dissolved oxygen (down to <10 ppb)
- Prevent deposition and corrosion of the steam generation system
- Prevent corrosion of the condensate system

Condensate Recovery and Recycle

Because of the high cost in making boiler feed water, it is economically desirable to recover condensates from throughout the plant. This recovery is discussed in some detail in the section "Components of the Steam System" under the subsection "Steam Traps and Condensate Systems" of this chapter. A couple of key points in that discussion are reiterated here:

- It is necessary to monitor the condensate return streams for hydrocarbon or other contamination by process fluids. Condensate "hot well" vapors can be monitored to identify leaks. Streams with leaks should not be reused.
- Surface condensers and other systems operating at vacuum will pull in air, becoming contaminated with dissolved oxygen. Condensate from these services should not be used in processes, but may still be used for BFW after deaeration.
- Condensate chemical treatment is just about as critical as BFW treatment to avoid corrosion in the condensate headers.

Prevention of BFW Contamination

As with most utilities, it is critical to avoid contamination of BFW with process fluids. This has been mentioned under condensate reuse, but consideration needs to be given to backflow prevention wherever BFW is introduced directly into a process.

As a minimum, the process injection point should have one or more check valves and a block valve. The injection point should be capable of being blinded when not in use.

Temporary connections of BFW into a process are at particular risk. These can occur as part of the shutdown or start-up procedures or during maintenance. It is a best practice to provide backflow prevention and to remove and blind off any temporary BFW connections to a process system when they are not needed and *before* the process system is pressured up.

A little care in preventing contamination of the BFW system will avoid unexpected problems.

Plant Water

For general use in a refinery, there is normally a plant water system (AKA industrial, utility, or yard water). This system (which we will call plant water) may be supplied from city water, wells, or other sources. It is not considered potable (drinkable). Plant water is used for area wash-down, flushing equipment, and other routine uses that do not require drinking water quality or have other requirements.

The plant water is normally supplied at ambient temperature and ~100–125 psig (~7–9 barg) through a dead-ended distribution system. The water is available at numerous "utility drops" located strategically throughout the units. The utility drops are usually capable of supplying something like 50 gpm (200 l/min) of water.

In many locations, there are provisions for heating the water by direct, live steam injection manually or through a self-contained control valve.

In cold climates, the plant water headers and drops may be winterized by tracing and/or a flowing loop. Usually, the tracing will be of the “stand-off” steam type or electrical to avoid boiling the water.

Potable Water

In some, usually remote, locations the facility may need to provide its own potable or drinkable water. This water is used for drinking, but must also be provided to safety eyewashes and showers. It would be used in change room for showers, also.

Governmental authorities define the required water quality for potable water. It normally has limits on the impurities and must be chlorinated or otherwise disinfected. The potable water system piping also requires disinfection. There are requirements for sampling the potable water. The local requirements need to be determined.

Table 5 provides a sampling of some key drinking water standards. This is presented for example only. You should consult the applicable regulations and authorities for current requirements. The US standards actually include limits on at least 88 different contaminants so you can see this is just a small sampling.

A typical potable water treatment system may include several steps as noted below. These processes are not detailed here. A civil engineer would normally be consulted in design of these systems.

- Flocculation or deep bed filtration of the water to remove solids
- Reverse osmosis or softening to manage hardness, dissolved solids, and potentially hazardous inorganic compounds
- Carbon filtration or treatment for organics
- Chlorination (with a required holding time) before distribution to the plant.

The potable water system must be protected against contamination from the process or any other source. For this reason, the potable water system should *never* be connected to the process or any other utility. Where potable water is used, backflow protection (such as air gaps, preventers, or air/siphon breaks) must always be applied.

Winterization of the potable water system normally takes the form of insulation with electric or warm water tracing. Never steam-trace potable water lines.

On the other hand, the normally-no-flow lines that go to safety eyewashes or showers may get very hot in the summer or in desert locations. These potable water lines are normally run below other piping in the rack to provide shade, underground, or are provided with insulation and cooling water tracing to keep them from getting hot enough to cause injury. Insulation alone is not adequate.

Table 5 Sample of typical drinking water standards (www.lenntech.com/applications/drinking/standards)

	US EPA (2013)		WHO (1993)	EU (1998)
Contaminant	Maximum	Recommended	Guideline max	Standard max
Arsenic, mg/l	0.01	Nil	0.01	0.01
Barium, mg/l	2	2	0.3	
Benzene, mg/l	0.005	Nil		0.001
Cadmium, mg/l	0.005	0.005	0.003	0.005
Chloride, mg/l	–	250	250	250
Chlorine, mg/l (Cl_2)	(min 4 residual)	(min 4 residual)	(5 residual)	
Chromium, mg/l	0.1	0.1	0.05 (Cr^{6+})	0.05 (Cr^{6+})
Copper, mg/l	1.3	1.3	2	2
Cyanide, mg/l	0.2	0.2	0.07	0.05
Fluoride, mg/l	4	4	1.5	1.5
Iron, mg/l	–	0.3		0.02
Lead, mg/l	0.015	Nil	0.01	0.01
Manganese, mg/l	–	0.05	0.5	0.05
Nitrate, mg/l	10 (as N)	10 (as N)	50 total as N (Nitrate & Nitrite)	50 (as N)
Nitrite, mg/l	1	1		0.5 (as N)
Phenols, mg/l	–	0.001		
Selenium, mg/l	0.05	0.05	0.01	0.01
Sodium, mg/l			200	200
Sulfate, mg/l	–	250	500	250
TDS, mg/l	–	500	500	
Toluene, mg/l	1	1	0.7	
Xylenes, mg/l	10	10	0.5	
Zinc, mg/l	–	5	3	
Turbidity, NTU	Specific treatment processes req'd			
Radioactivity, pCi/l	5 (as $Ra^{226, 228}$)	Nil		
Coliform bacteria	Negative test req'd	Nil		Nil in 100 ml

Fire Water

Water for fighting fires (AKA fire water) is distributed through a secure, redundant system throughout the refinery. Fire water is sometimes used when large quantities of water are needed for flushing, area wash-down, or hydrotesting systems. These uses are only intermittent.

The fire water system should never be connected permanently to any process equipment or systems. Backflow prevention to avoid contamination of the fire water system should always be used when firewater is involved. People have been unpleasantly surprised when fighting a fire to find their firewater is contaminated with gasoline because an unwise (or prohibited) connection was made somewhere in the system.

Additional discussion of facilities and practices for fire water systems is in the chapter entitled "▶ Fire Prevention and Firefighting in Petroleum Processing."

Compressed Air Systems

All petroleum processing plants require a supply of compressed air to operate the plant and for plant maintenance. There are usually two separate systems and these are:

- Plant air system
- Instrument air system

Plant Air System

Plant air is generally supplied by a simple compressor with an after cooler. Very often, when plant air is required only for maintenance, this is furnished by a mobile compressor connected to a distribution piping system. Air for catalyst regeneration and the like is normally supplied by the regular process gas compressor on the unit.

Instrument Air System

Instrument air should always be a separate supply system; although in some refineries, instrument air is provided from the plant air system on a priority basis, with plant air distribution cut off at low pressures.

In some refineries, there are additional emergency air compressors provided locally in the event main plant instrument air fails.

Compressed air for instrument operation must be free of oil and dry for the proper function of the instruments it supplies. This is a requirement which is not necessary for most plant air usage. A reliable source of clean dry instrument air is an essential requirement for plant operation. Failure of this system means a complete shutdown of the plant.

Instrument Air System Flow Sheet

Figure 17 shows a typical, dedicated instrument air supply system.

Atmospheric air is introduced into the suction of one of two compressors via an air filter. The compressors are usually reciprocating or screw type non-lubricated. Centrifugal type compressors have been used for this service when the demand for instrument air is very high. The air compressors discharge the air at the required

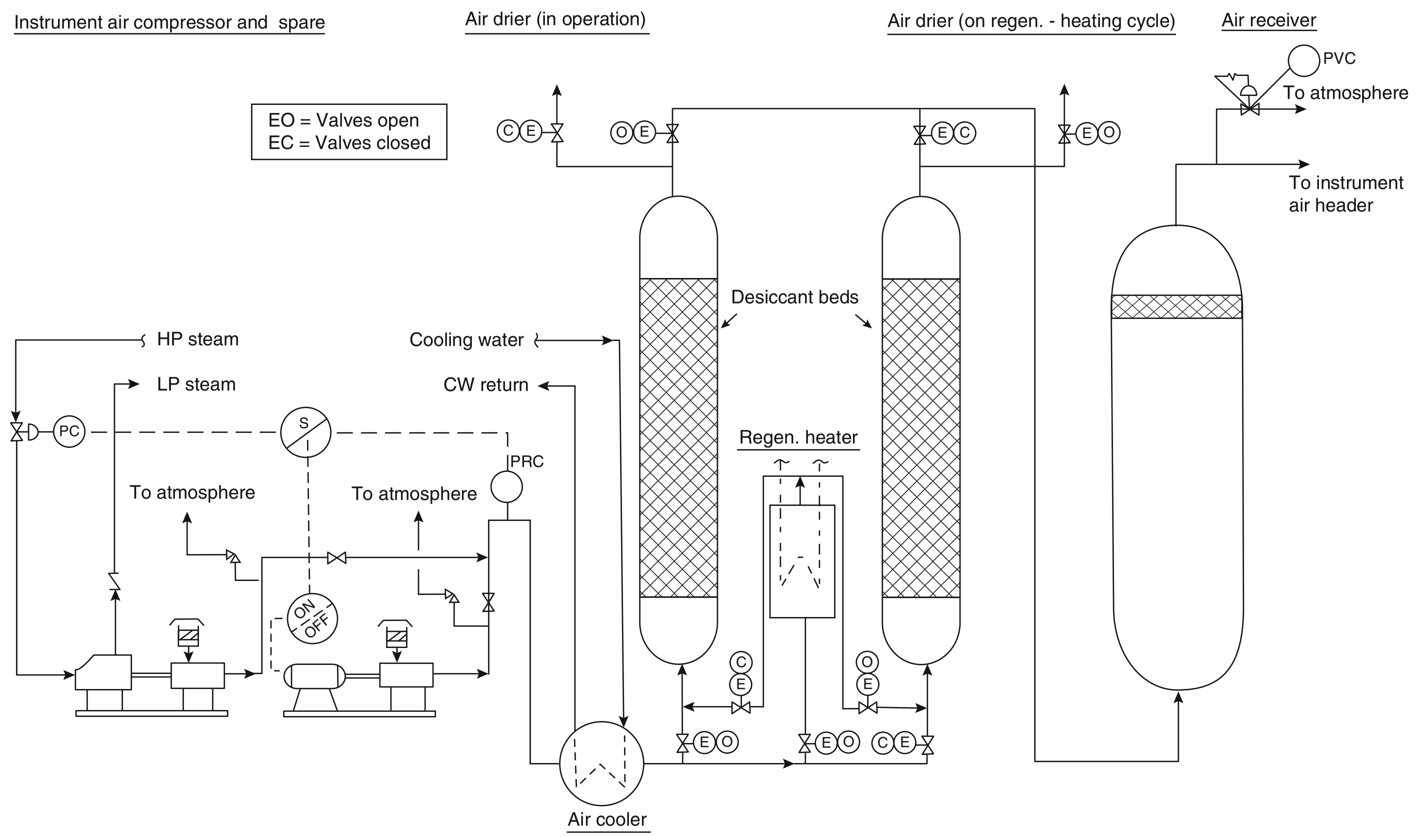


Fig. 17 A typical instrument air supply system

pressure (usually above 100 psig) into an air cooler before the air enters one of two dryers.

One of the compressors is in operation while the other is on standby. The operating compressor is usually motor driven with a discharge-pressure-operated on/off start-up switch. The standby compressor is turbine (or diesel engine) driven with an automatic start-up on low discharge pressure.

The cooled compressed air leaves the cooler to enter the dryers. There are usually at least two dryer vessels each containing a bed of desiccant material. This material is either silica gel, alumina, or, in special cases, zeolite (molecular sieve). One or more of the dryers is in operation with the compressed air flowing through to be dried and to enter the instrument air receiver. The desiccant in a spent dryer is simultaneously regenerated.

The regeneration cycle may be initiated manually, on a predetermined frequency, or by a moisture analyzer in the instrument air header.

Regeneration of a traditional desiccant bed is effected by passing a stream of heated air through the bed and venting the stream to atmosphere. This heated stream removes the water from the desiccant to restore its hygroscopic properties. At the end of this heating cycle, cooled air is reintroduced to cool down the bed to its operating temperature. When cool, the unit is ready to be switched into operation and to allow the other dryer to start its regeneration cycle. The various operating and regeneration phases are automatically controlled by a series of solenoid valves operated by a sequence timer switch control. These dryers (often including the compressor and receiver items) are packaged units supplied, skid mounted, and ready for operation.

There are also pressure swing adsorption (PSA) dryers for instrument air, normally using molecular sieves. These dryer beds are regenerated by dropping the bed pressure to atmosphere and purging the bed with dry air from the bed(s) in service. The regenerated bed is then repressured and swung back online. The sequence is controlled by a PLC.

The instrument air receiver vessel is a pressure vessel containing a crinkled wire mesh screen (CWMS) or other fine coalescing medium before the outlet nozzle. It is at high pressure protected by a pressure control valve venting to atmosphere and is also protected by a pressure safety relief valve (not shown in diagram). The air leaves the top of this vessel to enter the instrument air distribution system servicing all the units in the complex.

The instrument air must meet dryness specifications appropriate to the facility location. Very cold climates require much dryer air. Table 6 provides some typical instrument air specifications.

Table 6 Typical instrument air specifications

Specification	Typical maximum	Notes
Dew point	−40 °F (−40 °C)	Absolute max under any condition is 35 °F (2 °C)
Oil content	0.01 ppm	
Particulates	0.02 mg/m^3	100 % must be <100 μm
Supply temperature	110 °F (43 °C)	

The dry instrument air is usually distributed to the users at around 60–80 psig (say, 4–5.5 barg) by a utility header. For large, intermittent users, like pressure swing adsorption units, there may be local surge drums or additional knockouts.

Instrument Air Security and Prioritization

Instrument air is normally supplied by redundant compressors with redundant air dryers. Because instrument air is so critical, many facilities also provide emergency backup instrument air at critical locations in the plant. Approaches that have been used include:

- Standby local compressor sized to supply air to one unit. These are often non-lubricated machines with separate coalescers and knockout pots that tie into the instrument air system. They may be steam or diesel driven. These compressors must be tested regularly (weekly) to ensure they will work when required.
- Some facilities locate a large instrument air surge drum at a critical unit. The instrument air drum is held at full compressor discharge pressure (maybe 120 psig (say, 8–9 barg)). The drum is sized to contain enough air to operate the plant with no compressor for a period of time (usually something like 30 min) before the pressure decays to the point where control valves begin failing (usually around 40–60 psig (say, 2.5–4.0 barg)).
- Some locations may provide vaporized liquid nitrogen for backup to the instrument air. This approach has to be carefully managed, however, since the nitrogen will also enter control rooms and may cause suffocation, especially if the controls are heavily pneumatic. It might be acceptable for a few specific local controls where the vented nitrogen cannot reach an occupied or potentially occupied building.
- In an instrument air loss, some plants pressure their plant air into the instrument air header. This should only be temporary. Extended use of plant air as instrument air will likely foul the pneumatic instruments and control valves unless the plant air meets instrument air specs.

Connecting Instrument and Plant Air Systems

While the preferable approach to plant and instrument air is complete separation, many locations combine the systems up to the battery limit of a unit. In these cases, the entire air supply, both instrument and plant, is conditioned to meet instrument air specifications. The two services then separate. There is a valve on the plant air supply header that shuts that header off in the event of low air supply pressure – giving priority on air to the instrument system.

Instrument Air System Capacity

The required capacity for the instrument air system will be determined by the types and number of instruments consuming the air as well as the frequency with which they must act. Table 7 provides some typical air usage rates for pneumatic

Table 7 Some instrument air consumption rates and ranges (see references at the end of the chapter)

Device	Air requirement, scfm (Nm^3/h)
Signal converter (I/P, P/I, E/P, etc.)	0.35–0.60 (0.56–1.0)
Ball valve actuator	[73 cu in/opn (0.0012 m^3/opn)]
Diaphragm control valve, w/ positioner	0.3–0.75 (0.5–1.3) – stable flow
	7–15 (11–24) – unstable flow
Piston actuated control valve, w/ positioner	5 (8.5)
Panel-mounted instrument	0.5 (0.85)
Field-mounted instrument	0.5 (0.85)

instruments as a guideline. You can estimate the air rate by counting the number of instruments of each type in the control system, applying the appropriate consumption rate, and adding the rates. Commonly, a 25–50 % contingency is applied on top of these numbers to cover unknowns, emergency situations, and an allowance for expansion.

For detailed design, vendor data on air consumption for the instrumentation selected should be used for header and capacity sizing.

Plant Air System

In many respects, a plant air system resembles the instrument air system. The compressors are usually redundant. In cold climates, both types of the air will be dried. The plant air is then distributed by headers throughout the plant. It is also one of the utilities supplied at the utility stations or utility drops for general use in the facility.

The chief differences between plant and instrument air are in the level of security applied and the requirement for drying the instrument air. Anyone can use the plant air through a utility station. The usage rates can be much larger than for instrument air. Plant air may also be connected to the process at times, whereas instrument air is normally strictly excluded from process connections.

Plant air use tends to rise, because it is uncontrolled. It is advisable to manage the plant air users, just like any other utility users to ensure adequate air supply to more important users.

Protection of Air Systems

Care must be taken to protect the air systems from contamination. Instrument air should never be connected to a process system. Plant air should only be connected to the process through check valves. Air should never be left connected into a process line that is at higher pressure. It should always be disconnected and air gapped or blinded.

Contamination of plant and instrument air has been seen as the result of strange, unauthorized, or inadequately considered connections that have resulted in air systems full of nitrogen, oil, and water. Care must be taken at all times to ensure that this does not happen to you.

Electrical Power Supply

In today's petroleum processing facilities, electrical power is arguably the most important utility, competing with steam. Failure of electrical power for even 0.5 s usually means hours, if not days, of downtime and lost production accompanied by the potential for equipment damage or worse.

We will touch only slightly on this critical system in this handbook, but this is not a reflection on its importance.

Electrical Power Distribution System

The electrical power distribution system in a facility might look something like that depicted in Fig. 18. This is a very simple version of a one-line diagram. Electrical engineers (who may cringe at this diagram) have much more detailed diagrams for the power systems, but this will suffice for the discussion here. The diagram does not show all the breakers, motor controllers, switches, etc.

Power to a facility is generally supplied from an outside utility via a nearby set of transformers and switch gear. The utility protects itself from a problem in your facility with breakers. The utility power, usually 138 KV or higher from the long distance transmission lines, is transformed down to 13.8 KV entering a large facility.

For reliability, there are normally multiple feeder lines into a facility, preferably originating from different sources or transmission lines. This provides some level of protection against power loss, but often problems on one feeder tend to propagate to the others.

Facilities with cogeneration and power recovery units have some alternate sources of power, but these units can also be knocked out by an outside problem if they are not properly protected.

The 13.8 KV feeders are transformed down to 4,160 V, usually within the facility. The 4,160 V electricity goes to the plant power distribution centers (PDCs) where it is distributed to the high voltage users, like large induction and synchronous motors. These are usually over 250 HP (~188 KW). The large motors may be over 10,000 HP (7,500 KW).

The 4,160 V power is transformed down to lower voltages in steps to supply the smaller users. Usually, there are 480 V, 240 V, and 120 V users typically in the USA. These will include smaller motors, lighting, instrumentation, electronics, and other services.

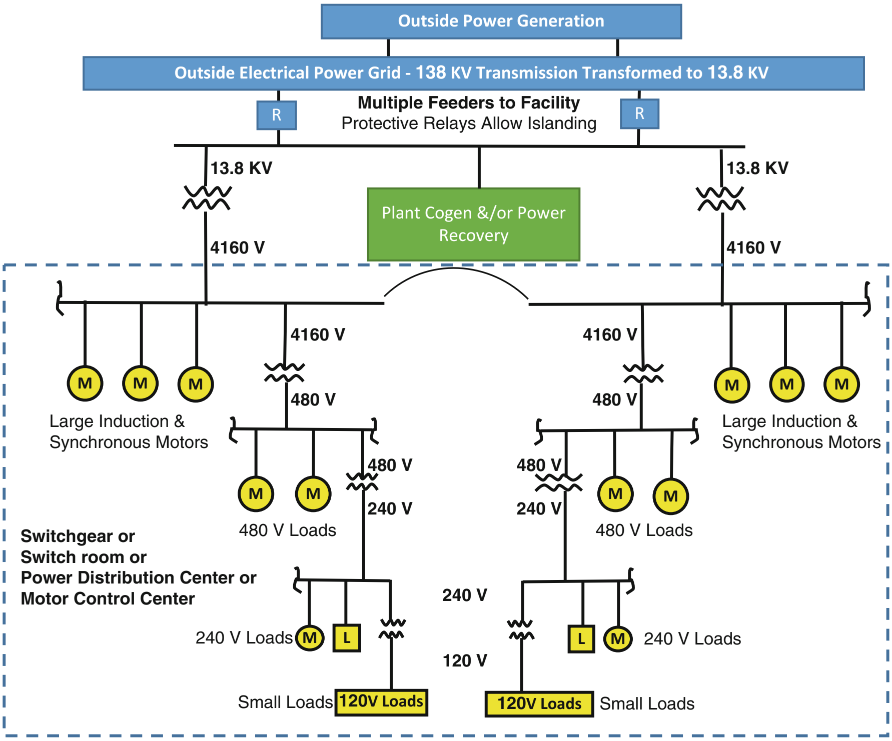


Fig. 18 A simplified electrical one-line diagram

There is usually an attempt to provide critical services with power from at least two different sources, even within a facility. For instance, two critical 480 V motors may be supplied from different 480 V lines supplied by different 4,160 V lines. Or, the redundant power supplies to the DCS may originate in different PDCs tracing back to different feeders. For control systems, power is usually automatically switched to an uninterruptable power supply (UPS, batteries) that is charged off the external power supply. The UPS normally is sized to provide continued power to the controllers for several minutes to hours.

Not really obvious in the simplified one-line diagram, the loads must be balanced among the power phases to avoid a phase imbalance and creation of high current in one phase. This is carefully considered by the electrical engineers in design and operation of the system.

Cogeneration and Power Recovery

Many facilities have surplus fuel gas available and they need steam. In these plants, cogeneration of power and steam is a good option. The large cogeneration units are available as packaged plants (many in the 50–75 MW range). The power is supplied by an aeroderivative gas turbine driving a generator, although there are engine-driven units, too. Excess heat leaving the turbine is used to raise steam, just like a conventional water-tube boiler. This system thus provides two critical utilities to the plant and allows the export of excess power to the utility grid.

Cogeneration units are normally very reliable, but they do experience shutdowns. The backup steam supply needs to be capable of taking over fast enough when the cogen trips. Sometimes, the cogen supplies so much of the plant steam demand that, when it trips, the boilers cannot fire up fast enough to supply the critical steam needs. In these cases, what starts as a cogen trip snowballs into a total utility failure and cold restart of the entire facility. To avoid this, the percentage of steam supplied by the cogen needs to be managed. It is possible to take surplus cogen steam to a separate steam turbine generator to make use of excess steam. Care needs to be taken in managing these situations.

Cogens can also be knocked down by a power disturbance in the outside utility grid. For this reason, many facilities provide protective relays that allow the plant to rapidly (automatically) isolate from the outside power grid and continue running with minimal disturbance. This is referred to as “islanding.” In these cases, the cogen generator and control system may need to be designed to handle the reactive power demand it will see when it is the primary power supply to an islanded facility.

Often there are other power recovery generators within a facility. One of the most common is a turbo-expander on the FCC flue gas. These generators are much smaller than cogens. A trip of one of the smaller generators usually has little facility-wide impact, unless they create a direct ground fault as they fail. If the generator is in a pressure-letdown service, a control alternative needs to be available. Usually there is a control valve or controlled louver/damper in parallel to a letdown generator, so a rapid switchover is possible if the generator fails.

Power Versus Emergency Steam Loads

Electrical power frequently replaces steam in prime drivers of rotating equipment. This is energy efficient, but it does present some hidden problems. If the plant depends on steam turbine drivers to back up the electric motor drivers, a sudden loss of power can place a huge, instantaneous load on the steam system. This is alluded to above in the discussion of cogeneration, but the concern applies in other cases as well.

There is a limit to how fast a boiler can increase its steaming rate. As a rule of thumb, a boiler can double steam production about every minute in an emergency without tripping and assuming it has adequate back pressure.

Let’s say a 250 Mlb/h (113,000 kg/h) boiler is operating at one fourth rate in parallel to a cogen that is supplying 88,000 lb/h (40,000 kg/h) of steam and there are several critical electrical services in the plant. If the cogen trips and the external electrical supply trips due to the sudden increased load (a common scenario), the boiler would pick up the cogen steam supply plus another, say, 100 Mlb/h of load from the spare steam-driven lube pumps, backup air compressors, etc., that kick on due to power failure. The new instantaneous steam demand is now about 250 Mlb/h (full boiler capacity). The boiler can increase steam rate from 63 to 125 Mlb/h within the first minute. And it gets to 250 Mlb/h after 2 min. Meanwhile the steam header pressure has sagged, and the emergency turbines are now using even more steam than they were (the nature of steam turbines). The boiler will have a hard time catching up without shedding load somewhere or reestablishment of electrical power. If the operator tries to fire the boiler faster, it will usually just trip on high steam drum level (due to the sudden increase in steam bubbles in the drum).

The point here is that you must balance the electrical and steam loads to enable transition from electricity to steam in critical services in an emergency.

Of course, the alternative is to accept that steam will fail along with the power and construct your emergency procedures for that event. That is a viable alternative and one which is often chosen. You are accepting the economic impacts of the outage in that case vs. the continued cost of higher steam generation rates.

Electrical Power Distribution Conclusion

Electrical power is one of the most critical utilities in a petroleum processing facility. It is normally supplied by an outside utility, but may be supplied or augmented by on-site generation.

Reliability of the power supply is critical. These systems normally are supplied by multiple feeders from the power company. If the facility has a cogeneration unit with sufficient capacity, it may be capable of islanding to operate off internally generated power. UPSs are normally provided for backup power to control systems.

Integration of the power and steam systems through a cogeneration unit or excessive reliance on power (with steam backup) needs to be carefully managed to avoid total utility failure in the event of a power trip. Boilers have to be capable of assuming the required plant steam load if power is lost.

Nitrogen System

General Discussion of Nitrogen Utilities

Nitrogen is a common gas provided throughout refineries for inerting, blanketing, and purging. Often nitrogen is supplied from a plant header to the continuous users, just like any other utility.

Nitrogen can be provided in several forms:

- Vaporized liquid (on-site or temporary vaporizers)
- Pressure swing adsorption
- Membranes
- Gas cylinders/tube trailers

Table 8 Typical nitrogen purity specification for purging and blanketing

Component	Limits
Nitrogen, v%	99.7 min
CO + CO_2, vppm	30–40 max
Hydrocarbon, vppm	5 max
Water, vppm	5 max
Oxygen, vppm	100 max

We will discuss the usual supply approaches briefly in the following sections. First we will look at the required purity for nitrogen within a plant.

Specifications

Nitrogen purity requirements will vary, depending on the service. Where the gas is used for hydrocarbon gas or oxygen elimination, the most common uses, the purity must be high or effectiveness is limited.

For equipment purging and blanketing, a typical purity specification for nitrogen is in Table 8:

This specification is normally satisfied by vaporized liquid nitrogen (or cylinders for small users). Purity is generally much higher than that shown. The intake source for the nitrogen plant can influence the composition. For instance, an intake near a freeway will show higher CO and CO_2 content than nitrogen recovered elsewhere. Often this is not a problem, but may become a problem if the nitrogen is used for inert vessel entry where CO is a criterion.

In some cases, a lower purity specification may be permitted, such as in gas blanketing service. This may be supplied by a PSA or membrane nitrogen plant. Still, attention has to be given to the disposition of vent gases. If the blanket gas contains some oxygen (usually the main contaminant), it may be unwise to vent it to flare or vapor recovery.

Typical Nitrogen Supply Flow Sheets

The most common nitrogen supply in a facility is provided by vaporized bulk liquid. Figure 19 shows the main parts of the LN_2 vaporizer systems commonly used. Two types of liquid supply are shown:

- *On-site liquid storage tank*. In this system, a large on-site cryogenic storage tank is installed. The tank is usually double walled and super-insulated to prevent external heating. A tiny amount of the liquid is lost through evaporation which cools the remaining liquid. Evaporative loss is usually something like 1 %. A small stream of LN_2 flows through vaporizer coils which pull heat from the air to turn the liquid to vapor. The vapor is distributed to the facility nitrogen headers at about 125–200 psig (8.5–13.8 barg) and ambient temperature.

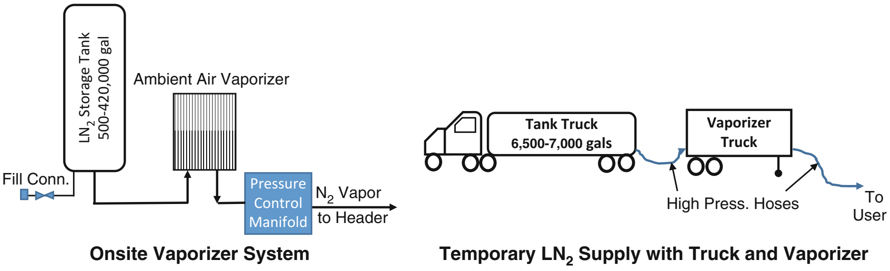


Fig. 19 Typical bulk liquid nitrogen supply options

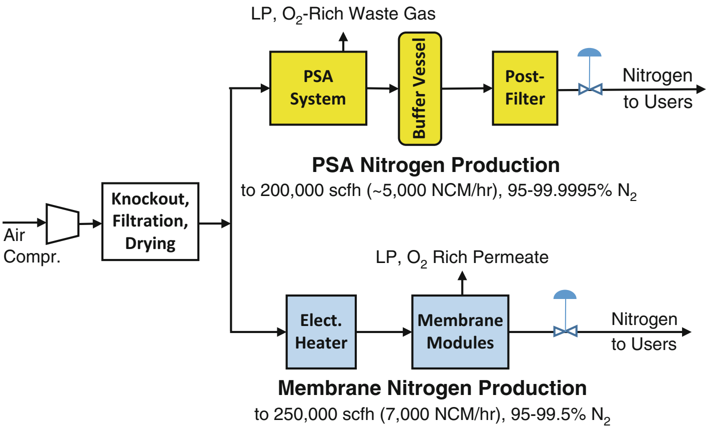


Fig. 20 On-site, non-cryogenic nitrogen generation options

There is backflow prevention to avoid contamination of the stored liquid. The tank and vaporizer are normally owned and maintained by the LN_2 vendor.

- *Temporary trailers and vaporizers*. The nitrogen vendor may supply his own LN_2 trailers and vaporizer. This is common during turnarounds when large quantities of nitrogen are needed for purging or inert entry. Full LN_2 tractor-trailer rigs are connected to a vaporizer truck. In the vaporizer truck, a propane-fired heater heats a circulating stream of, usually, oil or glycol solution, which then vaporizes the nitrogen. This system can supply liquid or gaseous nitrogen at elevated temperatures and pressures to 10,000 psi (690 barg). Care must be taken to avoid overpressuring process equipment or causing brittle fracture from unvaporized nitrogen liquid entering the system. The vendors are used to dealing with these issues.

On-site nitrogen generation is also an option by use of pressure swing adsorption and membranes. Packaged units for this are available from industrial gas suppliers. Simplified block flow sheets for these processes are shown in Fig. 20.

Nitrogen from these sources tends to be lower purity, although high purity is possible at higher cost.

Prevention of Nitrogen System Contamination

There are few worse feelings than purging a vessel with your plant nitrogen for an entire shift without success only to find your plant nitrogen supply is contaminated with hydrocarbon or hydrogen. Now you have to scramble to find a clean nitrogen supply quickly. If you are lucky, that is all you have to do.

There have also been occasions where someone has connected to the nitrogen header when they meant to tie into the plant air utility header. When the line goes into a building or enclosed space, this presents an asphyxiation hazard.

It is critical that the nitrogen utility system be protected from contamination by a foreign material and that it not be used for anything other than its intended purpose. In fairly common practice, contamination and unauthorized/unsafe use of nitrogen are prevented by specific steps:

- Nitrogen distribution header drops or outlets are separated from the normal utility stations and clearly marked with signs.
- The nitrogen drops have a specific nitrogen connection fittings on them – not the crow's feet used for air. The nitrogen fitting is often tack welded to the N_2 pipe to prevent removal.
- Special nitrogen hoses with nitrogen fittings are used which can only be connected to the nitrogen fittings on the utility drops.
- At the connection of nitrogen to each user, a special backflow prevention manifold is used. An example of such a manifold is in Fig. 21. Each company and facility will have their own standard for these manifolds.

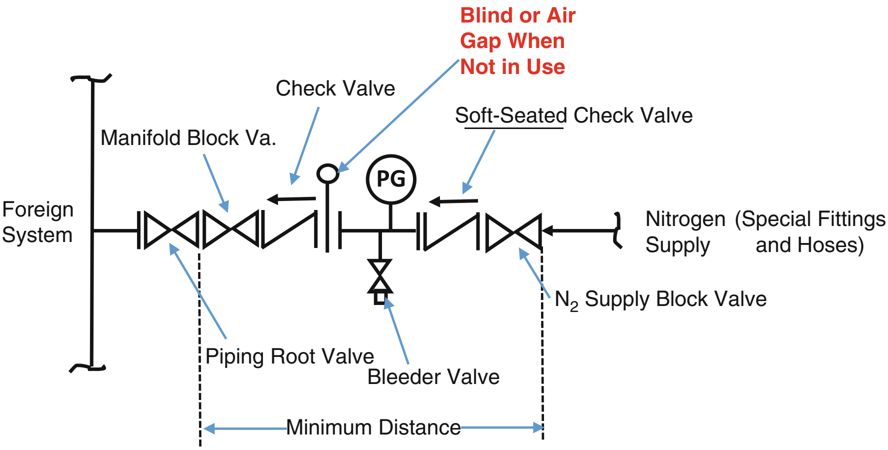


Fig. 21 Example of nitrogen backflow prevention manifold

- All nitrogen connections to the process or any other foreign systems, except permanent purge connections, are removed, blinded, or air gapped before pressure is raised on the foreign system.
- LN_2 brought into the plant should be tested for oxygen before it is used to ensure it is, in fact, nitrogen. There have been instances where liquid oxygen has accidently been unloaded into a nitrogen system – that is, about as bad as contamination can get.

Regardless of the precautions taken, it is still possible to defeat the protective measures. Constant diligence is needed to ensure that the nitrogen header provides the pure nitrogen expected.

Other Utility and Utility-Like Systems

In addition to the normally recognized utility systems, modern petroleum processing plants often have other systems that are distributed throughout a facility from a central supply location in the same manner as utilities. Among these are:

- Flushing oil
- Ammonia
- Oxygen for enrichment
- Hydrogen
- Caustic soda
- Amine solution

There are also several systems typically present in a processing facility that collect wastewaters, drainings, and other fluids from throughout the facility and convey them to a central location for disposition. Among these systems are:

- Process or oily water sewer
- Storm sewer
- Chemical sewers
- Slops or recovered oil

In this section, we will describe the functions and features of each of these systems. The discussion here will not be in the same detail as the foregoing utility discussions, but these systems are critical to operating a refinery or petrochemical plant and should not be overlooked in a comprehensive discussion.

Flushing Oil

Refineries processing heavy oils, vacuum resids, or tars with high pour points will often have a flushing oil utility available at strategic locations. The flushing oil is normally a straight-run diesel or light cycle oil. In very cold climates the flushing oil may be in the kerosene boiling range.

As an example, flushing oil may be used to dilute or cut the heavy oil and displace it from equipment when necessary. It may also be used to flush seals on heavy oil pumps when the pumpage is too heavy for a reliable seal flush.

In a flushing oil system, the oil is pressured into a dead-ended header at 50–100 psig (3.5–7 barg) and may be heated. The header may normally supply, perhaps, 100–200 gpm (370–750 l/m) – about a 2″ supply header. The users draw off the header as needed.

Flushing oil will often be tied into the process lines through a block valve and check, ready for use when needed. Some uses, such as continuous pump seal flushes, will be normally flowing, with the flushing oil going out of the pump with the pumpage.

Contamination of the flushing oil header with heavy oil by backflow is always possible, so check valves should be used at the injection points to reduce the risk. If heavy oil does get into the flushing oil system, it mostly presents a plugging problem and would have to be melted out.

Ammonia

The addition of selective catalytic reduction (SCR) and non-catalytic reduction (NCR) systems for NOx control from heaters and FCCs has resulted in some facilities providing ammonia for the reduction units as a utility throughout the plant. These systems may supply anhydrous or aqueous ammonia as a dead-ended, pressurized header throughout the facility from a central location. This consolidates the unloading and handling of the ammonia in one place, minimizing some of the handling risks.

The central ammonia facilities generally consist of a storage tank with connections for filling from a tank truck. There is a pressurizing pump that pulls from an elevated suction in the tank and provides pressure to the system – typically about 100 psig (~7 barg). Ammonia is distributed at ambient temperatures. Pumps for this service are normally positive displacement or gear pumps, with the excess flow spilled back into the storage tank on pressure control. The pumps are spared.

The ammonia is only routed to the local vaporizers or injection skids at each user from the central system. It is not provided as a utility drop.

There are a couple of idiosyncrasies about ammonia handling that can prevent a lot of problems:

- If the ammonia is for use in NOx reduction, be sure you get SCR grade. There are cheaper grades and more expensive grades. The cheaper grades have more impurities, and the expensive grades are unnecessary.
- Ammonia can have tiny amounts of oil and grease as well as other contaminants. Suction lines need to be elevated above the dead-bottom of the tanks so they do

not draw in the contaminants that settle as a sludge. It may be necessary to periodically draw the sludge out of the storage tanks.

- Aqueous ammonia is corrosive to carbon steel, despite what you may expect. This can be due to the use of undeaerated water for blending or the tendency of ammonia and deionized water to complex iron. In any event, the ammonia will have to undergo fine (submicron) filtration at each user if the distribution header is carbon steel. Once filtered, the piping should all be stainless steel. A stainless steel ammonia distribution header to the users would be nice, but probably not worth the expense.
- In vaporizers, because you are evaporating the ammonia completely, there will be an accumulation of hard deposits of iron and other materials from the ammonia. This is especially noticeable with aqueous ammonia. Watch for pressure drop in the vaporizers and plan to clean them on a regular basis. The spray-type vaporizers plug less than packed vaporizers. It is easy to set up a temporary vaporizer using bottled anhydrous ammonia and plant air mixed into the SCR supply header for emergencies. There is more discussion of this in the separate topic entitled "▶ Environmental Control and Engineering in Petroleum Processing" under SCR systems.
- Think about where you vent the relief valves from ammonia storage tanks and where you route tank drains or vents. Putting ammonia into a flare normally results in NOx emissions and/or plugging from ammonia salts. It is not unusual to route reliefs and drains to a nearby, dedicated atmospheric scrubber stack where the ammonia is absorbed in a water spray and the water is sent to the sewer.
- Avoid draining ammonia to the deck without a good-sized flowing water flush. The ammonia can easily overcome an operator.
- Secondary containment around ammonia storage facilities is required to manage spills.

So, if you have enough NOx control systems in your plant, an ammonia utility may be a viable alternative to the risks and problems with multiple delivery points and pumps.

Oxygen Enrichment Supply

Many facilities are choosing to de-bottleneck sulfur recovery units and FCCs using "oxygen enrichment." In these processes, atmospheric air that is used for combustion is augmented or enriched by injection of a controlled amount of pure or nearly pure oxygen. This is like increasing the size of the combustion air blower, without the capital cost of a new air blower. The practice is, of course, limited by temperatures in the system.

In facilities with O_2 enrichment, there may be an oxygen utility header provided. It may only be local to the unit(s) using the O_2. The oxygen is only routed to the specific users. It is not a plant-wide utility.

The options for supplying oxygen are similar to supply of nitrogen:

- Liquid oxygen with a vaporizer
- PSA oxygen (possibly the waste stream from a nitrogen generator)
- Membrane oxygen (possibly the permeate from a nitrogen generator)

Oxygen handling presents enhanced risks of fire where it may contact hydrocarbons, hydrogen, ammonia, or other combustibles. These need to be specifically managed.

Hydrogen Distribution

Because of the importance of hydroprocessing in meeting the fuel standards today, hydrogen is distributed in many refineries through one or more headers in the same manner as a utility. The systems for this are discussed in detail in the topic "▶ Hydrogen Production and Management for Petroleum Processing" in this handbook.

Caustic Soda

Sodium hydroxide or caustic soda finds uses in many units of a petroleum processing facility. In many cases it is received into a central facility and then distributed like a utility to the various users to minimize the bulk handling risks.

The caustic is usually received as ~50 w% solution, which may be sent to some users directly. At this concentration, the caustic freezes at 58 °F (14 °C). Lines carrying the 50 % caustic need to be electrically or cooling water traced to avoid freezing in many climates.

The 50 % caustic can be diluted down to 19 w%, which is a eutectic point, freezing at 18 °F (−28 °C). The 19 % caustic can then be distributed with less concern over freezing. The dilution can be done in a batch mode using cold condensate or other clean water. It is necessary to cool the solution as it is diluted to dissipate the substantial heat of solution or do the dilution slowly enough that the heat has time to dissipate. A circulating loop from the storage tank with injection of the dilution water and then flow through a cooler can be used. This system needs backflow protection to avoid contaminating the water stream. It should also ensure positive isolation of the water after use to avoid inadvertent water leakage into a tank that could create a high temperature.

Secondary containment around caustic storage facilities is required to manage spills and prevent groundwater contamination.

Caustic distribution would only go to the specific users in a facility.

Sulfuric Acid

Like caustic soda, sulfuric acid is also used at many units in a facility. Of course, a sulfuric acid alkylation unit would be a major user, but it will normally have its own dedicated supplies of acid. More commonly, acid is used in the cooling towers for pH control. In some facilities, it is supplied from a central location (often at the SA alky unit) through headers periodically to day tanks at the various users. This minimizes the hazards and risks in handling the bulk acid, which are substantial.

Secondary containment around all sulfuric acid storage and pumping facilities is required to manage spills and prevent groundwater contamination.

Also, like caustic, concentrated sulfuric acid has a high freezing point at about 50 °F. This means that sulfuric acid distribution headers need to be managed empty or traced and insulated, but the tracing temperature must be controlled to avoid rapid corrosion. Normally, carbon steel lines are fine for sulfuric acid, but, if a carbon steel sulfuric acid line is steam traced, it will only last a few minutes to a few hours before corrosion destroys it. Electric tracing to 60–70 °F and tracing with cooling water are the usual remedies.

Sulfuric acid lines also need to be protected from excessive ambient temperatures by insulation. Cooling water tracing also helps here. And, it must be protected against inadvertent dilution with water, which produces very high temperatures.

Amine Distribution

Many facilities have central amine solution regeneration, with the lean amine routed throughout the plant and rich amine returning to the central facility. The amine is routed only to the specific users and is not a normal utility drop.

Discussion of centralized amine facilities is included in the chapter entitled "▶ Refinery Gas Treating Processes" of this handbook.

Sewer Systems

Petroleum processing facilities generally have three types of sewer systems to collect aqueous fluids that are drained, purged, flushed, or are otherwise discharged and precipitation that falls on the facility. The most common systems are:

- Process or oily water sewer
- Storm sewer
- Chemical sewers
- Sanitary sewer

The following discussions provide some of the considerations in designing and operating these sewer systems.

Process or Oily Water Sewer (OWS)

Most petroleum processing plants have process or oily water sewers (OWS) as the main sewer system in the facility. These sewers accept any drained fluid from myriad sources which might be contaminated with oil or other process fluids.

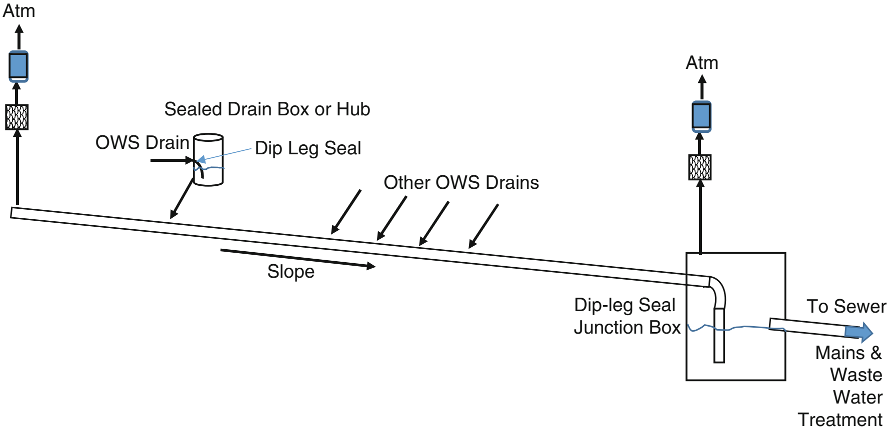


Fig. 22 Oily water sewer lateral

These sewers are located underground and convey the collected liquids to the wastewater treatment plant.

Figure 22 illustrates an oily water sewer lateral within a plant.

Some key design and operating considerations for the process or oily water sewer are:

- Drains to the sewer must be managed to avoid upsetting the wastewater treatment facilities. For instance, draining a large amount of soda ash solution to the OWS quickly will cause a pH excursion in the wastewater treatment facilities and the outfall or line to any publically owned treatment works (POTW) that receives the outfall. The same would be true if a large amount of sulfuric acid was dumped into the sewer. In the case of acid, in addition to a pH problem, the acid will cause corrosion in the treatment facilities. These would be potential permit violations.
- If a facility has a biotreatment unit, that unit is particularly upset by pH excursions, chlorine or bleach, biocides from cooling water treatment, phenols, heavy metals, and many other types of pollutants. The “bugs” get used to a regular diet of pollutants and don’t usually react well to big changes in their diet. Killing the bugs requires significant recovery time.
- In many facilities, especially in the USA, the oily water sewer VOC emissions must be controlled, as seen in Fig. 22. This is normally done by providing closed, dip leg-sealed drain hubs for connections into the OWS. The hubs can be opened for inspection as needed. The dip leg-sealed junction boxes and manholes are also sealed from the atmosphere, but these must be vented to the atmosphere in order to function. To ensure the closed sewer flows, in the seal boxes and at the end of each OWS lateral, there is normally a vent to a high point through a flame arrestor and a carbon canister or drum.

- The OWS hubs are usually elevated slightly above grade so that they only collect the oily water and storm water is collected in drains located at grade. Of course, if the OWS backs up, the overflow will go to the storm sewer, which has to be designed to manage this flow. More on this is under "storm sewers."
- Drained material to the OWS can often be very hot, such as when a vessel is being steamed out or for blowdown coming from a boiler via a flash drum. The sewer needs to be able to handle the high temperatures. Typically, the design temperature is around 160 °F (70 °C) for the underground lines. In some cases, a cooler stream, like plant water or cooling water blowdown, may be flushed into the sewer along with the hot stream to reduce temperatures.
- The grade or slope in the oily water sewer must be sufficient to avoid backup. Commonly, the slope of the OWS lines is a few inches for every 10 f. of line (a few cm per meter). Slope drains generally toward the wastewater treatment facility.
- Fluids that can set up or leave deposits should never be introduced into the OWS lines. This would include things like molten sulfur.
- High vapor pressure hydrocarbons, hydrogen, H_2S, and other light combustibles or toxic gases should never be sent to the oily water sewer. They should be routed to a flash drum, and only aqueous drains from the flash drum should be allowed in OWS.
- The multiple dip leg seals or subsurface seals are important in this system as a means of preventing combustible gases and explosions from propagating through the sewer.
- The OWS is usually steel and single wall. Older OWSs may be vitreous clay tile or even redwood. Some localities may require the OWS to be double walled with leak detection.

Storm Sewer

For precipitation events, facilities have to be able to manage the large influx of water. Storm water flow rates generally dwarf any other sewer flows. It is common to have a separate storm sewer to minimize the quantity of contaminated water that the wastewater treatment plant has to deal with.

A storm sewer will generally run in parallel to the oily water sewer. The storm sewer lines are much larger than the OWS lines to handle the flows. Sizing of these gravity drain lines must include a few other runoffs, in addition to storm water.

Most notable of the added capacity requirement is the water load from firefighting in an emergency. This load can easily exceed storm water loads. Unit storm sewers may be sized to handle 5,000–12,000 gpm (~1,100–2,700 m^3/h) of fire water or as required by the capability of the firewater system. This water will contain oil, solids, debris, fire retardants, chemicals, and foam – all of which must be managed in the wastewater treatment.

Generally, the storm water flow and the firefighting load are not considered simultaneously in sizing the storm sewer. The larger load sets the sewer size.

There are advantages to keeping the OWS and storm sewer separate. If they are separated, the initial storm flow can be captured for processing through the wastewater treatment plant and, after the sewer system, has been well flushed by storm water, the remaining storm water can usually be diverted and discharged without further treatment.

Sometimes, the oily water sewer and the storm sewer are combined, however. This can be less expensive, but it means there is no difference in treatment requirements between the waters. All storm water has to be intercepted and processed just like oily water.

A storm water sewer generally consists of local open surface drains and open catch basins (with water seals) located along lateral sewer lines. There will be several catch basins, drains, and laterals in a unit.

The laterals flow to junction boxes where each line is sealed by dip leg (or subsurface entry). The junction boxes connect together into larger and larger lines ending at the wastewater treatment plant (WWTP).

In some low-point locations, there may be a lift sump where the storm waters are intercepted and pumped to the WWTP. Normally, the inlet basins and boxes at the WWTP allow the storm water to be processed through the API separator and other facilities at a controlled rate, within the capacity of the equipment. When the allowable processing rate is exceeded, the excess storm water overflows or is diverted into one or more large holding basins. It will then be brought back into the WWTP processes as capacity allows.

As noted above, some plants have permits allowing direct discharge of non-contaminated storm water after a certain amount of rain has fallen. In these plants, the potentially clean storm water will be diverted away from the wastewater facilities into a clean water basin. It is usually checked for potential contaminants before being discharged.

The multiple dip leg seals or subsurface seals are important in this system, as in the OWS, for preventing combustible gases and explosions from propagating through the sewer.

Storm sewers are generally single pipe systems, i.e., they do not usually require any double containment. The storm water holding basins, however, are often double lined with plastic.

Chemical Sewers

Chemical sewers are present in many facilities in localized areas. These are designed to accept relatively clean drain fluids containing predominantly a specific chemical that can be collected and reused or sent off to disposal. These are materials you generally do not want in the OWS and certainly not in the storm sewer.

For instance, a chemical sewer is often available within a unit for amine solutions. Level bridle drains, pump drains, equipment drains, sample purges, etc., in amine circulation systems are all collected in a holding tank or drum to be pumped back into the process periodically. The drum is usually located in a below-grade vault, so the chemical sewer can flow by gravity into the holding tank. The chemical sewer piping leading to the holding tank is often a double-walled pipe, and the vault may also be double walled. There is leak detection provided between the walls. A vertical pump pulls the solution out of the tank and pumps it back into the process. The chemical sewer can also be used to empty vessels for maintenance and save good solution.

The chemical sewer hubs are normally closed, or piping is directly connected to the chemical sewer line. The sewer line may be vented to the atmosphere at a safe location, or an equalization line may be provided from the holding tank back to the end of the sewer line. These systems may also be purged or blanketed with inert gas under slight pressure.

Care must be taken to avoid contaminating the chemical sewer. If the sewer does get contaminated, the holding tank contents may have to be sent out for disposal and the system cleaned. This would be the case if oil got into the amine sewer, for instance, since the oil would cause foaming.

Often the vault around the holding tank is open to atmosphere. The top rim is usually elevated 6–12 in. (0.15–0.3 m) above grade to avoid acting as an area catch basin, but it will still collect some rainwater. The vault usually has a drain that is normally closed. When it collects rainwater, the collected water is drained to the OWS manually, and the drain valve is immediately blocked back in.

Sanitary Sewer

The final type of sewer we will consider is the sanitary sewer. These are normally vitreous clay or plastic pipe installations that carry the sanitary wastes from occupied facilities to the sanitary sewage treatment plant. They gravity drain (with an occasional lift sump) to the treatment plant either on-site or a POTW off-site. Local municipal codes govern the sanitary sewer installation. Care must be taken to avoid contaminating the sanitary sewer. Conversely, you need to avoid sending sanitary sewage to the other sewer systems unless they are specifically designed to handle sanitary waste.

Slops and Recovered Oil

There are several locations in a plant where it is necessary to get rid of oil, emulsion, oily water, and so on, but it does not belong in the sewer. This is usually because the amount of oil involved is substantially greater than what the wastewater treatment system can or should handle. For these situations, we have hydrocarbon slops or recovered oil systems.

Uses for slops may include:

- Off-spec products
- Oil flushed before taking a sample
- Oil skimmed off wastewater and flash drums
- Oil collected in the flare drums
- Oil from vessels and other equipment being removed for maintenance
- Level bridle drains that are primarily oil
- Drains from compressors, pumps, etc.
- Emulsions from desalting or other processes
- Essentially anything that is predominantly oil

The oil streams that make up the slops are collected, usually at the source, and brought to the slops tankage area. There are commonly intermediate drums for surge, forwarding, and separation from water. The streams all end up in one or more slops or recovered oil tanks.

From the slops/recovered oil tanks, the oil is sent back to an appropriate unit in the facility. Often, fairly clean oil is sent to the crude unit and reprocessed. If the oil is heavy or has undesirable components, it may go to the delayed coker where it can be injected into the coke drum during part of the coking cycle.

Emulsions are a particular problem. They may be sent to a separate emulsion-breaking tank. An emulsion-breaking tank is usually equipped with good mixing and circulation facilities, emulsion-breaking chemical injections, and circulation through an external, steam-heated exchanger. The emulsion-breaking tank is controlled and treated to break whatever emulsions are encountered. Normally the process chemical vendor works with plant personnel to ensure the emulsion-breaking system works.

Once the emulsion is separated, the oil goes on to recovered oil tanks and the water goes to sour water. There is always a residual solid or floc that will build up in the emulsion-breaking tank until the tank is taken out of service for cleaning. Multiple suction elevations are necessary to stay above the sludge. Emulsion-breaking tanks do require more frequent cleaning than other tanks, so they are normally relatively small.

The slops rate produced within a refinery should not be more than 1 % of the total crude input. With attention to draining and sampling practices as well as controls, the slops rate can be much lower.

It is only possible to paint a picture of slops and recovered oil facilities with a broad brush as these are so dependent on the processes used in the plant and how well the processes are managed.

Summary of Practices to Prevent Utility System Contamination

Rounding out the discussion of utilities, we should reemphasize the importance of avoiding contamination of these critical systems:

- Plant water, air, flushing oil, steam, and almost any other utility should only be connected into a process or foreign system through an anti-backflow manifold that includes the equivalent of double block and bleed, with a check valve and a blinding point. In this case, foreign systems include connections to other utilities. These manifolds should be removed or blinded after use before the foreign system is pressured up above the utility supply pressure.
- Potable and city water connections can only be made to foreign systems using a code-approved backflow preventer with an atmospheric vent.
- Nitrogen connections to a foreign system require special anti-backflow precautions and managed, so the foreign system cannot enter the nitrogen under any condition.

- Air gap utility connections when not in use.
- Think before connecting a utility into a foreign system.

In spite of the precautions, utility systems will become contaminated. Monitor the systems for potential contamination and deal with it before it becomes a serious problem.

Utilities Conclusion

This concludes the discussion of utilities in petroleum processing plants. Each of the topics, covered briefly here, has been the subject of countless articles and books.

There is a tendency to ignore the utilities until you have a problem. Then the problem utility becomes the most important thing there is in the plant – until the problem is solved. The keys to reliable, trouble-free, economical utilities are:

- Good utility design practices that emphasize reliability
- Routine monitoring and early action on issues
- Educated operators and staff
- Routine preventative maintenance
- Good utility operations management
- Attention to preventing contamination

Following these keys should enable a facility to focus primarily on running the main process units, trusting that the utilities will be there to support them.

References

Steam and Condensate Systems

R.C. Andrade et al., (Drew Chemical Corp., 1983), Controlling boiler carryover. Chem. Eng. 51–53 (1983)

J. Colanniono (Colannino Consultants, 1993), Prevent boiler tube failures, Parts 1 and 2. Chem. Eng. Prog. 33–36 (Oct 1993); 73–76 (Nov 1993)

S.T. Costa, (Calgon Corp., 1994), Bulletin: Factors affecting the selection of an industrial boiler water treatment program. Bulletin. 10–327 (1994)

L. Huchler, (MarTech Systems, 2000), Basics of boiler water chemical treatment, Hydrocarb. Process. 20, 87 (2000)

B. Liptak, (Bela G. Liptak Associates, 1987), Improving boiler efficiency. Chem. Eng. 49–60 (1987)

Water Systems

B. Buecker, (CEDA, Inc., 2000), Control water chemistry in HRSGs. Chem. Eng. Prog. **9**, 55–61 (2000)

F. Caplan, Quick calculation of cooling tower blowdown and makeup. Chem. Eng. 10 (1975)
Corrosion Doctors, Item: Scaling Indices. www.corrosion-doctors.org. Accessed 9 Feb 2014
S.T. Costa, (Calgon Corp., 1994), Bulletin: Factors affecting the selection of an industrial boiler water treatment program. Calgon Bull. 10–327 (1994)
R.H.L. Howe, R.C. Howe, (Eli Lilly & Co., 1981), Combining indexes for cooling water evaluation. Chem. Eng. 157–158 (1981)
L.A. Huchler, (MarTech Systems, Inc., 1998), Select the best boiler-water chemical treatment program. Chem. Eng. Prog. **11**, 45–50 (1998)
L.A. Huchler, Can you reduce your cooling tower blowdown rate? Hydrocarb. Process. 100, 121 (2000a)
L.A. Huchler, Whatever happened to deaerator cracking? Hydrocarb. Process. 131 (2000b)
L.A. Huchler, What about Legionella in industrial cooling towers? Hydrocarb. Process. 115 (2000c)
L.A. Huchler, Basics of boiler water chemical treatment. Hydrocarb. Process. 20, 87 (2000d)
L.A. Huchler, Basic cooling water treatment. Hydrocarb. Process. 123 (2001a)
L.A. Huchler, What do scaling indices mean? Hydrocarb. Process. 167 (2001b)
L.A. Huchler, Oxidizing biocides: How about chlorine? Hydrocarb. Process. 181 (2001c)
L.A. Huchler, (MarTech Systems, Inc., 2009), Cooling towers, Part 1: Siting, selecting, and sizing. Chem. Eng. Prog. 51–54 (2009a)
L.A. Huchler, (MarTech Systems, Inc., 2009), Cooling towers, Part 2: Operating, monitoring, and maintaining. Chem. Eng. Prog. 38–41 (2009b)
F.N. Kemmer, J. McCallion (eds.), (Nalco Chemical Co., 1979), *The Nalco Water Handbook* (McGraw-Hill Book, New York, 1979)
Lenntech website, Boiler feed water, www.lenntech.com. Accessed 11 Feb 2014
Lenntech website, WHO’s drinking water standards 1993 (1993). www.lenntech.com. Accessed 11 Feb 2014
Lenntech website, WHO/EU drinking water standards comparative table. www.lenntech.com. Accessed 11 Feb 2014
J.R. Macdonald, (Nalco Chemical Co., 1987), Choosing the correct cooling water program. Chem. Eng. 135–137 (1987)
H.K. Miyamoto, (MacLaren Plansearch), M.D. Silbert (Marvin Silbert & Assoc.), A new approach to the Langelier stability index. Chem. Eng. 89–92 (1986)
Multiple authors (Nalco Chemical Co. & ABB Lummus Global, 2001), Cooling towers. Chem. Eng. Prog. 29–41 (2001)
Nalco Chemical Company, Bulletin: An introduction to boiler feedwater treatment. Bulletin. 30 (1978)
Nalco Chemical Company, Technifax bulletin: Boiler system sampling. (1984)
P.R. Puckorius, (Puckorius & Assoc., Inc., 2013), Selecting the optimal cooling tower fill. Chem. Eng. Prog. 31–34 (2013)
W.J. Scott, (Hercules, Inc., 1982), Handling cooling water systems during a low pH excursion. Chem. Eng. 21–126 (1982)
S.D. Straus et al., Boiler water treatment for low and moderate-pressure plants. Power **30**, S-1–S-16 (1987)
U.S. EPA, Bulletin: National primary drinking water regulations. Bulletin EPA 816-F-09-0004, May 2009
U.S. FDA, Item: Flow diagram of a reverse osmosis system. www.fda.gov. Accessed 9 Feb 2014
Wikimedia.org, Photo: Cooling tower. www.commons.wikimedia.org. Accessed 2014
P. Zisson, (Buckman Labs. Intl., 1997), Chemically treating boilers. Chem. Process. 9 (1997)

Compressed Air Systems

B.D. Bullough, (Sebesta Blomberg & Assoc.), Piping design of instrument air distribution systems

Chere Resources, Instrument air consumption – preliminary estimates. www.chereresources.com. Accessed Feb 2014

Instrumentation Portal, Instrument air consumption calculation. (2011). http://instrumentationportal.com. Accessed Feb 2014

Electrical Power Supply

T. Brown, J.L. Cadick, (Electro Technology Laboratories, Inc., 1979), Fundamentals of electricity. Chem. Eng. 72–76 (1979)

Cleaver Brooks Div. of Aqua-Chem, Inc. Bulletin: How to read schematic wiring diagrams. (1974)

V. Ganapathy, (ABCO Industries, 1997), Efficiently generate steam from cogeneration plants. Chem. Eng. 187–190 (1997)

Nitrogen System

Air Products, *Safety Bulletin: Liquid Nitrogen*. Air Products, Safetygram 7 (2013)

Grasys, Item: Membrane nitrogen plants and packages. (2014). www.graysys.com. Accessed Feb 2014

S. Ivanova, R. Lewis (Air Products, 2012), Producing nitrogen via pressure swing adsorption. Chem. Eng. Prog. 38–42 (2012)

R.L. Lewis, D.J. Stookey, (Permea, Inc., 1992), Pressure-swing adsorbers and membrane systems: Alternative nitrogen sources. Chem. Process. 41–46 (1992)

S. Shelley, Out of thin air. Chem. Eng. 30–39 (1991)

Off-Site Facilities for Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments, LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_18

Abstract

In a refinery, “offsites” are the facilities outside the main refining units that support those process units. The discussion in this chapter focuses on storage tanks, product blending, loading and receiving, waste hydrocarbon disposal, and effluent water treating. A procedure and example are provided for estimating tank heat loss and heater sizing.

Keywords
Offsites • Tanks • Jetty • Effluent Water • Slops • Flare • Blending • Loading

Introduction

In most refineries the off-sites facilities are a major capital cost center, second only to the process plants themselves. Indeed in some instances, where the off-sites include one or more complex jetties, they can be the principal capital cost center.

Among the major off-sites facilities found in most refineries are:

- Storage
- Product blending
- Road and rail loading
- Jetty facilities
- Waste disposal
- Effluent water treating

Many refineries consider the flare as part of the safety systems. To a large extent this is justifiable as most relief valves exhaust to the flare as do the process and other vent systems. For the purpose of this publication, however, the flare system is considered as part of the off-sites and specifically comes under the discussion of waste disposal.

We will explore each of these types of facilities in more detail within this chapter.

Storage Facilities

The crude oil feed and the processed products are held in storage tanks of various sizes and types. These tanks are usually collected and located together in the refinery area suitably defined as “the tank farm.” There will be many other tanks (usually much smaller than those in the tank farm) which will contain chemicals to be used in the processes and the slop/recovered oil or spent chemicals from the various processes and utility plants. Most refinery storage tanks fall into the following three categories:

- Atmospheric storage
- Pressure storage
- Heated storage

Atmospheric Storage

As the name implies, all atmospheric storage tanks are open to the atmosphere or are maintained at atmospheric pressure by a controlled vapor blanket. These tanks fall into two categories:

- Cone-roof tanks
- Floating-roof tanks

Cone-Roof Tanks

Among the most common atmospheric storage tanks is the cone-roof tank shown in Fig. 1. This tank is used for the storage of nontoxic liquids with fairly low volatility. In its simplest form the roof of the tank will contain a vent, open to the atmosphere, which allows the tank to "breathe" when emptying and filling. A hatch in the roof also provides access for sampling the tank contents. In oil refining this type of tank is used for the storage of gas oils, diesel, light heating oil, and the very light lube oils (e.g., spindle oil).

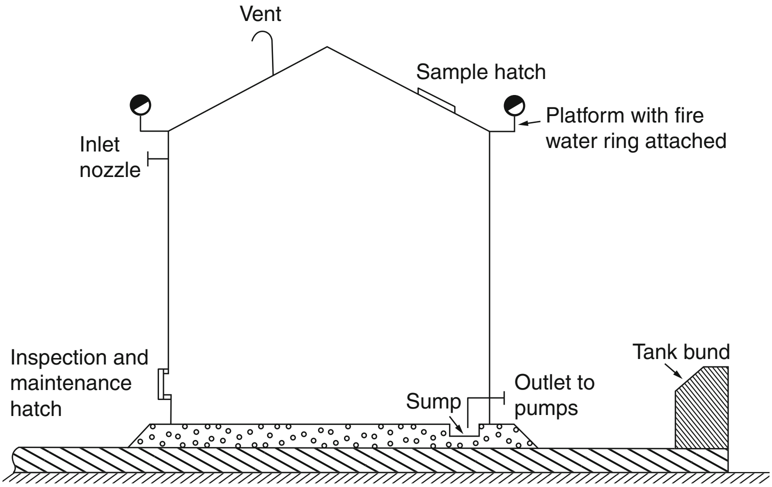


Fig. 1 Cone-roof tank

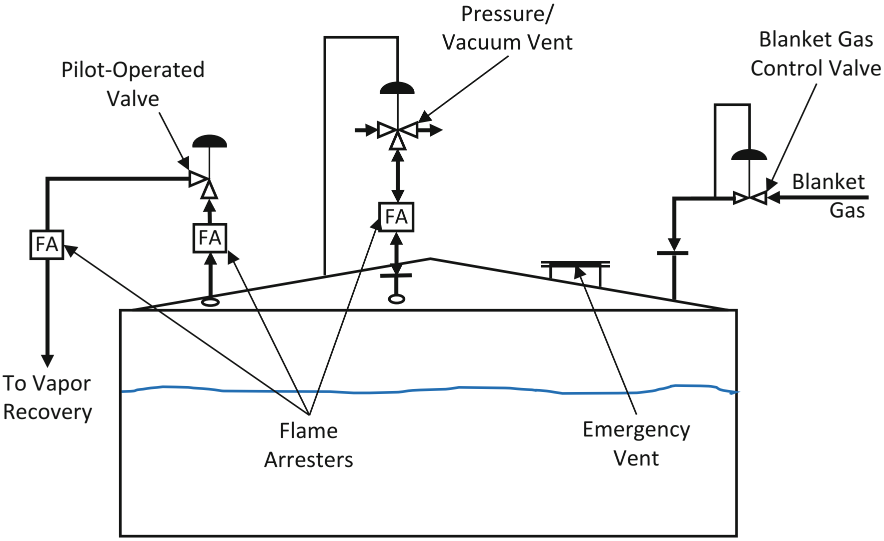


Fig. 2 Blanket gas or padding system on a tank

In keeping with a company's fire protection policy, tanks containing flammable material will be equipped with foam and fire water jets located around the base of the roof. All storage tanks containing flammable material and material that could cause environmental damage are contained within a diked area or bund. The size and volume of the bund area are fixed by regulation. Usually the bund has to contain the total contents of one of the tanks included in the area. The number of tanks per bunded area is also fixed by regulation.

Many commodities need to be protected from atmospheric oxygen exposure. This is normally done in cone-roof tanks using an inert gas blanket or padding system. The inert gas blanket is controlled tightly using a very sensitive control system that keeps the blanket pressure in about the +0.5 to +2.0 in. water range. Inert gas (usually natural gas or nitrogen) is brought in at low pressure and is vented at high pressure. The vented gases go to a vapor recovery system, usually through a small liquid ring compressor or similar device, to prevent emissions. The system uses special control valves or regulators. Blanketed tanks will also have regular pressure and vacuum vents in case the blanket system fails or the rate of change in tank inventory exceeds the blanket system capability. Figure 2 illustrates the blanket gas system concept. Note that the blanket gas inlet is opposite the outlet to help ensure a good sweep of the tank vapor space with inert gas.

Floating-Roof Tanks

Light volatile liquids may also be stored at essentially atmospheric pressure by the use of "floating-roof" tanks. A diagram of this type of storage tank is given in Fig. 3.

The roof of this tank literally floats on the surface of the liquid contents of the tank. In this way the air space above the liquid is reduced to almost zero, thereby

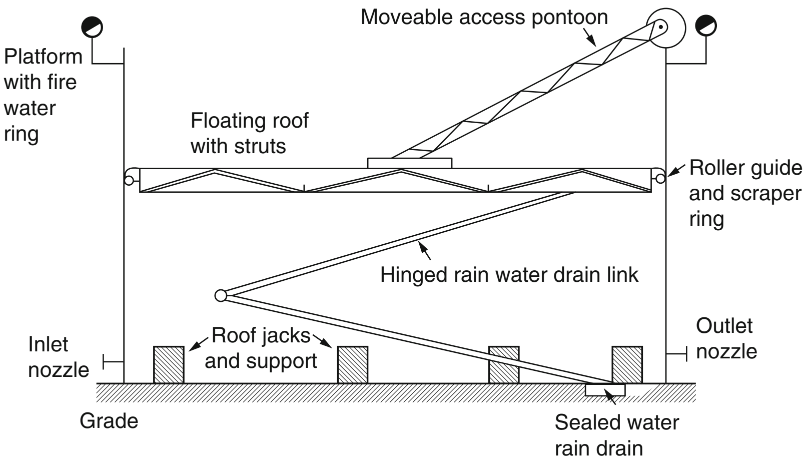


Fig. 3 Floating-roof tank

minimizing the amount of liquid vaporization that can occur. The roof is specially designed for this service and often contains a top skin and a bottom skin of steel plate, held together by steel struts. These struts also provide strength and rigidity to the roof structure. The roof moves up and down the inside of the tank wall as the liquid level rises when filling and falls when emptying. The roof movement is enhanced by guide rollers between the roof edge and the tank wall. A scraper ring or a set of shoes located around the periphery of the floating roof are pressed tightly against the tank wall to ensure a primary seal between the contents and the atmosphere. The primary seal also provides additional guide to the roof movement and stability to the roof itself.

To further reduce tank emissions, in many areas, the primary seal is supplemented by one or more secondary seals. These are tubes or wipers made of resilient material (like rubber) that press against the tank wall and seal any remaining gap from the primary seals.

In some tanks, the floating roof may only be a single roof skin. There are floats around the circumference. This is referred to as a “pan” design. The other tank design features in a pan floating roof are similar to those described above.

When the tank reaches the minimum practical level for the liquid contents, the roof structure comes to rest on a group of pillars at the bottom of the tank. These provide the roof support when the tank is empty. There is a space between the roof and the tank bottom. This space is required to house the liquid inlet and outlet nozzles for filling and emptying the tank which, of course, must always be below the roof. The space is also adequate to enable periodic tank cleaning and maintenance.

In many floating-roof tanks, the maintenance support pillars or legs move up and down with the roof. They are pinned to penetrations through the roof at a low level. The advantage of this design is that when the tank is emptied for maintenance or switching services, the roof can go almost all the way to the bottom (or at least as low as any internals). This leaves less remaining heel to deal with, effectively minimizing waste. For maintenance, then, the roof can be refloated with water to a level where the legs are reset to support the roof when the tank is entered. After maintenance, the roof is refloated with water, the pins are pulled, the roof is dropped to minimum level, the legs are re-pinned, and then the tank is filled with oil.

A drain line running inside the tank from the roof to a “below-grade” sealed drain provides the facility for draining the roof of rain water. These roof drains may be hard piping connected together by swivel joints (like hinges), or the drain may be a coiled, large-diameter flexible tubing. The flexibility in the drain line allows the line to move up and down with the roof movement.

A pontoon-type access pier from the platform around the perimeter at the top of the tank provides access to the sample hatch located at the center of the roof. This “pontoon” also moves upward and downward with the roof movement.

Automatic bleeder vents are provided on all floating-roof tanks. They vent air from under a floating roof when the tank is being filled initially from empty. After the liquid rises high enough to float the roof off its supports, the vent automatically closes. Likewise when the tank is being emptied, the vent automatically opens just before the roof lands on its support, thereby preventing the development of a vacuum under the roof.

Other accessories include rim vents, float gauges, anti-rotation devices, and manholes.

Liquids stored in this type of tank have relatively high volatilities and vapor pressures such as gasoline, kerosene, jet fuel, and the like. In oil refining the break between the use of cone-roof tank and floating-roof tank is based on “flash point” of the material. Flash point is that temperature above which the material will ignite or “flash” in the presence of air. Normally this break point is 120 °F.

Nozzle Arrangement and Location Considerations

Most tanks have multiple connections into the commodity storage section of the tank. The locations of these connections affect how the tank will operate. Typical connections include:

- Inlet lines
- Outlet lines
- Subsurface foam lines
- Water draw
- Roof drain (floating-roof tank)
- Sample lines (which may be attached to a floating pantograph)
- Low-low suction line
- Mixer
- Circulating system return
- Bayonet heater
- Maintenance manway

Some specific considerations when designing and managing these connections include:

- Inlet and outlet lines should be separated from each other by at least 10 f. (3 m) horizontally to avoid short circuiting. It is best if the lines connect to the tank on opposite sides, far apart.
- If sludge buildup is expected (and it almost always occurs), there should be high and low inlet and outlet connections. The low lines are usually a nominal distance above the tank floor, like 2–3 f. (0.7–1 m). The high lines are usually about 4 f. (1.3–1.5 m) higher.
- Many tanks use subsurface foam lines, in addition to or in lieu of the foam generators around the top of the tank. These need to be evenly spaced around the periphery. Each should enter through a backflow prevention device.
- The water draw should come from the lowest point in the tank. Usually the water draw takes suction from the bottom of the tank sump. It may exit the sump underground in a drain-dry tank.
- The roof drains for floating-roof tanks normally pass through the tank commodity to a nozzle on the wall near a sewer hub or drain sump leading to the oily water sewer. Some refiners leave these drains open in service to avoid sinking the roof in a sudden rain storm. Others are concerned about leakage of the joints or pipe leading from the roof drain (which is common), with subsequent loss of hydrocarbon to the sewer or atmosphere. Everyone follows practices based on their experience.
- Tanks often have multiple sample taps to the shell or connected to a pantograph that floats on the commodity. These are used to get top, middle, bottom, and dead-bottom samples from the tank. In the case of emulsion-breaking tanks, there are often taps every 12 in. (0.3 m) up the side of the tank to help find the oil/water interface. Tank sample taps should always be plugged when not being used. Sometimes the taps are all routed to a local drain or sink where the samples are taken. In many tanks, the samples are actually circulated from a tap back into the tank to ensure an accurate sample.
- When a tank has to switch commodities or batches frequently, it will often have a low-low suction line. This line is as close as possible to the tank floor vertically and may even originate in a sump below the floor. It allows the tank to be emptied almost completely. This “zero” NPSHA situation needs to be considered in pump design.
- As noted above, some tanks have mixers installed through the tank wall. These may be propeller-style or jet nozzles, which include venturis. The location and orientation of these is important. Propeller mixers usually enter through a packing gland, which must be maintained. Propellers often can be moved to different angles in the tank to prevent accumulation of sludge in one area. Where mechanical mixers are used, the stresses imposed on the tank wall by the mixer action will require reinforcement of the shell where the mixer nozzle is located.
- Where a circulating system is provided on a tank, either for heating or mixing, the return needs to be across the tank from the suction line to ensure proper blending action.

- Bayonet or coil heaters are installed in some tanks. These are inserted through the tank wall near grade level. It is best to encase the heater elements in an enclosure that will allow the elements to be removed for maintenance without having to empty and clean the tank. There are some tanks where steam-heating coils are installed over the tank floor. In these cases, the steam inlet and condensate outlet nozzles are usually close to each other. If a regular floor-mounted steam coil leaks, it must wait until the tank can be drained for repairs.
- Most tanks have a large maintenance manway for access when the tank is serviced. In very large tanks, this flanged manway is large enough to drive a small front-end loader through. The manway should be pointed toward the easiest access point in the tank dike, usually toward a ramp down into the dike. Sealing these manways is often difficult after use. In recent practice, some refiners have chosen to eliminate the manway and just cut an access hole in the tank when it requires servicing. The access hole is welded up after each use. Since the turnaround frequency on tanks is about 20 years, this can be an acceptable approach.

Tank Internals

Many tank internals have been described in the previous tank discussion. It is important to remember that most tanks are not just empty volumes. Tanks may contain:

- Internal mixing nozzles (sometimes they disappear in service)
- Mixing venturis
- Propeller or other mechanical mixers
- Dip lines down into the sumps
- Roof drains
- Sample pantographs
- Sample tap extensions
- Water draw lines
- Inlet line extensions
- Outlet line extensions
- Roof support legs (cone as well as floating roof)
- Drain sumps
- Gauging instruments
- Stilling wells

Once a tank is closed, you will not be able to easily examine any of these internals. It is a good practice to photograph each internal and maintain these photos on file for reference. The function, nozzle number, location (angle), and elevation of each internal should be attached to each internal photo. You will never remember what is in the tank once it is closed.

Sumps and Drain-Dry Tanks

Switching services in a tank or changing product specifications requires that as much of the previous tanks' contents be removed as possible before the new material is introduced. In most tanks this is accomplished by flushing out the tank two to three times with the new commodity while the level is kept low. This does accomplish the task, but has the disadvantages of potentially downgrading product and not completely eliminating the previous commodity. It may generate a lot of slops. The effectiveness of this approach is limited by the tank internals, the suction line elevation, the outlet pump NPHSR, and the minimum heel in the tank.

Many tanks have a drain sump located at the lowest point in the tank. This sump helps drain a tank to a low level during commodity switches, but the level is usually still limited. The biggest value for the sump is normally draining accumulated water.

Many tanks today use a “drain-dry” design. This design is limited mostly to clean services. In a drain-dry tank, there is nothing to prevent the tank from being almost completely drained by taking suction from the drain sump below grade. Only a few inches of commodity is left in the tank, instead of 2–4 f. of heel in a normal tank.

Pressure Storage

Pressure storage tanks are used to prevent, or at least minimize, the loss of the tank contents due to vaporization. These types of storage tanks can range in operating pressures from a few inches of water gauge to 250 psig. There are three major types of pressure storage. These are:

- Low-pressure tanks – these are dome-roof tanks and operate at pressures of between 3 in. water gauge and 2.5 psig.
- Medium-pressure tanks – these are hemispheroids (which operate at pressures between 2.5 and 5.0 psig) and spheroidal tanks (which operate at pressures up to 15 psig).
- High-pressure tanks – these are either horizontal “bullets” with ellipsoidal/hemispherical heads or spherical tanks (spheres). The working pressures for these types of tanks range from 30 to 250 psig. The maximum allowable pressure is limited by tank size and code requirements. For a 1,000 bbl sphere, the maximum pressure is 215 psig. For a 30,000 bbl tank it is 50 psig. These pressure limits can be increased if the tank is stress relieved.

Although it is possible to store material in tanks with pressure in excess of 250 psig normally when such storage is required, refrigerated storage is usually a better alternative.

Heated Storage Tanks

Heated storage tanks are more common in the petroleum industry than most others. They are used to store material whose flowing properties will restrict flow at normal

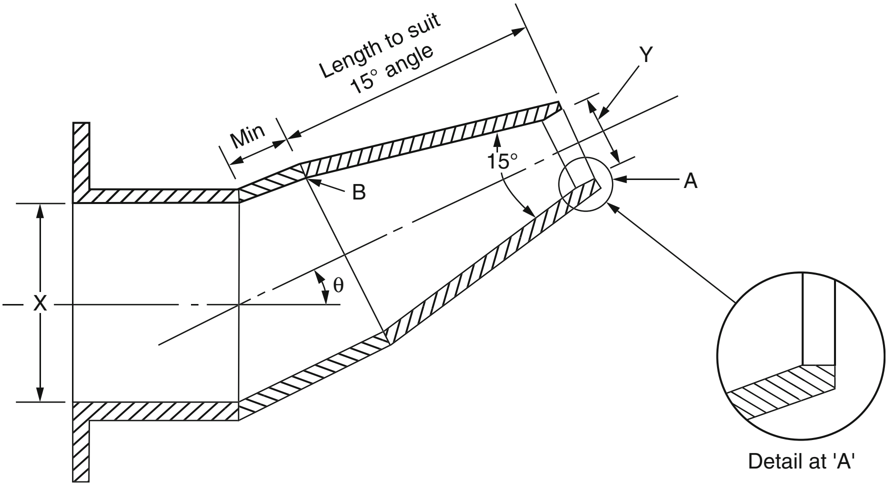


Fig. 4 Jet mixing nozzle

ambient temperatures. In the petroleum industry, products heavier than diesel oil, such as heavy gas oils, lube oil, and fuel oil, are stored in heated tanks.

Generally speaking, tanks are heated by immersed heating coils or bayonet-type immersed heaters. Steam is normally used as the heating medium because of its availability in petroleum complexes, although smaller tanks or tanks containing heat-sensitive materials may be heated electrically. You will find some tanks heated by circulation through an external heat exchanger. External tank heating is used when there is a possibility of a hazardous situation occurring if an immersed heater leaks or to enable easier heater repairs.

Very often where immersed heating is used, the tank is agitated, usually by side-located propeller agitators for large tanks. Where external circulating heating is used for tanks, the contents are mixed by means of jet mixing. Here the hot return stream is introduced into the tank via a specially designed jet nozzle as shown in Fig. 4.

Heat loss and the heater surface area to compensate for the heat loss may be calculated using the procedure outlined in Appendices 1 and 2 of this chapter.

A Few Other Tank Management and Design Considerations

Tanks and tank farms require specific management practices and may have some special design features. These include operation of the tanks as well as maintenance and record keeping. Each refiner has its own practices, but some common themes are noted here:

- When a tank is built, one of the first activities before use is strapping the tank. This means filling the tank with water that is precisely metered. The tank's contained volume is noted every inch or two. The results are published as strapping tables (which may be electronic) that will be used for the life of the tank or until the strapping is repeated. More recently, strapping tanks by laser methods has become feasible. By either method, the strapping tables, with any corrections for temperature, are the most accurate gauge of contained volume in a tank.

- Each tank is normally manually gauged at least every day. In some cases, they may be gauged several times during a shift. The readings are recorded and are considered company records for regulatory purposes. Gauging usually involves going to each tank and manually activating the gauge device to get a reading. In some services, gauging may require the operator to go to the top of the tank and use the gauging hatch to drop a weighted tape into the tank through a stilling well. These manual gauges are compared to readings on the remote gauging system, if any, to verify readings and indicate when repairs are needed. A change in level of a tank that is unexpected is investigated. It may indicate a lineup error or a leak.
- The safety of the operators working around tanks needs to be considered, especially when going up to the roof of the tanks. It is common practice for an operator to let the control room know when he enters and exits a tank dike area. Many refiners also require an operator to wear fresh air and have a standby operator in fresh air when manually gauging tanks or going onto a tank roof for any reason. The low spots represented by the tank dike and the top of a floating-roof tank, as well as the vapor space in a cone-roof tank, can accumulate hydrogen sulfide or other gases in sufficient quantity to pose a hazard to personnel.
- Tanks collect water in service. The amount of water collected is usually determined by “water cutting” the tank when it is manually gauged. Water cutting is accomplished by coating the gauge tape with a special water-indicating paste and then dropping the gauge tape through the gauge hatch. When the tape is removed, the water level will be seen by color change on the tape, so the gauging gets you both oil and water levels. Some newer instruments for gauging tanks may also indicate water level.
- When the water level reaches a predetermined depth (or on a defined frequency), the water needs to be removed by “water drawing” the tank. This means that the valve from the water draw sump (at the lowest point in the tank) is opened and the drawn liquid sent to the oily water sewer until the drawn liquid is mostly oil. This is a manual operation. When water drawing a tank, the operator should stand by the draw point or in the immediate area to ensure minimal hydrocarbon is sent to the sewer.
- The tank dike is intended to accept the contents of the tank in the event of rupture. A dike has a drain sump (usually the same one where water draws go). The sump will be routed to the oily water sewer through a block valve located outside the berm or dike. Depending on the refiner, the decision needs to be made to leave the block valves open or closed. If the valves are managed normally closed, then rain water will accumulate in the dike and have to be periodically

drained. Accumulated rain water will also corrode the tank shell if left for an extended period. If the valves are managed open, a tank failure will easily overwhelm the wastewater-treating facilities. Many refiners opt to keep the valves closed and then drain the dikes after a rain at a predetermined rate. This helps keep the wastewater treatment plant to a reasonable size and provides a controllable discharge rate.

- Many tanks today have double bottoms to help prevent loss of hydrocarbon to the ground, even inside the dike. These double bottoms have provisions for leak detection between the two bottom skins. They can be retrofitted to existing tanks with a small loss of capacity.
- Tanks are normally set on sand pads. In modern tank design, it is common for the pad to also contain an impervious (plastic) membrane. A small tank leak will then be indicated by oil seepage collected on the membrane.
- The primary corrosion risk around tanks, as well as the underground piping leading to and from them, is from contact with the ground. This corrosion attacks the floor of the tank or the walls of the pipes from the outside. Tank farms may be protected by impressed current systems or buried zinc electrodes. Because of the long times between turnarounds, it is important to keep the corrosion prevention systems in good working order.
- Tanks are generally in service for many years between turnarounds. A typical service interval is 20 years. Attention to management of these facilities is important to prevent leaks and sludge buildup in the tanks.

Product Blending Facilities

Blending is combining two or more components to produce a desired end product. The term in refinery practice usually refers to process streams being combined to make a saleable product leaving the refinery. Generally these include gasolines and middle distillates (jet, kerosene, diesel, and heating oil). Other blended finished products will include various grades of fuel oil and lube oil. The blending of the process streams is accomplished either by batch blending in blending tanks or by in-line blending by in the pipeline itself.

In-Line Versus Batch Blending

In batch blending, the components are routed separately into a single receiver tank. They are mixed in this tank to meet the finished product specification. In the case of in-line blending, the component streams are routed through automatically operated flow control valves to a finished product tank. With modern computerized control technology, in-line blending is the more common form of blending process. In the case of gasolines and lube oils in particular, in-line blending is extensively the accepted method. Middle distillates and residuum blending by batch still has some advantage because there are fewer components to be handled, although the quantities involved are usually greater.

As a word of caution, in-tank, batch blending of butanes into gasoline for RVP control is a very dangerous practice. It has resulted in multiple fatalities, because the butane does not initially and quickly dissolve in the gasoline. Only in-line blending should be used for butane in gasoline.

The In-Line Blender Operation

An in-line blender is essentially a multiple stream controller with feedback. The controller itself is a computer into which the recipe for the blend is keyed. Such blending recipes have been covered in some detail in the chapter entitled "▶ Introduction to Crude Oil and Petroleum Processing" of this handbook. The controller automatically starts the pumps for the blend components and manipulates the flow control valves on the component lines to meet the required component quantities. In most cases the component lines join together to form the blended product, which is then routed to the finished product tank. A series of online analyzers, located in the blend rundown lines, monitor the finished product properties and, in turn, reset the controller adjusting the component quantities to meet the end product specifications.

The In-Line Blender Design

Most refinery companies have their own proprietary component blending recipes for their finished products. These will be in computer program form and usually use the linear programming techniques described in the chapter "▶ Petroleum Refinery Planning and Economics" of this handbook. It is this program software that is installed into the blender controller to activate the respective component systems. The blender controller acts to start the selected pumps and the control valves. It also receives data from the online analyzers located in the product rundown line.

The design of the blending system as a whole is the combined effort of the process engineer, the instrument engineer, and the computer specialist. It will be the duty of the process engineer or the blender to develop the blending recipe in terms of component percentages and quantities to meet a particular product specification. The instrument engineer will ensure that the control valves, pump starting arrangement, and the onstream analyzers meet the process requirements. A typical list of the instrument engineer's responsibilities in this regard includes:

- The control panel, panel instruments, instrument power supply, annunciators, pump switches, indicating lights, graphic display, and all panel wiring
- Turbine meters and preamplifiers
- Control valves with positioners
- Stream analyzers
- Field transmitters (flow, temperature, pressure)

Finally it will be the computer specialist's duty to translate these requirements into the software program for the controller computer.

Recent developments in online analyzers, especially NIR analyzers, are allowing these devices to keep blenders optimized continuously during the blend. The newer analyzers can accurately determine octane, cetane, and several other key specifications. They are more reliable than some of the older online methods, such as online knock engines. It is still necessary to final certify a product blend, however.

Component Tankage

Because the in-line blender permits the rapid conversion of the components to finished products, the ratio of component to finished product tankage should be quite large. For good flexibility this ratio should be 4 or 5 to 1.

The most significant process requirement for successful blending is that the properties of the individual components must not change during the blending operation. Alkylates and catalytically cracked naphtha vary little, unless feeds or unit operations are changed. Reformates and straight-run naphtha, however, have a greater variability due to changes in source crude feed quality. These are often stored in separate "running gauge" tankage, the quality of the contents of which are tested when full.

Lube oils are a particular problem in component storage, because of the tendency of the oils to "stratify" to a greater extent than other stocks. That is, these oils tend to separate in storage with the higher density and viscosity portion of the oil sinking to the tank bottom. In most cases the contents of these tanks are continually mixed using propeller-type mixers. Many companies adopt this system to all heavy component tankage such as gas oils and fuel oil product components to avoid stratification in those services, also.

When blending ethanol and many other renewable components, it is necessary to prevent exposure of the renewable components to water. These components will absorb water and then release the water in a vehicle tank later when the gas tank cools. Ethanol is particularly bad in this regard. Renewable blend stock tanks usually have cone or geodesic dome roofs, sometimes with inert purges, to prevent absorption of atmospheric moisture and collection of rain water.

Finished Product Tankage

Finished product tankage is needed even with the most efficient in-line blender. This is because of required product disposal rates and product certification. However, in many design cases, in-line blending will still only require about one half the product storage required by batch blending.

Actual requirements of product tankage will usually be dictated by the manner in which the product is to be certified and shipped from the refinery. The blend rate is usually sized to blend a day's production in a certain number of hours.

The maximum rate of an economically sized blender will usually be too slow to blend into an ocean-going tanker.

Thus, product tankage and loading pumps are needed to supplement the blender. Conversely, the minimum rate of a blender will usually be too fast to blend directly into a road tanker. In some cases, however, this is done by limited volume transfer pumps taking suction directly from component tankage.

As with blend stock tankage, product tanks containing ethanol blends or other renewable blends normally require protection from water intrusion with a roof or dome.

Road and Rail Loading Facilities

The extent of product shipping facilities required in a chemical or petroleum complex depends on the size of the complex, the local market, the number of different products to be shipped, and the market to be supplied. Normally the shipping facilities installed in most plants are sufficient to cater for normal product handling and the flexibility required for seasonal demands. The capacity of these facilities will almost invariably exceed the plant's total production.

The most common method of shipping product is by road or rail in suitably designed tanker cars. In the case of large complexes located on coastal or riverside sites, shipping by barge or ships carries the bulk of the plant products. This section, however, will deal only with dispatch by road and rail. Note that many of these same considerations can be applied to receiving facilities for crudes or intermediates by truck and rail, also.

Loading Rates

Loading rates for road and rail tankers vary from as low as 150 GPM to as high as 1,000 GPM, but most terminals load at rates between 300 and 550 GPM. Road tankers have capacities from 1,300 to 6,500 gal, and one tractor can haul two 6,500 gal tankers.

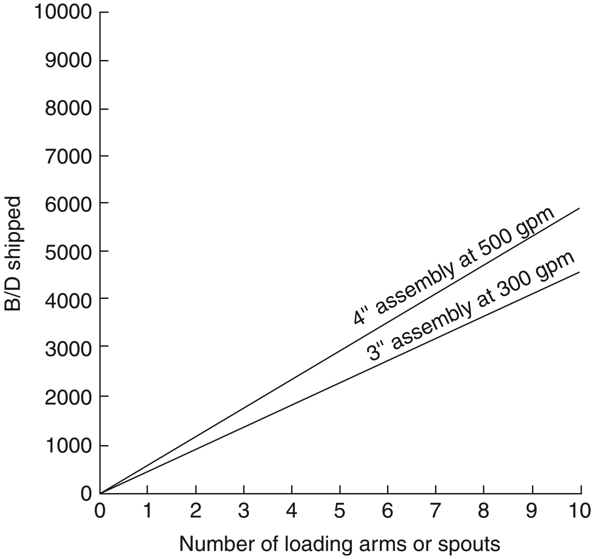
The number of loading arms required for each product to be loaded varies with:

- Truck size
- Number of loading hours per day
- Number of loading days per week
- Time for positioning, hookup, and de-positioning of the truck

Figure 5 gives the number of arms or spouts required for loading a 3,500 gal truck under various conditions.

The conditions shown in Fig. 5 are for filling at a rate of 300 GPM (bottom curve) and for 500 GPM (top curve). time The loading is taken as the filling time per tank truck plus 10 min. Thus loading time is

Fig. 5 Number of loading arms for quantity shipment



$$[(\text{Tank truck capacity, gals})/\text{GPM}] + 10 \text{ min} \tag{1}$$

Tank car capacity is taken as 3,500 gal. Thus for the lower curve loading time is 22 min per tanker and for the upper curve 17 min per tanker. Assuming that a single product is loaded over 4 h in an 8-h day 5 days a week, then the number of trucks required per barrel/day is

$$\begin{aligned}&(\text{BPD} \times 42 \times 5 \text{ days} \times 8 \text{ h/day})/(3{,}500 \text{ gals/truck} \times 20 \text{ h loading per week})\\&\quad = 0.024 \text{ trucks per barrel/day}\end{aligned}$$

Then for 1,000 B/D, the number of trucks per working day = 0.024 × 1,000 = 24 trucks/day of 4 h filling.

Time to load trucks at 300 GPM filling rate = 24 × 22 min = 528 min.

To complete the loading in 4 h, the number of arms required = 528/240 = 2.2 arms.

Continuing with this calculation for several more shipping capacities and for filling rates of 300 and 500 GPM produces the data given in Fig. 5.

Loading Equipment

Figure 6 is a schematic drawing for a typical road or rail loading facility.

The loading pumps, which are located close to the product storage tanks, take suction from these tanks. The loading pumps are high-capacity, low head type with flat head/capacity characteristics. They operate between 35 and 45 psi differential head.

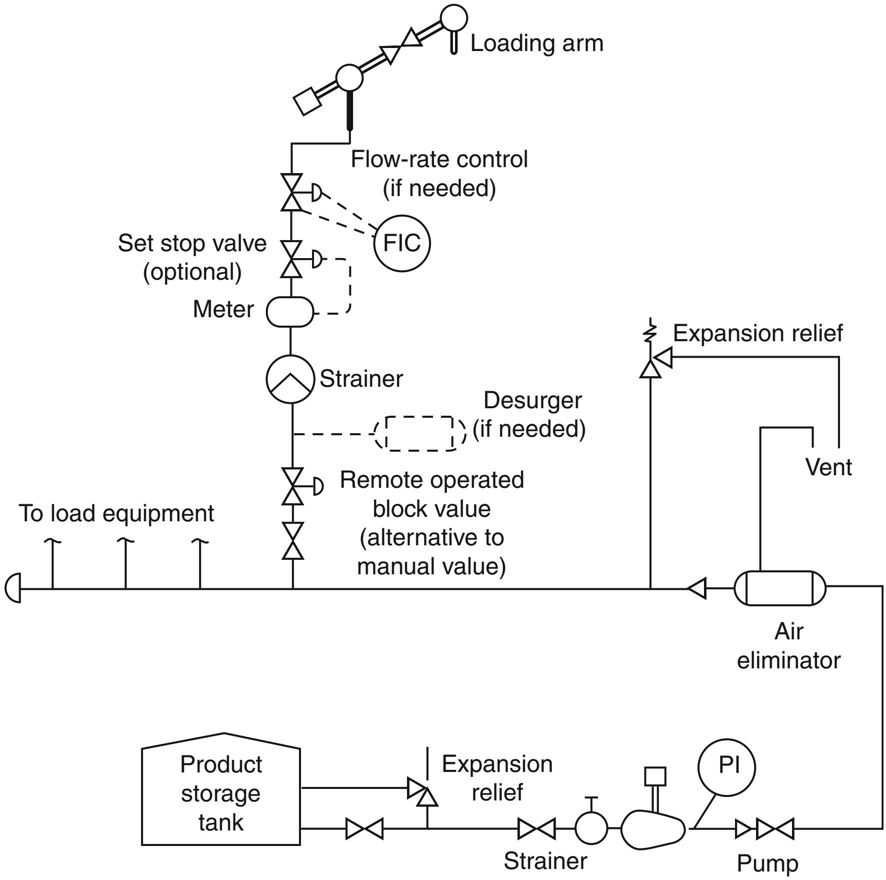


Fig. 6 Schematic diagram of a loading facility

These pumps discharge through an air eliminator drum into the loading header. Several loading arm assemblies are connected to the loading header. Each of these assemblies includes a remote-operated block valve followed by a desurger (optional) and then a strainer located before the loading meter. The product flows from the meter into a swivel-jointed loading arm and nozzle. Tank trucks and rail cars are loaded through their top hatches into which the nozzles of the loading arm fit.

Air eliminators are used to disengage air and other vapors which would interfere with the accuracy of the meters. Disengaging of the vapors is accomplished at about 3 psig. Should there not be sufficient static head at the disengaging vessel, a back pressure valve must be provided to obtain this pressure. The meters are positive displacement type, and desurgers are installed to decrease hydraulic shock resulting from quick shutoff.

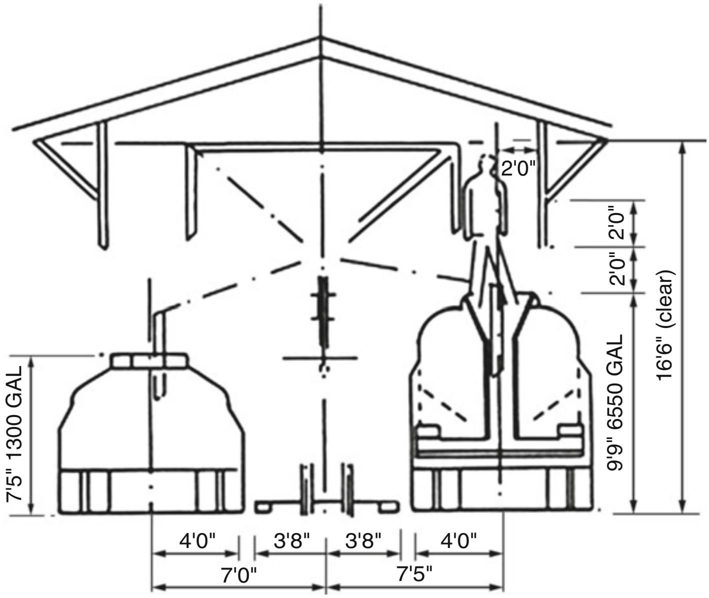


Fig. 7 Tank truck loading facility

Loading Facilities Arrangement

Figures 7 and 8 show typical arrangements of loading facilities for truck and railcar, respectively.

The dimensions shown on the diagram are applicable to one world area and may not be applicable to other localities. The equipment and its arrangement shown in the diagrams, however, are similar for most of these facilities.

In truck loading the meters and strainers are located at the loading station. The connection of the loading arm is made by an operator actually standing on the car itself. In the case of the truck loading facilities, the loading arm is operated from an adjacent platform. As in the case of truck loading, the meter and strainer, together with the on/off valve, are located near the loading site. In many newer trucks and rail cars, the connections are usually located on the bottom of the tanker. This is safer for loading personnel and less expensive. The same general facilities are used, however.

Jetty and Dock Facilities

Tankers and barges are loaded and unloaded at jetties or docks. In almost all circumstances these facilities for handling petroleum products are separate from those used for general cargo. Very often tankers, particularly the modern “super-tankers,” are loaded and unloaded by submarine pipelines from a deepwater

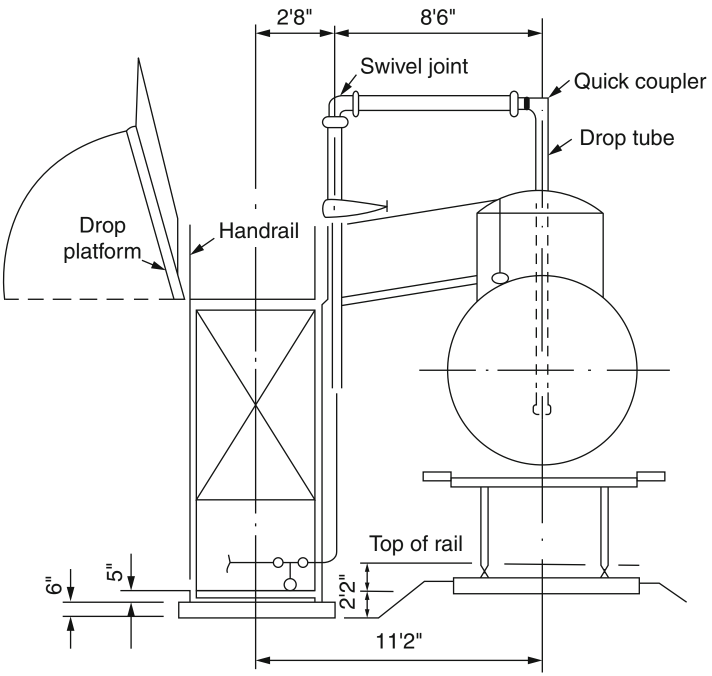


Fig. 8 Rail car loading facility

anchorage. This section of the chapter, however, deals only with onshore docking facilities.

Jetty Size, Access, and Location

Tanker sizes range from small coastal vessels of 10,000 bbl capacity to supertankers in excess of 250,000 bbl capacity. The more common tanker size is about 140,000 bbl capacity, and this size tanker is labeled a T2. This tanker is usually used for product carrying. It can carry as much as three different product parcels at the same time. The larger tankers are usually used for crude oil transportation.

Ideally the jetty size should be sufficient to accommodate several sizes of tankers and usually at least a couple of sizes at the same time. In some refineries which have jetty facilities, these usually include barge loading items also. The barge loading may, however, be located on remote docking facilities from the larger sea-going tankers.

The location of the jetty itself must consider the following:

- There is sufficient deep water to accommodate the larger crude-carrying tanker.
- It is located as close as possible to the refinery's tank farm.
- It is in an area that has a good approach road and park.

- There is sufficient room for a product/crude pipeway.
- There is sufficient waterway in which to maneuver and handle tanker docking.

A fully loaded T2 tanker has a maximum draft of 30 ft. The larger crude-carrying tankers would have a maximum draft around 45 ft. It is important to minimize rundown pipe lengths to and from the jetty loading area and the refinery tank farm. The first is a piping cost factor and the second is that often the pumping characteristics may have a negative static head during the pumping program.

A good onshore jetty approach road is mandatory for the operation of the jetty. This is required for safety reasons and the easy approach way for emergency vehicles (such as fire engines and ambulances). The approach road is also required for the transportation of the operating staff, ship's crew, and the ship's chandler vehicles. Usually this approach road is dedicated for jetty use and will be independent of any adjacent refinery road.

There must be room on shore and on the jetty itself for the loading and unloading pipeway(s). This can be extensive, depending on the refinery size and the number of products that are exported. There are several options for the location and size of this pipeway configuration. On the jetty itself, it may be carried on overhanging supports on both sides of the jetty pier, or it can be supported by an independent pipe rack adjacent to the jetty pier (much more expensive, however), and this pipe rack could be multi-tiered. On shore, the pipeway can be located along the roadway at ground level or elevated with two or more tiers. It could also be elevated and run above the roadway. This does, however, restrict access by limiting vehicle height using the roadway.

Finally the location of the jetty must allow sufficient waterway room for tankers to be berthed properly. Tankers arriving from the open sea must have room so that tugs can handle and turn the ship around to face the open sea before tying up at the jetty.

A layout plan for a typical tanker jetty is shown in Fig. 9.

Equipment

The equipment required for tanker loading includes pumps, hoses or flexible loading pipes, and handling cranes or structures. The loading pumps are located at the tank farm. These are centrifugal type with discharge pressures in excess of 100 psig. This is dependent on rundown pipe lengths, but pressure drop through the loading hoses or flexible loading pipes is within 10–25 psig. Also, and as mentioned earlier, there is often a static head loss to the deck manifold of an empty tanker.

When a rubber hose is used, it is supported by a dockside derrick plus the tanker boom. Some installations employ a combination of hose and pipe or flexible assemblies of pipe and swivel joints supported by structures. Automatic adjustment for tide and tanker draft is incorporated in this equipment. Hose and various assemblies are available in sizes from 2 to 12 in. diameter with the 8 and 10 in. most frequently used for products.

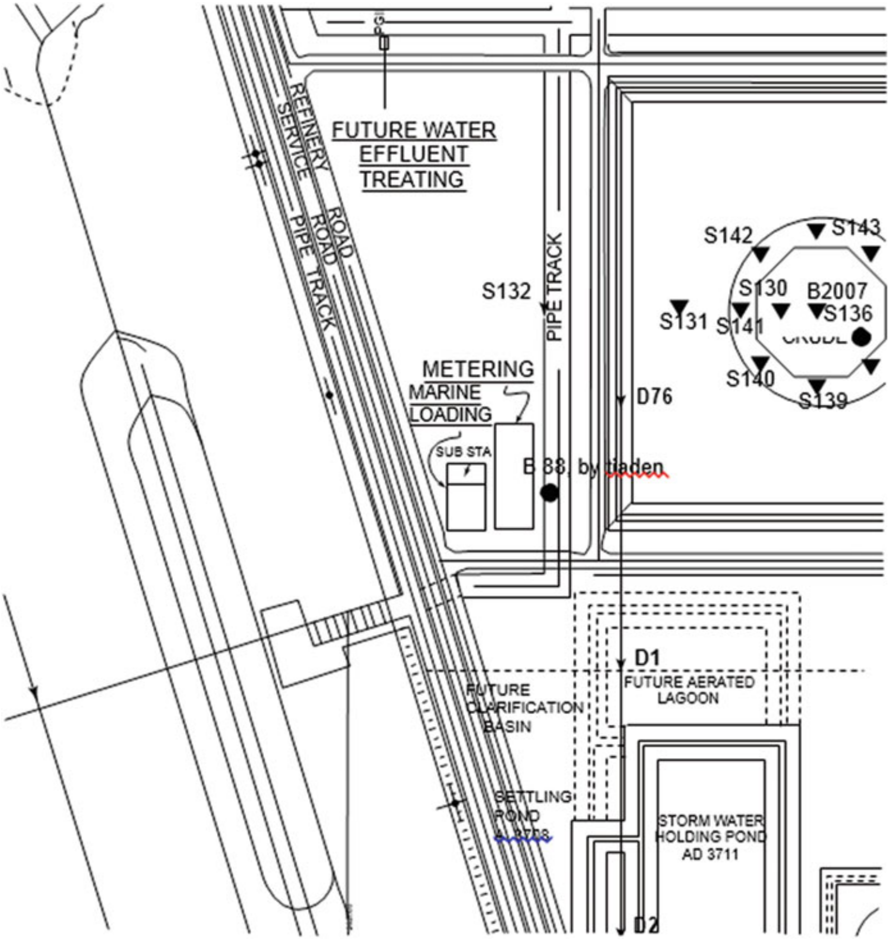


Fig. 9 A typical tanker jetty layout

Barges are usually loaded through hoses supported by dockside derricks or, in some cases, by derricks on the barges. To conserve space, barges are frequently moored two or three abreast with the loading hose being manhandled across the inboard barges to the outboard barges. This hose is accordingly limited in size to a 6 in. diameter weighing about 8 lb/ft.

Loading Rates

Tanker piping and pumping systems are designed for relatively high rates. The unloading pumps for the T2 tanker size can handle up to 8,000 bph. Supertankers unloading crude have pumps that can handle quantities of 22,000 bph or more.

A desirable product loading rate for each product is 8,000–10,000 bph. It is common practice to load two products simultaneously. Loading rates for barges are usually limited to 2,000 bph. Barges have capacities ranging from 600 to 2,000 bbl. Barges are flat-bottomed shallow draft vessels used to transport products short distances in canals, harbors, or inland waterways.

Quantities loaded aboard tankers are measured by metering storage tanks and tanker compartments. Products loaded into barges are measured by metering. Meters are located on the dock near the hose connections. These metering facilities include strainers and flow controllers, similar to truck or rail loading.

Other Features

Some of the other features that are considered in the establishing of jetty facilities are:

- Ship ballast handling
- Vented gas handling or incineration
- Tanker mooring facilities
- Slop and spill collection facilities
- Lighting and communication facilities

Ship ballast water is handled using specially allocated onshore tanks to collect the water, which will be contaminated. This contamination will be the petroleum product residue remaining in the ship's tanks after product unloading. Ships arriving at the refinery jetty under ballast are usually the smaller product tankers. These are the vessels that will load at the refinery with the finished products for shipment. The ballast water is pumped from the ship's tanks to the onshore ballast water tankage by the ship's pumps. From the ballast water tanks, the content is drained off to the refinery's effluent treating facilities. The hydrocarbon contaminants are removed from the water in the treating plant and routed to the refineries' slop/recovered oil system to finally enter the refinery processes. The treated effluent water may be drained back to the sea, unless prohibited by regulation.

As the tanker or barge is filled, gases in the holds have to be vented. In many locals, this vented gas must be incinerated or flared by regulation. A packaged incinerator, with appropriate flame arrestors and backflow prevention, is usually used. Many modern tankers contain inert gas systems which provide a blanket on the tanks using engine exhaust gases. These blanket gases will not readily support combustion, so any incinerator will require supplemental fuel gas to ensure complete combustion.

The length of the jetty's loading/unloading wharf, where the ships are moored, is sized to accommodate two or more tankers of fixed length (say two T2s). The allocated space for these vessels must conform to standard conditions usually established by the particular Port Authority Regulations. One of these regulations, which affects the length of the wharf, is that the space between moored vessels should be such that the stern and aft mooring lines of adjacent vessels, measured at an angle of 45° to the center line of the vessels, cannot overlap.

Slop and spill facilities around loading or unloading vessels at the wharf may include a temporary boom installed around the vessel during these operations. Any spillage is contained by the boom and is subsequently disposed of by the same route as the ballast water.

Jetty lighting is based on the main refinery lighting code and practice. This means that all access ways and roads will have general street lighting. Areas where personnel are employed on a 24-h basis will be floodlit between the hours of sunset and sunrise. This lighting will be supplemented by the ship's lighting facilities as required for loading/unloading activities and for ship berthing and departure. Ship to onshore communication by means of telephone, radio, and company computer systems is activated as soon as the ship has been berthed.

Waste Hydrocarbon Disposal Facilities

Although every attempt is made for economic and regulatory reasons to minimize waste hydrocarbon gases and oils, all process plants, including oil refineries, produce quantities of toxic and/or flammable material during periods of plant startup, shutdown, upset, or emergencies. A properly designed flare and slop handling system is therefore essential to the plant operation. This section describes and discusses typical disposal systems currently in use in the oil refining industry where the hydrocarbon is immiscible with water. Where the chemical is miscible in water, special separation systems must be used.

Figure 10 shows a completely integrated waste disposal system for the light ends section of an oil refinery. The system shown here consists of three separate collection systems being integrated to a flare and a slop (or recovered oil in more recent terminology) rerun system.

A fourth system is for the disposal of the oily water drainage with a connection to the flare and a separate connection for any oil-laden skimming. This later connection would be to route the skimmed oil to the refinery slop tanks.

In the three integrated systems, the first collects all the vapor effluent streams from the relief headers. The contents of this stream will be material that is normally vapor at ambient conditions. It would be the collection of the vapors from the relief valves and the vapor venting on plant shutdown or upset conditions.

The second of the three systems is the liquid hydrocarbon drainage. The material in this system is liquid under normal ambient conditions and is collected from drain headers used to empty vessels during shutdown or upset conditions.

Both the first and the second collection systems are routed to the flare knockout drum. The second (liquid system) may also be routed to the light ends slop storage drum. The liquid phase from the flare knockout drum is also routed to the slop storage drum.

The third system is the light ends feed diversion. This allows the light ends unit to be bypassed temporarily by sending the feed to the slop drum for rerunning later.

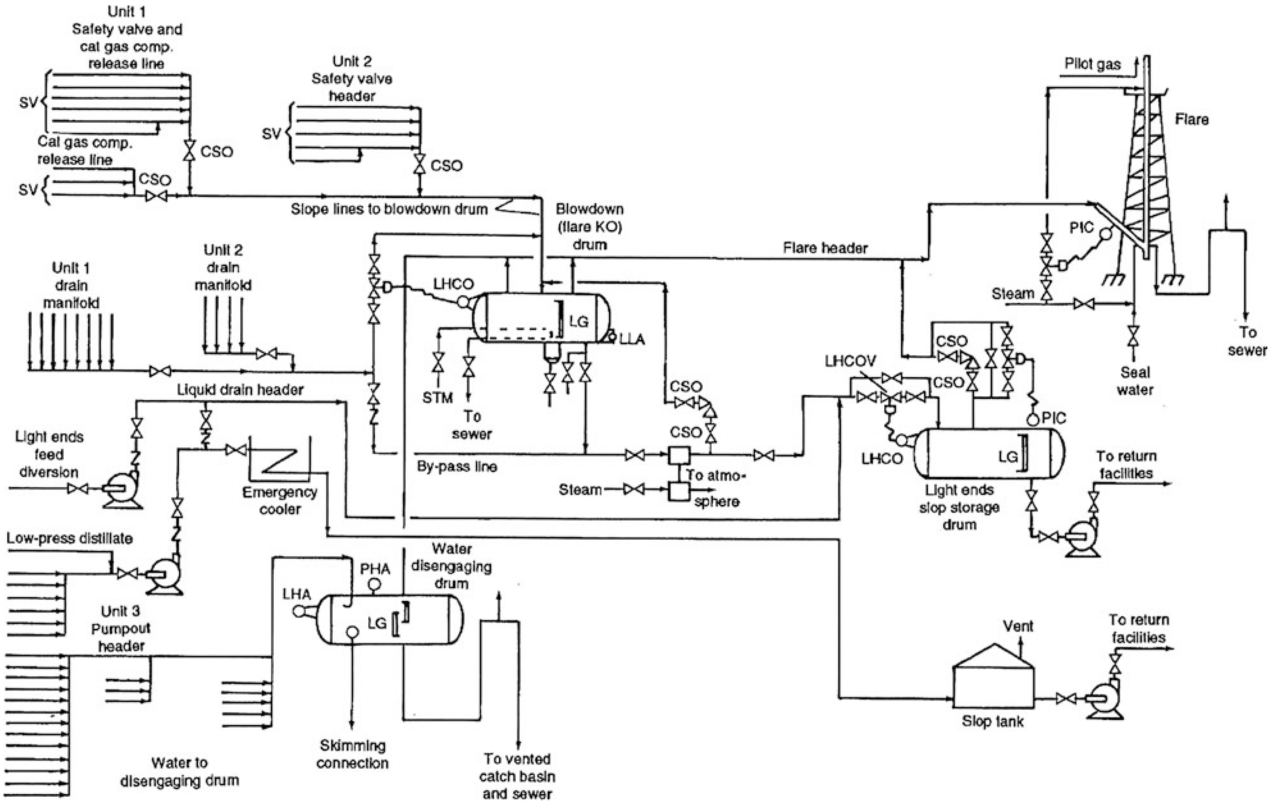


Fig. 10 An integrated waste disposal system

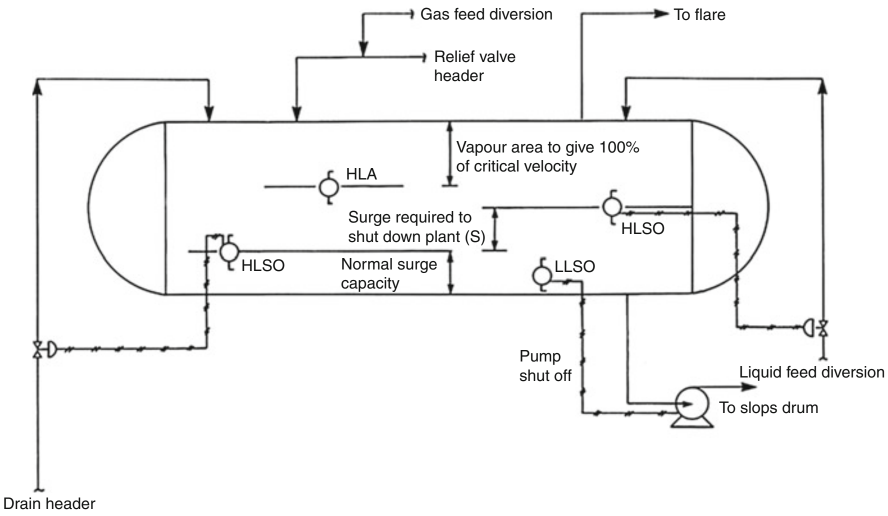


Fig. 11 A noncondensable blowdown drum

Further description and discussion of these disposal systems is given in the following sections:

- Blowdown and slop disposal
- Flares

Blowdown and Slop/Recovered Oil

This system generally consists of the following drums:

- Noncondensable blowdown drum
- Condensable blowdown drum
- Water disengaging drum

A typical noncondensable blowdown drum is shown in Fig. 11. These types of drums are provided for handling material normally in the vapor state and high volatility liquids. These drums receive and disengage liquid from safety valve headers and drain headers.

Blowdown drums are often referred to as flare knockout drums as the disengaged vapor is routed directly to a flare. The drum is basically a surge drum and therefore should be sized as one using the following criteria:

1. Normal liquid surge is based on the daily liquid draw-off to drain per operating day of 24 h. This includes spillage, sample point draining, etc.

2. The surge capacity between the HLSO (high level shutoff) for normal drainage and the HLSO for feed diversion should be such as to contain the total feed to a unit routed to this drum for a period sufficient to shutdown the unit producing the feed stream. Should there be more than one unit routed to the drum, then this surge capacity should be for the largest of a single feed stream.
3. The capacity between the highest HLSO and the high level alarm (HLA) should be sized to handle the largest liquid volume that can be discharged in 30 min by the relief valves constituting any single risk.
4. The drum must be sized for a vapor velocity above the HLA at a maximum of 100 % of the critical figure calculated by

$$V = 0.157[(\rho_l - \rho_v)/\rho_v]^{0.5} \tag{2}$$

where:

$V =$ critical velocity in ft/s.
$\rho_l =$ liquid density in lbs/cuft.
$\rho_v =$ vapor density in lbs/cuft at drum temperature and pressure.

5. Drum pressure: The operating pressure for this drum will be about 0.5 psig or that of the water disengaging drum tied to the same flare header. In relief conditions, the pressure in the drum may be substantially higher, however. Typically, design pressure for these drums is 50 psig.

A condensable blowdown drum and system are used for collection and containment of heavier hydrocarbons with low volatility. For example, this would account for the middle and waxy distillates (kerosene, gas oils, and the like).

Figure 12 illustrates a typical blowdown drum with quench. The material entering this system is generally above ambient temperatures. Very often hot streams directly from operating units find their way into this system. To handle these materials the condensable blowdown drum is designed as a direct contact quench drum. The blowdown material leaves the unit in a drain collection system to enter the bottom section of the drum. Cooling water is introduced at the top of the drum and passes over a baffled tray section to contact the hot blowdown stream at the drum base. Any hot vapors rising from the blowdown stream are condensed in the baffle section of the drum and carried down to the bottom of the drum. Uncondensed material leaving the top of the vessel is routed to the flare. The aqueous mixture containing the condensed blowdown leaves the bottom of the drum through a seal system to enter the chemical or oily water sewer for separation and treatment.

This design works if the fluids in the drum are below about 212 °F. If the collected fluids are above 212 °F, then you absolutely do not want to introduce water into the drum. This would cause a steam explosion and likely rupture the drum. In systems where the fluids are very hot, the blowdown drum is provided with cooling by an external circulation loop. The drum may be sized to hold the largest “hot blow” volume until the collected fluid can be cooled to a temperature at which it can be sent to slop or recovered oil.

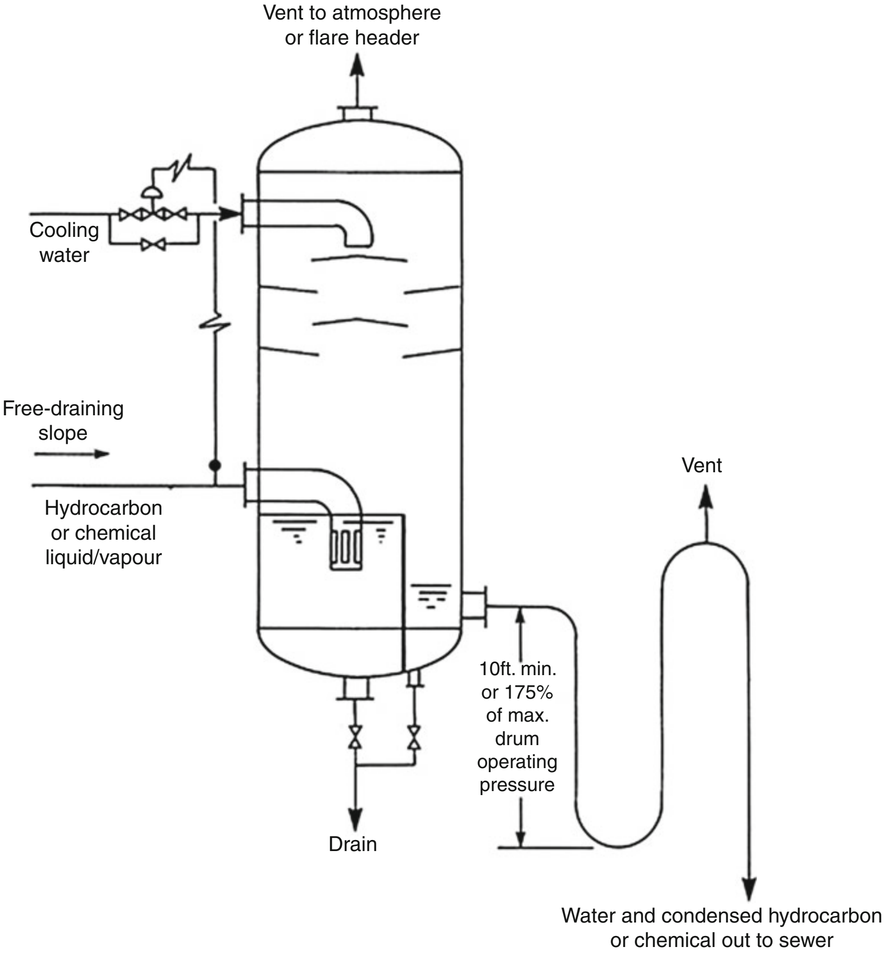


Fig. 12 A typical blowdown drum with quench

The following criteria are used to size a blowdown vessel with internal quench:

- The vapor load on the drum is based on the safety valve(s) constituting the largest single risk.
- The maximum operating pressure for the drum is usually 1–2 psig.
- The stack may vent to the atmosphere rather than the flare if desired. However, if vented to the atmosphere, the stack should vent at least 10 f. above the highest adjacent structure. Unfired vent stacks are strongly discouraged after multiple fatality incidents related to these stacks. In any case the vent should not release to atmosphere below 50 f. above grade. Snuffing steam should also be provided.
- The cooled effluent leaving the drum should be at 150 °F or colder. The cold water supply should be controlled either by effluent temperature or inlet

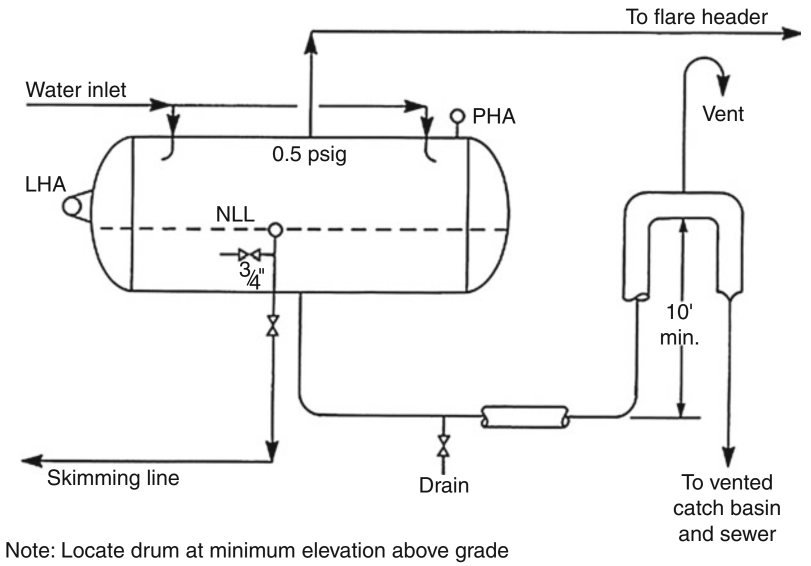


Fig. 13 A water separation drum

blowdown stream flow. There should, however, be a bypass flow of water entering the drum at all times.

- The drain system from the unit(s) to the drum should be free draining into the drum. The drum therefore should be located at a minimum height to grade. Where very waxy materials are likely to be handled, steam tracing of lines and a steam coil in the drum should be considered.

The water separation drum arrangement is shown in Fig. 13. The purpose of this drum is to remove any volatile and combustible material from certain water effluent streams before they enter the sewer or sour water system.

Thus:

- All water from distillate drums which have been in direct contact with flammable material such as light hydrocarbons is sent to the disengaging drum before disposal to the sewer. The exception is where a sour water stripper is included in the plant; then these streams are sent to this stripper.
- Cooling water drainage from coolers and condensers which may have been contaminated with flammable high volatility material is sent to the disengaging drum. So, too, are steam condensate streams which fall in the same category.

The drum is located at a minimum height above grade. It operates at about 0.5 psig and vents into the flare system. The pressure and the liquid level in the drum are maintained by the free draining of the effluent through a suitable seal. For sour water flash drums, the water would be pumped to sour water tankage.

Design criteria used for the sizing of this drum are as follows:

- The vapor load on the drum will be the result of high volatile material flashing to equilibrium conditions at the drum pressure. This design load is based on the largest amount of vapor arising from a single contingency. For exchangers this contingency will be due to a fractured tube. For liquid from a distillate drum, this will be due to a failed open control valve on the water outlet.
- The liquid seal must be such as to eliminate air from the sewer system and to allow free drainage from the drum.
- An oil or chemical skimming valve is located at the water NLL. This allows for the draw-off of the oil phase from time to time. A high interface level alarm is often included.

The Flare

Vapors collected in a closed safety system are disposed of by burning at a safe location. The facilities used for this burning are called flares. The most common of these flares used in industry today are:

- The elevated flare
- The multi-jet ground flare

The elevated flare is used where some degree of smoke abatement is required. The flare itself operates from the top of a stack, usually in excess of 150 f. high. Steam is injected into the gas stream to be burnt to complete combustion and thereby reduce the smoke emission.

The multi-jet ground flare is selected where luminosity is a problem, for example, at locations near housing sites. In this type of flare, the vapors are burned within the flare stack thus considerably reducing the luminosity. Steam is again used in this type of flare to reduce the smoke emission.

Figure 14 shows a typical arrangement of an elevated flare, and Figs. 15 and 16 show that for a multi-jet ground flare.

The Elevated Flare

This type of flare is the normal choice in the larger process industries such as the petroleum refining industry. It consists of a flare stack over 150 f. in height that contains an igniter system, pilot flame(s), and the flare pipe itself. The flare header enters the stack through a water seal at the base of the stack immediately above an anchor or concrete plinth. The water seal maintains a back pressure of around 0.5 psig on the flare header. The waste gas to be flared moves up the stack to exit at the top.

At the stack top there is an assembly of igniter and pilot gas which ensures the safe burning of the waste flare gases. A typical pilot assembly is shown in Fig. 17. It consists of three tubes all external to the stack itself and each supplied with the

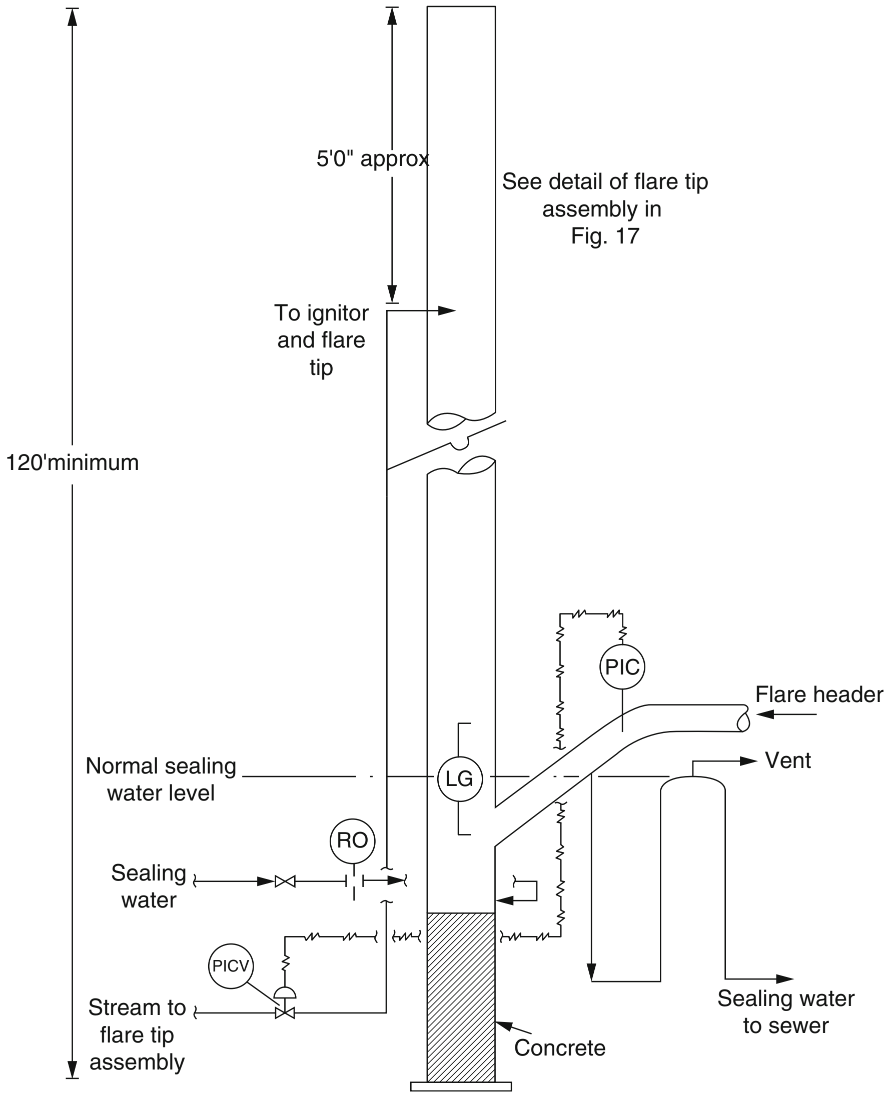


Fig. 14 An elevated flare

plant fuel gas. In some cases, the first and largest of these tubes is the igniter. Here the fuel gas supply is mixed with air (plant or instrument air supply) before passing upward through a venturi tube to an igniter chamber. A spark is induced in the igniter chamber by an electric current of 15 Amp. The chamber and the venturi tube are located near grade, and a sight glass on the igniter chamber enables the operator to check on the igniter's operation. The flame front from the igniter travels up the igniter tube to contact the waste gases that are to be flared as they exit the top of the

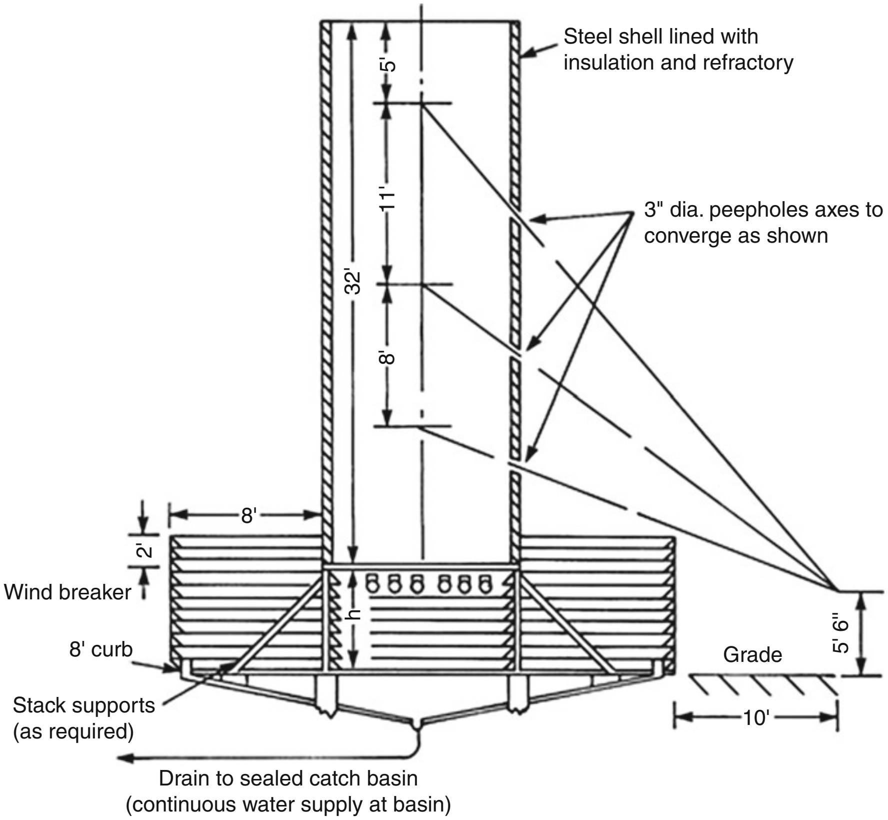


Fig. 15 A multi-jet ground flare and stack

flare stack. The same flame front ignites the "on and off" pilot burner which is the center tube of the three and initially ignites the permanent pilot burner(s) at the stack top.

The outlets of these three tubes are located at the stack top such that the prevailing wind ensures that the flame from them is blown across the stack exit.

Other configurations also exist for igniting the pilots. In one common system, there is a direct spark ignition at each pilot tip that is automatically triggered every few seconds to ensure each pilot stays lit.

Steam is often injected into the stack at some point near the top to complete combustion and eliminate or at least reduce smoke emission. The amount of steam normally used for this purpose depends on the character or composition of the waste gases. Aromatics and olefins when burnt produce a smoky flame: steam injection allows the free carbon which makes up the smoke to convert into CO and CO_2 which, of course, are invisible gases. An estimate of the amount of steam required for smoke abatement is given in Fig. 18. From a practical standpoint, steam rates above 1.0 lb steam per lb vented gas are normally unrealistic.

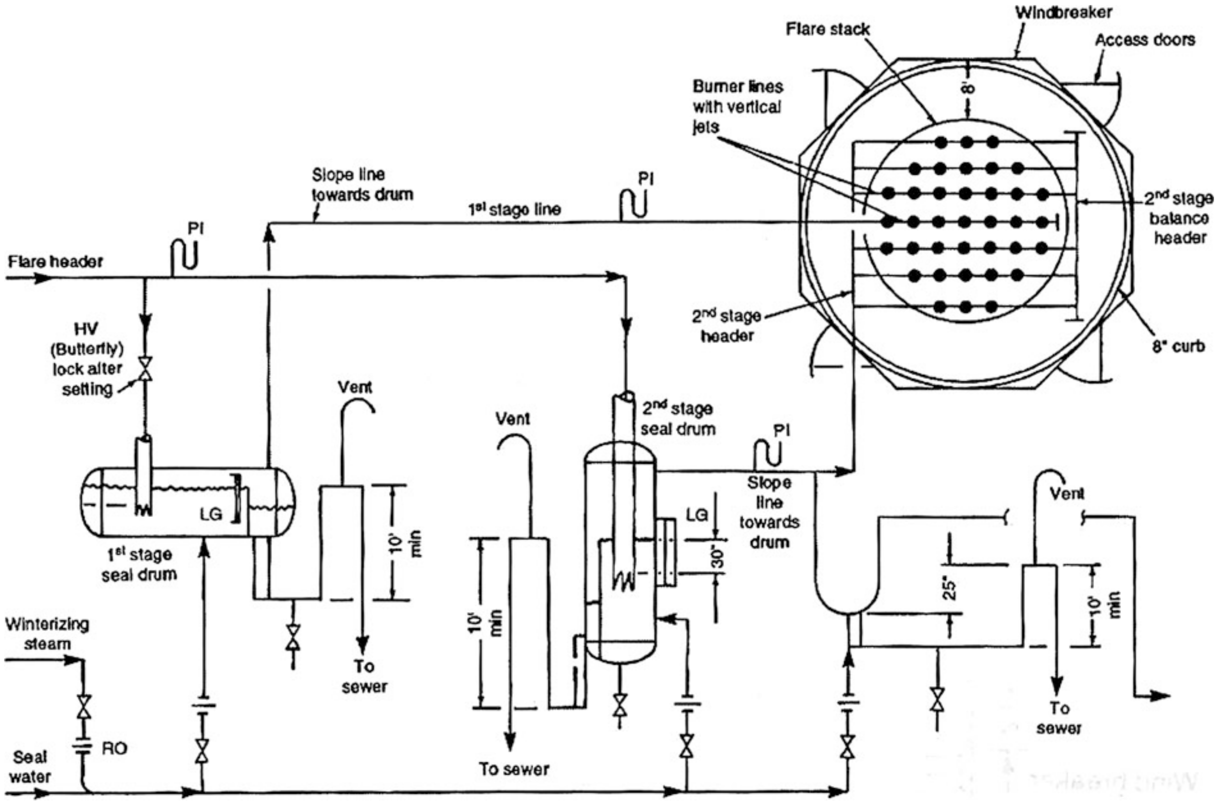


Fig. 16 Multi-jet flare plan with seal details

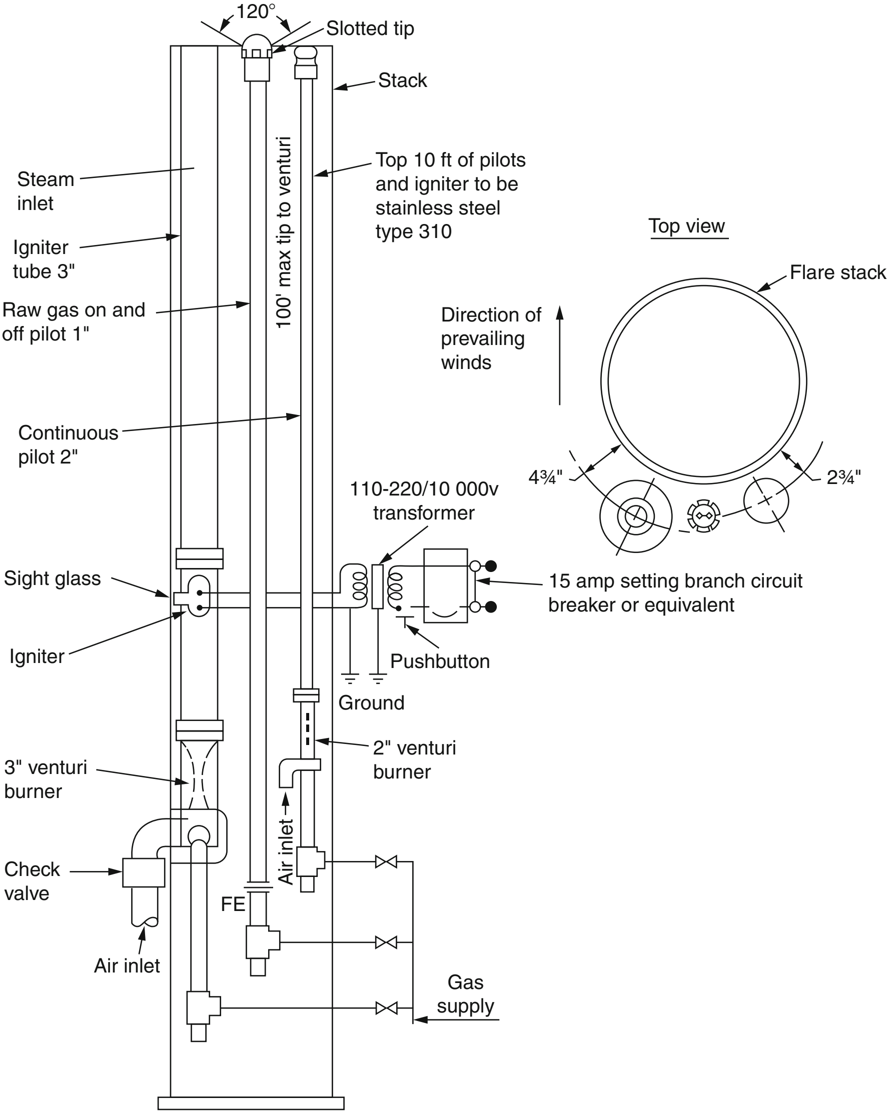


Fig. 17 Flare tip igniter assembly

A clear space around an elevated flare is required to allow for the effect of heat radiation from the flare to the ground. Flares which have a heat release of 300 million to 1 billion Btu/h should be located at least 200 f. from the plant property line or any pond, separator, tankage, or any equipment that could be ignited by a falling spark. The stack also must have a spacing of at least 500 f. from any structure or plant whose elevation is within 125 f. of the flare tip.

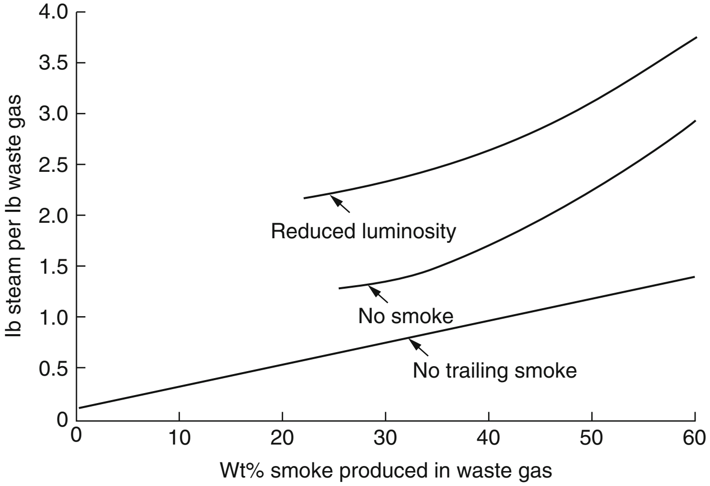


Fig. 18 Approximate amount of steam for smoke abatement

Flare tips today tend to be molecular seal types. In these proprietary tips, there is a baffle-like arrangement to trap a gas that is heavier than air, like propane, or a gas much lighter than air, like methane, in the tip to prevent air ingress back into the stack that can cause an explosion. This system is used in addition to a water seal and a purge.

The elevated flare stack is designed to maintain a gas velocity of between 100 and 160 ft/s during a major blowdown to flare. This rate is based on the maximum single emergency plus any steam added to improve the burning characteristics. Above a velocity of 160 ft/s, noise becomes a problem, and the maintenance of ignition also is dubious unless multiple ignition tubes or the intermittent spark ignition system is used. Some proprietary flare tip designs, however, do claim ability to handle satisfactorily velocities up to 400 ft/s. By API guidelines, the maximum flare tip velocity should not exceed 0.5 mach.

The Multi-jet Ground Flare

The multi-jet flare provides a completely noiseless, nonluminous flaring at a reasonable cost. At normal loads the flare is also essentially smokeless and is particularly useful where continuous flaring is required. Figures 15 and 16 show the elevation of the flare stack and the plan arrangement of a two-stage multi-jet flare, respectively.

The two-stage arrangement shown here shows the flare header being directed to one of two seal drums or to both. The first-stage seal drum operates at a back pressure of 20 in. of water at the first-stage burners at its design capacity. The second-stage burners are activated when the pressure in the flare header reaches 30 in. of water gauge.

Very often, particularly in large process complexes, the ground flare is designed to operate in conjunction with an elevated flare. The multi-jet flare takes a gas stream up to say 80 % of its rated capacity. Additional flow is then diverted to an elevated flare system. Thus, if there is need for the continuous flaring of a reasonably small quantity, the ground flare accommodates it. In an emergency or surge, the elevated flare comes into operation automatically to take the additional load.

The burners of a multi-jet flare are jet nozzles approximately 15 in. in length of 1 in. diameter stainless steel pipe. They discharge vertically from the horizontal burner lines which run across the bottom of the stack. The number of jets is based on gas velocity and is expressed by the equation:

$$N = 16.4V \tag{3}$$

where:

N = number of jets.
V = flare design capacity in MMscf/day.

The jets are placed on a square or rectangular pitch of 18–24 in. A first estimate of the required pitch may be obtained from the expression:

$$P = \left(100 \times D^2\right)/(N \times C) \tag{4}$$

where:

P = pitch in inches.
D = stack ID in feet.
N = number of jets.
C = distance between burner center line in inches.

No jet should be placed closer than 12 in. from the inside of the stack.

The inside diameter of the stack is based on the rate of heat release at design capacity. It is calculated using the following equation:

$$D = 0.826\ Q^5 \tag{5}$$

where:

D = stack inside diameter in feet.
Q = heat release at max design in MM Btu/h.

The stack height for diameters up to 25 f. is 32 ft, and the steel shell of the stack is lined with 4″ of refractory material. A windbreaker completes the construction of the stack. This is necessary to prevent high wind gusts from extinguishing the flames.

Flame holders are installed above the burners to prevent the flames “riding” up to the top of the stack. These are simply solid rods of 1″ refractory material supported horizontally above each burner line. The position of these flame holders relative to the bottom of the stack is critical to the proper operation of the burners. The stack itself is elevated to allow air for combustion to enter. The minimum space between grade and the bottom of the stack is set at 6 f. or 0.3D whichever is the larger.

As for any flare, a continuous pilot burner is recommended. The proper operation of this pilot is important with respect to multi-jet-type flares because of the danger of un-burnt flammable material escaping outside the flare at ground level. A gas pilot is provided at each end of the primary burner to minimize this risk.

Effluent Water Treating Facilities

This section of the "off-site system" discussion deals with the treating of wastewater accumulated in a process complex before it leaves the complex. Over the years requirements for safeguarding the environment have demanded close control on the quality of effluents discharged from chemical and oil refining plants. This includes effluents which contain contaminants that can affect the quality of the atmosphere and those that can be injurious to plant and aquatic life. Effluent management in the oil industry has therefore acquired a position of importance and responsibility to meet these environmental control demands.

Water effluents that are discharged from the process and other units are collected for treating and removal or conversion of the injurious contaminants. In many oil refineries, imported water, in the form of ship's ballast water, is also collected on shore for treatment before discharging back to the sea. Figure 19 is a schematic of the water effluent treating system for a major European oil refinery.

Normally the water effluent treating facilities for a complex would be located at the lowest geographical point in the plant. In this way very little pumping is required to move the wastewater to and from the treating plants. The schematic in Fig. 19 is for a refinery that was sited below the sea level, so more pumps are used than would be typical.

The primary contaminant to be removed in the system shown in Fig. 19 is, of course, oil. Five separate systems are used in this refinery's treatment plant.

The first is that for handling ballast water from sea-going tankers. The second is the handling of clean water. This is included because the system bypasses all the treating processes except the last "guard" process which, in this case, are the retention ponds. The third system is also for handling non-oily water but water that would be high in certain chemicals. This system also discharges into retention or storm water ponds. The water is held in these ponds to ensure that there is no contamination. If the storm water is contaminated, it would be returned into the appropriate treating process(es) for removal of the contaminants.

The last two systems shown are for the handling of contaminated water from the refinery's paved areas, various tank and process plant drainage, and the like. These oily water systems and the ballast water stream are treated for oil removal. In the case of the ballast water, the water drained from the bottom of the holding tanks is routed through an API separator. This is a specially designed pond that reduces the

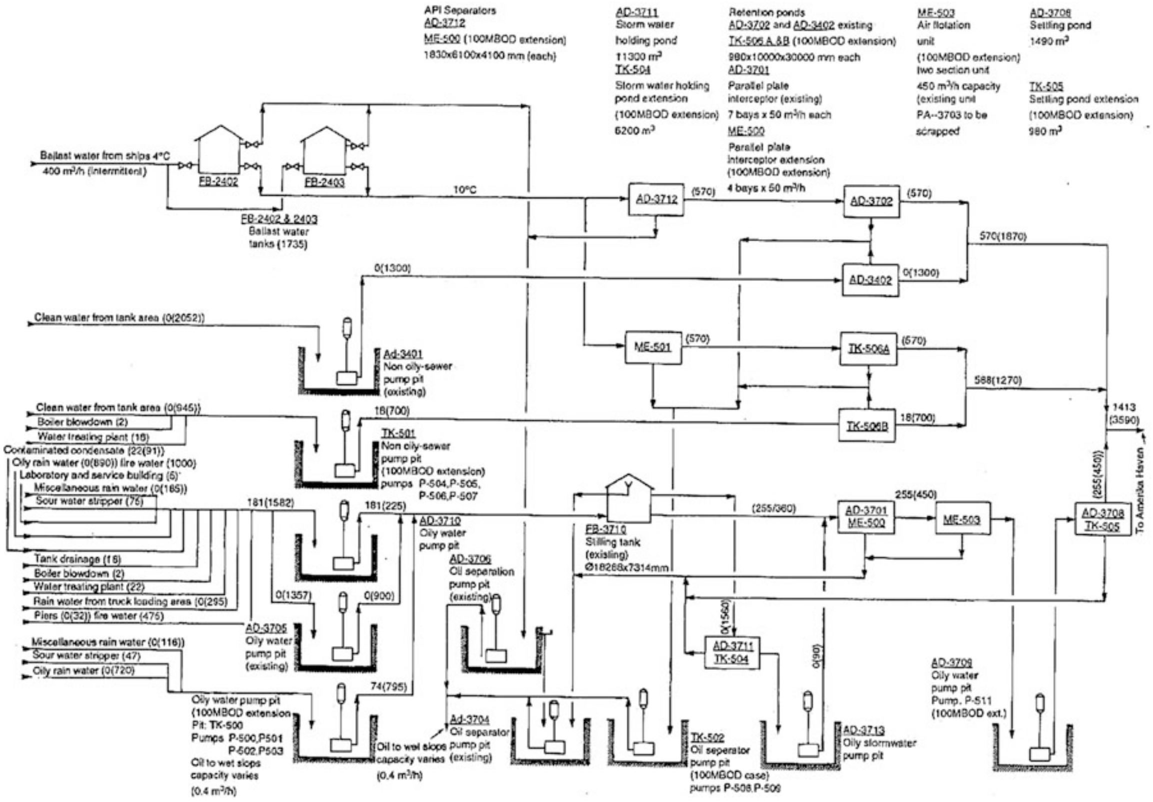


Fig. 19 A schematic of a water effluent treating system

forward velocity of the water stream to allow the separation of oil from the water by settling or gravity.

The water/oil separation for the other refinery streams takes place in a series of settling ponds. Final cleanup in this case is accomplished by the use of parallel plate interceptors and an air flotation process. The principle of the parallel plate interceptor is to force the water stream to change direction several times in rapid sequence and thus “knocking out” any oil entrained in the stream. The air flotation unit causes the contaminated water stream to be agitated so as to force the lighter oil phase to the surface where it can be removed by skimming or by baffled overflow.

There is often sludge accompanying the water. API separators and plate interceptors have provisions to collect the sludge for disposal. In many cases, the sludge is sent to the coker unit for disposal. In the US, API separator sludge is a hazardous waste by definition. Effluent and sour water treatment processes are discussed in much more detail in the handbook chapter “▶ Environmental Control and Engineering in Petroleum Processing.”

Other Effluent Water Treating Systems

Most chemical plants and indeed a few oil refining plants require more complex methods for clarifying their effluent water to meet environmental requirements for its disposal. The four more common methods are:

- In-line clarification using coagulation, flocculation, and filtration
- Plain filtration
- Sedimentation
- Chemically aided sedimentation using coagulation, flocculation, and settling

Clarification is a process that removes suspended (usually organic) matter that gives the stream color and turbidity. The removal of this matter, especially in a colloidal form, requires the addition of chemicals to cause coagulation and flocculation to promote settling and separation of suspended solids. Coagulants and coagulant aids added to the influent stream chemically react with impurities to form precipitates. These, together with particles of enmeshed turbidity, are flocculated into larger masses that are then readily separated from the bulk liquid.

There are essentially three steps in the chemically aided clarification process. These are:

- Mixing of the additives
- Flocculation
- Settling

Coagulation encompasses the process of mixing the contaminated water with additives to form agglomerates, or floc. This is carried out in a series of separate compartments, with the settling basin occupying the largest volume. Coagulation is the singular most important step in the clarifying process.

Because it involves the buildup of colloidal-type particles, the chemicals and the process rate are specific to the material that is to be clarified. There are companies that specialize in the design construction and the operation of this type of effluent treating. These companies use their experience in handling the complex electrochemical kinetics associated with flocculation and coagulation principles.

Biochemical Oxygen Demand Reduction

As discussed above, the primary function of effluent treating is removal of oil and other contaminants from refinery wastewaters. In many locations, it is also necessary for the refinery to reduce the BOD or COD of the refinery effluent before discharge to a waterway or before sending the effluent to a publically owned treatment works (POTW).

This is usually accomplished by processing the water through a biological digestion system. Systems that have been used for this purpose have included:

- Trickle filters
- Activated sludge units
- Activated carbon
- Aerated ponds

The design of these systems is beyond the scope of the current Handbook.

Sanitary Sewage Treatment

In some remote refinery locations, the facility must provide its own sanitary sewage disposal. This is normally accomplished with a packaged bio-treatment unit and/or aerated holding basins. A trickle filter may also be used. We will not discuss these systems in more detail here, as they are not common.

Appendix 1: Calculating Heat Loss and Heater Size for a Tank

Heat loss and the heater surface area to compensate for the heat loss may be calculated using the following procedure:

Step 1. Establish the bulk temperature for the tank contents. Determine the ambient air temperature and the wind velocity normal for the area in which the tank is to be sited.

Step 2. Calculate the inside film resistance to heat transfer between the tank contents and the tank wall. The following simplified equation may be used for this:

$$h_c = 8.5(\Delta t/\mu)^{0.25}$$

where:

h_c = inside film resistance to wall in Btu/h sqft °F.

Δt = temperature difference between the tank contents and the wall in °F.

μ = viscosity of the tank contents at the bulk temperature in cPs.

The heat loss calculation is iterative with assumed temperatures being made for the tank wall.

Step 3. Using the assumed wall temperature made in step 2, calculate the heat loss to the atmosphere by radiation using Fig. 20. Then calculate the convection heat loss from the tank wall to the atmosphere using Fig. 21. Note the temperature difference in this case is that between the assumed wall temperature and the ambient air temperature. Correct these figures by multiplying the radiation loss by the emissivity factor given in Fig. 20. Then correct the heat loss by convection figure by the factors as described in step 4 below.

Step 4. The value of h_{co} read from Fig. 21 is corrected for wind velocity and for shape (vertical or horizontal) by multiplying by the following shape factors:

Vertical plates	1.3
Horizontal plates	2.0 (facing up)
	1.2 (facing down)

For the wind velocity correction, use:

$$F_w = F_1 + F_2$$

where:

F_w = wind correction factor.

F_1 = wind factor at 200 °F calculated from:

$F_1 = (\mathrm{MPH}/1.47)^{0.61}$

F_2 = read from Fig. 22

Then the corrected h_{co} is

$h_{co} \times$ shape correction $\times F_w$.

Step 5. The resistance of heat transferred from the bulk of the contents to the wall must equal the heat transferred from the wall to the atmosphere. Thus:

Heat transferred from the bulk to the wall = "*a*"

$$= h_c \text{ from step } 2 \times \Delta t \text{ in Btu/h/sqft}$$

where Δt in this case is (bulk temp – assumed wall temp).

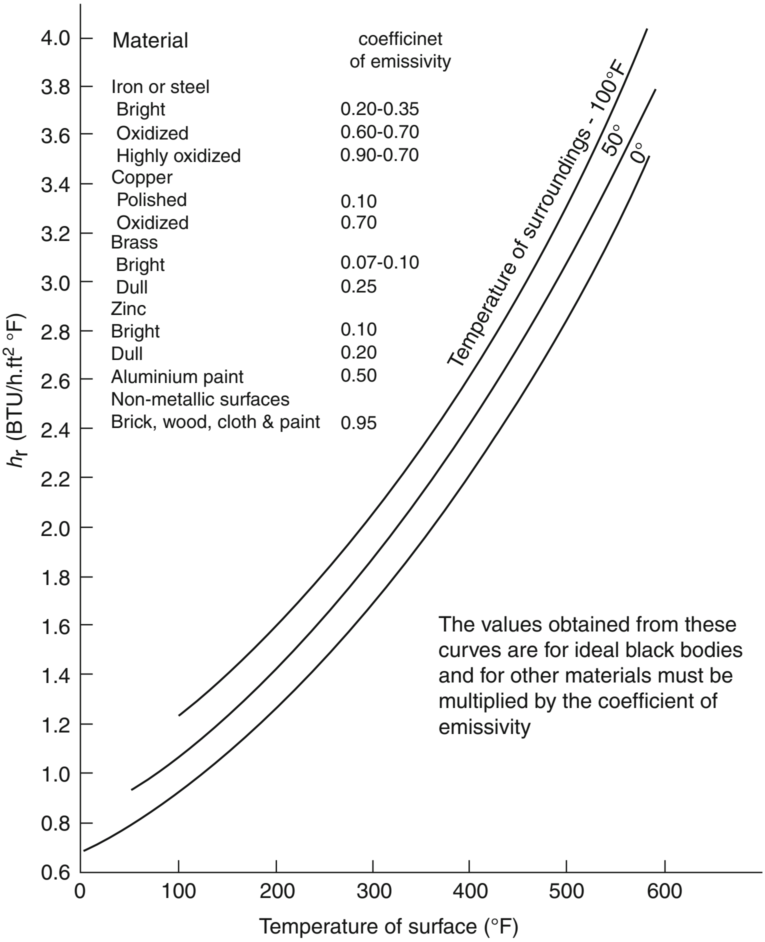


Fig. 20 Heat loss by radiation

Heat transferred from the wall to the atmosphere = "*b*"

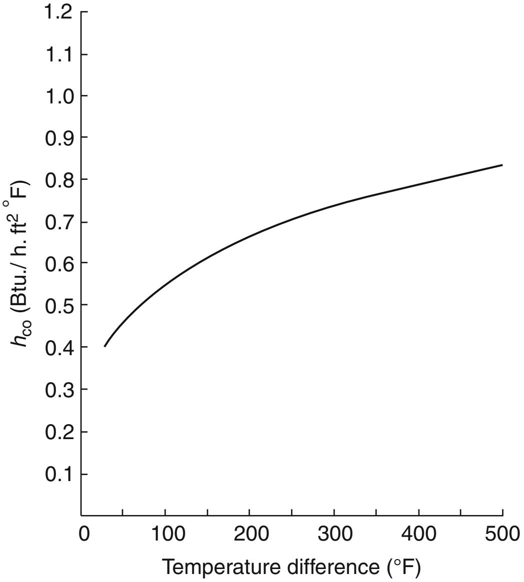
$$= (h_{co} + h_r) \times \Delta t \text{ in Btu/h/sqft}$$

where Δt in this case is (assumed wall temp – air temp).

Step 6. Plot the difference between the two transfer rates against the assumed wall temperature. This difference ("*a*" – "*b*") will be negative or positive, but the wall temperature that is correct will be the one in which the difference plotted = 0. Make a last check calculation using this value for the wall temperature.

Step 7. The total heat loss from the wall of the tank is the value of "*a*" or "*b*" calculated in step 6 times the surface area of the tank wall. Thus:

Fig. 21 Heat loss to the atmosphere by natural convection



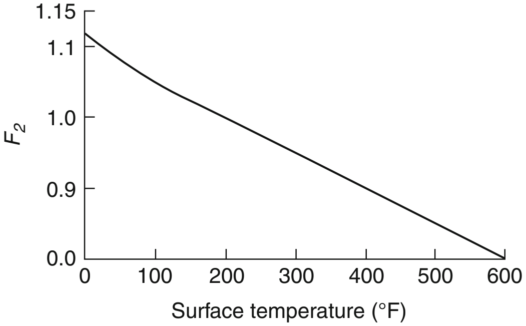


Fig. 22 Plot of “F2” versus surface temperature

$$Q_{\text{wall}} = h_{\text{c}} \times \Delta t \times (\pi D_{\text{tank}} \times \text{tank height})\text{in Btu/h}$$

Step 8. Calculate the heat loss from the roof in the same manner as that for the wall described in steps 2–7. Note the correction for shape factor in this case will be for horizontal plates facing upward and the surface area will be that for the roof.

Step 9. Calculate the heat loss through the floor of the tank by assuming the ground temperature as 50 °F and using

$$h_{\text{f}} = 1.5 \text{ Btu/h sqft °F}$$

Step 10. The total heat loss then is:

$$\text{Total heat loss from tank} = Q_{\text{wall}} + Q_{\text{roof}} + Q_{\text{floor}}$$

Step 11. Establish the heating medium to be used. Usually this is medium pressure steam.

Calculate the resistance to heat transfer of the heating medium to the outside of the heating coil or tubes. If steam is used then take the condensing steam value for h as 0.001 Btu/h sqft °F. Take the value of steam fouling as 0.0005 and tube metal resistance as 0.0005, also.

The outside fouling factor is selected from the following:

Light hydrocarbon = 0.0013.
Medium hydrocarbon = 0.002.
Heavy hydrocarbons, such as fuel oils = 0.005.
The resistance of the steam to the tube outside = $1/(h + R)$
where $R = r_{\text{steamfouling}} + r_{\text{tube metal}} + r_{\text{outside fouling}}$

Step 12. Assume a coil outside temperature. Then, using the same type of iterative calculation as for heat loss, calculate for "*a*" as the heat from the steam to the coil outside surface in Btu/h/sqft. That is,

$$\text{“}a\text{”} = h \times \Delta_{\text{ti}}$$

Calculate for "*b*" as the heat from the coil outside surface to the bulk of the tank contents.

Use Fig. 23 to obtain h_o, and again "*b*" is $h_o \times \Delta t_o$ where the Δt_o is the temperature between the tube outside and that of the bulk tank contents. Make further assumptions for coil outside temperature until "*a*" = "*b*".

Step 13. Use "*a*" or "*b*" from step 12, which is the rate of heat transferred from the heating medium in Btu/h/sqft, and divide this into the total heat loss calculated in step 10. The answer is the surface area of the immersed heater required for maintaining the tank content's bulk temperature.

An example calculation using this technique is given in Appendix 2 of this chapter.

Appendix 2: Example Calculation for Sizing a Tank Heater

Problem We need to calculate the surface area for a heating coil which will maintain the bulk temperature of fuel oil in a cone-roof tank at a temperature of 150 °F. The ambient air temperature is an average 65 °F and the wind velocity averaged over the year is 30 MPH. The fuel oil data are as follows:

Viscosity (μ) = 36 cPs at 150 °F.
SG at 150 °F = 0.900.

The tank is to be heated with 125 psig saturated steam. The tank dimensions are 60 f. diameter by 180 f. high. It is not insulated, but is painted with nonmetallic color paint.

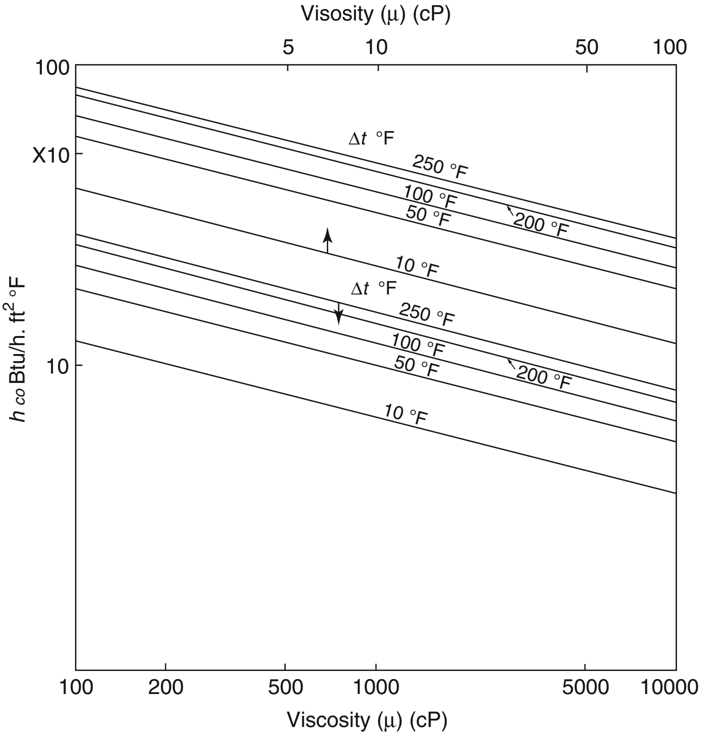


Fig. 23 Convection heat transfer coefficient

Solution (Note: figure numbers refer to Appendix 1 in this chapter)
1.0 Calculating the heat loss from the wall
1st trial. Assume wall temperature is 120 °F.

$$h_i = 8.5(\Delta t_i/\mu)^{0.25}$$

where:

$$\Delta t_i = 150 - 120 = 30\ \ ^\circ\mathrm{F}.$$

$$h_i = 8.5 \times 0.955 = 8.12\ \ \mathrm{Btu/h.sqft^\circ F}.$$

$$\text{“}a\text{”} = 8.12 \times 30 = 243.6\ \ \mathrm{Btu/h.sqft}.$$

Δt_0 is the temperature difference between assumed wall temp and the ambient air = 120 − 65 = 55 °F.

$h_{\mathrm{co}} = 0.495 \times 1.3$ (from Fig. 21).

Wind correction factor F_w is as follows:

$$\begin{aligned} F_1 &= (\mathrm{MPH}/1.47)^{0.61} \\ &= 6.29 \\ F_2 &= 1.04(\text{from Fig. 22}) \\ F_w &= 6.29 + 1.04 = 7.33 \end{aligned}$$

$$h_{co}\ (\text{corrected}) = 0.495 \times 1.3 \times 7.33 = 4.20\ \text{Btu/h.sqft °F}$$

Heat loss from wall due to radiation h_{ro} is found from Fig. 20 =1.18 Btu/h.sqft °F.

Corrected for emissivity $h_{ro} = 1.18 \times 0.95 = 1.123$ Btu/h.sqft°F:

$$\begin{aligned} \text{“}b\text{”} &= (h_{co} + h_{ro}) \times \Delta t_0 \\ &= (4.21 + 1.12) \times 55 = 293\ \text{Btu/h.sqft} \end{aligned}$$

$$\text{“}a\text{”} - \text{“}b\text{”} = 244 - 293 = -49\ \text{Btu/h.sqft}$$

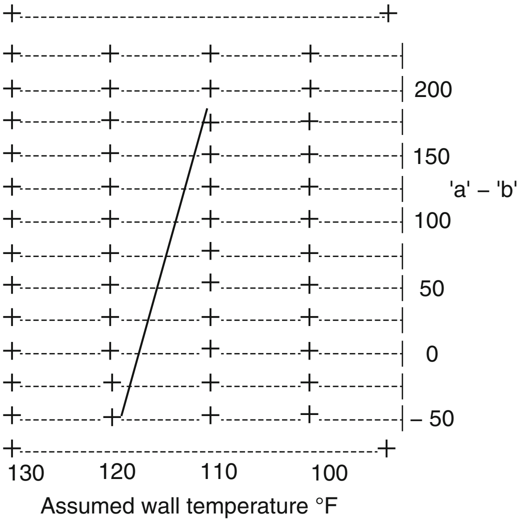
2nd trial. Assume wall temperature is 110 °F.

Carrying out the same calculation procedure as for trial 1: “*a*” – “*b*” = +172 Btu/h.sqft

3rd trial. Assume wall temperature is 115 °F.

Again carrying out the calculation procedure as for trial 1: “*a*” − “*b*” = +35

The results of the above trials are plotted linearly below:



Final trial. At wall temperature of 117 °F,

$$\begin{aligned}
&h_{\mathrm{io}} = 8.31\ \ \mathrm{Btu/h.sqft^\circ F}\\
&\text{“}a\text{”} = 8.31 \times (150 - 117) = 274\ \ \mathrm{Btu/h.sqft}\\
&h_{\mathrm{co}}(\text{corrected}) = 4.18\ \ \mathrm{Btu/h.sqft^\circ F}\\
&h_{\mathrm{ro}}(\text{corrected}) = 1.12\ \ \mathrm{Btu/h.sqft^\circ F}\\
&\text{“}b\text{”} = (4.18 + 1.12) \times (117 - 65)^\circ\mathrm{F} = 275.7\ \ \mathrm{Btu/h.sqft}
\end{aligned}$$

“*a*” and “*b*” are close enough to call the total heat loss 275.7 Btu/h.sqft:

$$\text{Surface area of wall} = \text{circumference} \times \text{height} = \pi D \times 180\,\mathrm{ft} = 33,929\,\mathrm{sqft}$$

$$\text{Total heat loss through wall} = 275.7 \times 33,929 = 9.35\ \ \mathrm{MMBtu/h}$$

2.0 Calculating heat loss through roof

Trial 1. Assume roof temperature is 116 °F:

$$h_{\mathrm{i}} = 8.38\ \ \mathrm{Btu/h.sqft^\circ F}$$

$$\text{“}a\text{”} = 8.38 \times (150 - 116)^\circ\mathrm{F} = 284.9\,\mathrm{Btu/h.sqft}$$

$$h_{\mathrm{co}}\ (\text{corrected}) = (0.470 \times 2.0) \times 1.04 \times 6.29 = 6.35\,\mathrm{Btu/h.sqft^\circ F}$$

(Note: the number read from Fig. 21 is multiplied by 2.0 in this case as the roof is an upward facing plate.)

$$\begin{aligned}
&h_{\mathrm{ro}}\ (\text{corrected}) = 1.165 \times 0.95 = 1.11\,\mathrm{Btu/h.sqft^\circ F}\\
&\text{“}b\text{”} = (6.35 + 1.11) \times (116 - 65)^\circ\mathrm{F} = 380\,\mathrm{Btu/h.sqft}\\
&\text{“}a\text{”} - \text{“}b\text{”} = -95\,\mathrm{Btu/h.sqft}
\end{aligned}$$

Trial 2. Assume a wall temperature of 110 °F.

“*a*” − “*b*” in this case = +23 which is within acceptable limits.

The heat loss is taken as an average of “*a*” and “*b*” = 338 Btu/h.sqft

Total roof heat loss = roof area × 338 = 2,827 sqft × 338 = 0.956 MMBtu/h

3.0 Calculating the heat loss through the floor

Assume the ground temperature is 50 °F, and the heat transfer coefficient is 1.5 Btu/h.sqft°F:

$$\text{Then heat loss} = 1.5 \times (150 - 50) \times 2,827\,\mathrm{sqft} = 0.424\,\mathrm{MMBtu/h}$$

4.0 Total heat loss from the tank

Heat loss from the walls = 9.350 MMBtu/h.

Heat loss from the roof = 0.956 MMBtu/h.

Heat loss from the floor = 0.424 MMBtu/h.

Total heat loss = 10.730 MMBtu/h.

5.0 Calculating the tank heater coil surface area required

The heating medium is saturated 125 psig steam.

Temperature of the steam = 354 °F.

Steam side calculations:

Approx. resistance of steam, $h_s = 0.001$ h.sqft°F/Btu
Fouling factor on steam side, $r_1 = 0.0005$ h.sqft°F/Btu
Tube metal resistance $r_2 = 0.0005$ h.sqft°F/Btu
Outside fouling factor $r_3 = 0.005$ h.sqft°F/Btu

$$\begin{aligned}\text{Steam side heat transfer coefficient} &= 1/(0.001 + 0.0005 + 0.0005 + 0.005)\\ &= 143\,\text{Btu/h.sqft°F.}\end{aligned}$$

Oil side heat transfer coefficient is obtained from Fig. 23.

1st trial. Assume a tube wall temperature of 310 °F.

For steam side "*a*" = 143 × (354 − 310) = 6,292 Btu/h.sqft.

For oil side ho = 31 Btu/h.sqft°F (Fig. 23),

$$\text{“}b\text{”} = 31 \times (310 - 150) = 4{,}960\ \text{Btu/h.sqft}$$

$$\text{“}a\text{”} - \text{“}b\text{”} = +1{,}332$$

2nd trial. Assume a tube wall temperature of 320 °F.

"*a*" in this case was calculated to be 4,862.

"*b*" was calculated to be 5,355.

"*a*" − "*b*" = −493

Plotted on a linear curve, the tube wall temperature to give "*a*" = "*b*" was 317 °F.

Final trial. At a tube wall temperature of 317 °F,

$$\begin{aligned}&\text{Steam side} = 143 \times (354 - 317)\\ &\text{“}a\text{”} = 5{,}291\,\text{Btu/h.sqft.}\end{aligned}$$

Oil side ho =31.2 (From Fig. 23):

$$\text{“}b\text{”} = 31.2 \times (317 - 150) = 5{,}210\,\text{Btu/h.sqft}$$

"*a*" − "*b*" = +81 which is acceptable.

Make the rate of heat transfer the average of the calculated rates:

$$U = (5{,}291 + 5{,}210)/2 = 5{,}251\ \text{Btu/h.sqft.}$$

Coil surface area required is:

$$A = 10.73\ \text{MM Btu/h}/\ 5{,}251\,\text{Btu/h.sqft} = 2{,}043\,\text{sqft.}$$

Environmental Control and Engineering in Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_19

Abstract

Operating a petroleum processing facility cleanly is a requirement for doing business. The environmental regulations that affect refineries and other facilities have become increasingly restrictive and the trend is expected to continue. This chapter explores the range of relevant regulations, processes, and practices that apply to modern refineries and other petroleum processing facilities for environmental management. Topics include air emissions, water effluents, solid wastes, and noise. Detailed design examples are provided for a sour water stripper and an oil/water separator.

Keywords
Refinery • Environment • Emissions • Effluent • Hazardous waste • Noise

Introduction

During the last half of the 1900s, control of contaminants from processing crude oil became an increasingly important driver in the design and operation of refineries and other petroleum processing facilities. The topic "▶ Petroleum Products and a Refinery Configuration" in this handbook discusses some of the changes that have taken place in the specifications for petroleum products to meet legislative environmental control. These products have been singled out because they impact more prominently on the daily lifestyle and health of the general public, particularly in the more advanced industrial countries. The product specifications continue to ratchet downward with respect to sulfur. At the same time, the requirements are becoming more stringent for fuel quality.

Similar changes and legislative controls have been adopted on the levels of emissions and streams leaving the petroleum processing facilities in the air, water, and solid wastes. These changes have become more restrictive as greater knowledge of their effects on the environment and health has developed.

This chapter deals with many of the measures adopted in the design and operation of processes to meet these environmental protection measures. We will focus on four areas of direct environmental controls in facilities, with several sub-areas:

- Air – sulfur, volatile organic carbon (VOC), nitrogen oxides, carbon monoxide, particulate matter, carbon dioxide, ozone, and other emissions
- Water effluents – oxygen demand, oil and grease, sulfides, ammonia compounds, phenols, caustic, benzene, selenium, metals, and other potential contaminants

- Solid wastes – sludge, catalysts, waste oils, and characteristic hazardous wastes
- Noise levels – internal, fenceline

Table 1 highlights some of the environmental concerns in air, water, solids, and noise from refineries, providing a map to potential areas of concern in each type of process. This chapter will explore each of these areas in more detail.

Table 1 Some key areas of environmental concern for oil refining process unit streams

Process area	Air	Water	Solids	Noise
Atmospheric & vacuum distillation	Flue gases, fugitives	Sour water (NH_3, H_2S, amines), desalter water (oil), spent caustic	Sludges, exchanger cleaning	Rotating equipment, fluid flow
Coking, thermal cracking	Flue gases, fugitives	Sour water, coke cutting water, process waste water	Sludges, exchanger cleaning, coke	Rotating equipment, fluid flow
Fluid catalytic cracking, unsaturated gas plant	Flue gases, fugitives, regenerator gas	Sour water (NH_3, H_2S, phenols), spent caustic, process waste water	Spent catalyst, exchanger cleaning	Rotating equipment, fluid flow, catalyst flow
Hydroprocessing units	Flue gases, fugitives	Sour water (NH_3, H_2S, oil), process waste water	Spent catalyst, exchanger cleaning	Rotating equipment, fluid flow, HP relief, venting
Hydrogen plants	Flue gases, deaerator/ degasifier vent		Spent catalyst, exchanger cleaning	Rotating equipment, fluid flow, hydrogen vents
Saturated gas plant, alkylation		Spent caustic and acid, process waste water	Exchanger cleaning	Rotating equipment, fluid flow
Catalytic reforming	Flue gases	Process waste water	Spent catalyst, exchanger cleaning	Rotating equipment, fluid flow
Sulfur plant, sour water stripping	Flue gases, incinerator, sulfur pit or tank vent (SO_X, H_2S)	Sour water, tail gas unit fluid	Sludges, sulfur, exchanger cleaning	Rotating equipment, fluid flow
Waste water treating	Fugitive vapors	Refinery effluent, storm water	Sludges	Rotating equipment, fluid flow
Tankage areas	Fugitive vapors	Tank dike drains, tank water draws	Tank sludges	Rotating equipment, fluid flow

(*continued*)

Table 1 (continued)

Process area	Air	Water	Solids	Noise
Flare	Combustion gases	Sour water, oily water		Flare noise, emergency vents, rotating equipment
General refinery concerns	Fugitive vapors, cooling towers	Storm water, oily water drainage	Trash (hazardous and non-hazardous)	

Air Emissions

Introduction

Air emissions limits today are largely driven by government legislation and the resulting regulations that have been promulgated. Some of the key air pollution regulations with which petroleum processing plants must contend include those listed below, among many others.

- US Clean Air Act (CAA) and amendments – this act, initially passed in 1970, contained a number of innovative provisions to reduce air pollution. With amendments, it is still a primary driver behind air emissions control design and practices in the United States today. Some of the important provisions and regulations resulting from the act include:
  - Roles for both the federal and state governments
  - Environmental Protection Agency (EPA) sets limits on air pollutants anywhere in the United States – states can regulate levels lower, which is particularly notable in California.
  - EPA reviews and approves State Implementation Plans (SIPs).
  - CAA includes provisions for interstate and international pollution limits.
  - Prevention of Significant Deterioration (PSD) – classified areas in the United States into attainment (meeting all standards) or non-attainment (do not meet some standards) with different permitting for facilities in each type of area.
  - Established a permitting system for emitters.
  - Enforcement provisions – including both civil and criminal penalties.
  - Requires public participation in permitting.
  - Market incentives for reduction of pollutants.
  - New source performance standards (NSPS) for facilities – best available control technology (BACT).
  - Air toxics rules – Maximum Achievable Control Technology (MACT) and Residual Risk and Technology Reviews (RTR).

- European Union (EU) regulations and directives
  - EU climate package – targets 20 % reduction in greenhouse gases (GHGs) by 2020 (vs. 1990) along with 20 % increase in renewables use and 20 % reduction in total energy use
  - Standards for higher fuel quality and diesel production
  - Industrial Emissions Directive (IED) – limits SO_2, NOx, particulates, and VOCs from industrial sources – integrated approach, best available technologies (BATs), and local conditions by local authorities
  - Thematic Strategy on Air Pollution (TSAP) – recommends emission limit values (ELVs) be consistent with local impacts
  - Energy Taxation Directive (ETD) – still proposed (2014) – potential taxes on energy content and CO_2 emissions
  - Renewable Energy Directive – affects product specifications
  - Fuel Quality Directive – affects product specifications, GHG emissions
- International Maritime Organization (IMO) legislation
  - International Convention on the Prevention of Pollution from Ships (MARPOL 73/78 or MARPOL Convention) – regulates maximum sulfur in fuel oil and emissions for ships – mostly product quality impacts, but more sulfur to deal with in the refinery.
- State regulatory decisions
  - California Air Resources Board and local air districts – these have been leaders in ratcheting down allowable emissions in refineries. Often, US regulations follow the actions of the California authorities within a few years.
  - Fuel oils – there is a drive to reduce the sulfur in fuel oils used primarily on the US East Coast. Individual states are adopting ultra-low sulfur fuel oil requirements ahead of the EPA deadlines. This is resulting in more sulfur to deal with in refineries.
- Asia
  - The focus has been on SO_2 reduction primarily – especially driven by severe conditions in some areas.
  - China has limits on allowable SO_2 based on an area classification, e.g., protected areas like scenic spots, historical sites, and protected habitats have a more severe limit than other areas – Regional Air Quality (RAQ) regulations (took effect in 2014) – SOx, NOx, particulates.
  - India Environment (Protection) Act – initially 1986 – SOx, NOx, VOCs, etc.

Impacts and Sources of Refinery Emissions

Table 1 provided an initial indication of some of the air emissions sources and the pollutants of concern. Here we will look more closely at the most common air emissions that are regulated, with additional attention to where these emissions may arise in the refinery. Specifically, we will talk about:

- Sulfur (SOx, H_2S, organic sulfur compounds)
- Nitrogen oxides (NOx)
- Carbon oxides (CO, CO_2)
- Particulate matter (esp. PM-10)
- Volatile organic carbon (VOC)
- Ozone
- Ammonia
- Methanol
- Lead
- Mercury

Table 2 provides a summary of some of the refinery sources, health effects, environmental effects, and property damage aspects of each of these pollutants.

Controlling Air Emissions

We will now examine the most common approaches to controlling the types of air emissions listed in Table 2.

Sulfur Compounds

Sulfur Oxides (Primarily SO_2)

For most combustion sources of sulfur oxides, the primary control approach is elimination of sulfur compounds from the fuel. Refinery gas treatment is discussed extensively in the chapter entitled "▶ Refinery Gas Treating Processes" of this handbook. We will not repeat that material except to note that the normal treatment approach is scrubbing of sour refinery gases with an amine (or other) solution to absorb H_2S (the primary sulfur compound) creating a low sulfur fuel gas. The amine is regenerated to release the H_2S, which is routed to the sulfur plant for sulfur recovery (to be discussed later).

Amine absorbers do not remove all sulfur compounds from the gases. COS and mercaptans will usually still be present. Normally, the levels of sulfur remaining are low enough that the gas can be used as fuel, but sometimes the level is still too high after removal of H_2S. In these cases, the options are:

- Caustic treatment (e.g., Merox or Merifining) to remove the mercaptans
- Physical solvent, sorbent treatment or hydrotreating to remove COS

Caustic Treating

A typical caustic treating system is illustrated in Fig. 1. In the caustic treater, the vapor containing mercaptans and other sulfur compounds is contacted with a circulating caustic stream containing a proprietary catalyst. The caustic absorbs the sulfur compounds selectively. Any residual H_2S will also be absorbed. Absorption occurs by reaction of mercaptan with caustic in solution:

Table 2 Sources and impacts of air emissions from a refinery

Air pollutant	Vapor sources	Health effects (in air)	Environmental effects (in air)	Property damage (in air)
Sulfur compounds				
Sulfur dioxide (primarily $S0_2$)	Fired heaters and other combustion sources burning the sulfur compounds fuels, sulfur recovery plant exhaust and vents, some processes (e.g., Edeleanu), combustion of pyrophoric iron sulfide in foulants. FCC regenerator	Short term: respiratory problems (irritation, bronchoconstriction, asthma symptoms). Long term: similar respiratory symptoms, decreased lung function	Reacts with other compounds in the air to form particulates and aerosols (smog). Increased respiratory problems in general public. Primary source of acid rain	Corrosion of stone and structures from sulfurous and sulfuric acids in low concentrations
Hydrogen sulfide (H_2S)	Sewer vents, tank seals (especially sour water storage tanks), process releases or leaks, fugitive emissions from sour streams, and maintenance activities	Highly toxic. Short term: maximum 10 ppm (8 h shift) with the max exposure of 15 ppm (15 mins). Short exposure above 500 ppm may be fatal. See the chapter "▶ Hazardous Materials in Petroleum Processing." Long term: damage to lungs, upper respiratory tract, eyes, and the central nervous system	Severe odor issue near a facility, H_2S would be oxidized to sulfur oxides and have similar environmental impacts to $S0_2$	See $S0_2$
Organic sulfur (R-SH)	Fugitive emissions from piping, valves and tanks; leaks	Using ethyl mercaptan as a guide. Short term: respiratory or skin irritation, cough, loss of sense of taste, nausea, vomiting, organ damage, unconsciousness, and coma. Long term: central nervous system damage in addition	Severe odor issue near a facility; RSH would be oxidized to sulfur oxides and have similar environmental impacts to $S0_2$	See $S0_2$

(*continued*)

Table 2 (continued)

Air pollutant	Vapor sources	Health effects (in air)	Environmental effects (in air)	Property damage (in air)
Nitrogen oxides (NOx, primarily NO_2)	Burning of gasoline, fuel gas, fuel oil, natural gas, coal, etc. Vehicles are an important source of $N0_2$ from refined product use	Lung damage, illnesses of breathing passages and lungs (respiratory system)	Ingredient of acid rain (acid aerosols), which can damage trees and lakes. Acid aerosols can reduce visibility	Corrosion of stone and structures from nitrous and nitric acids in low concentrations
Carbon oxides				
Carbon monoxide (CO)	Incomplete burning of vehicle fuels, fuel gas, fuel oil, natural gas, coal, etc. FCC regenerator	Reduces ability of blood to carry oxygen. May exacerbate heart or circulatory problems and respiratory damage	Oxidation to $C0_2$ with similar effects	No particular issues noted as CO
Carbon dioxide (CO_2)	Burning of vehicle fuels, fuel gas, fuel oil, natural gas, coal, etc. SMR hydrogen plants. Incinerators. FCC regenerator	Short term (acute): asphyxiant, respiratory distress, headache, dizziness, circulatory problems, irritation, excitation, vomiting, unconsciousness, fatality. Long term: low-level exposure: no significant impacts. Rapid unconsciousness >10 %	Primary greenhouse gas. Factor in acid rain. Positive impact on plant growth at normal concentrations of a few hundred ppm in air	Similar to $S0_2$ in very high concentrations
Particulate matter (especially PM-10) – dust, smoke, soot	Fuel combustion, industrial activities, catalyst handling, construction activities, unpaid roads, activities from outside the refinery. FCC regenerator	Nose and throat irritation, lung damage, bronchitis. Early death with long-term, heavy exposure. Hazards of chemicals in dust may present hazards: e.g., silica and nickel in catalyst dusts	Particulate haze reduces visibility. Chemicals in some dusts may have environmental impacts	Ashes, soots, smokes, and dusts can dirty and discolor structures and other property, including clothes and furniture. Some dusts may promote corrosion

(*continued*)

Table 2 (continued)

Air pollutant	Vapor sources	Health effects (in air)	Environmental effects (in air)	Property damage (in air)
Volatile organic carbon (VOC)	Incomplete burning of fuel, solvents, light hydrocarbon fugitive emissions and leaks (e.g., benzene, toluene, xylene, naphtha, etc.), paints, glues, vehicles, chemical fugitives or leaks, flares, and vents	In addition to ozone (smog) effects, it can cause serious health problems such as cancer and other effects. Many are hazardous air pollutants, which can cause varying serious illnesses (e.g., benzene)	In addition to ozone (smog) effects, some VOCs such as formaldehyde and ethylene may harm plants	Some solvents and organics can damage paint, elastomers, and fabrics
Ozone (O_3)	Chemical reaction of other pollutants normally: VOCs and NOx. Some cooling water or wastewater treatments use ozone	Breathing problems, reduced lung function, asthma, irritates eyes, stuffy nose, reduced resistance to colds and other infections, may speed up aging of lung tissue	Can damage plants and trees; smog can cause reduced visibility	Damages elastomers, rubber, paints, fabrics, etc.
Ammonia (NH_3)	NOx reduction system leaks, sour water leaks and tanks, hydrogen plant degasifier, other fugitive emissions	Irritant and corrosive to skin, eyes, respiratory tract, and mucous membranes. High concentrations may cause chemical bums. Low concentrations are an irritant	Potential oxidation to $N0_2$. In normally expected concentrations, NH_3 is not a major environmental issue. Could be a wastewater issue	Not significantly corrosive as a vapor in normally expected concentrations
Methanol (CH_3OH)	Leaks and fugitive emissions, hydrogen plant degasifier	Toxic in high concentrations. Primarily an irritant. Sensitizer on long-term skin contact and toxic to some organs. May be absorbed through skin	Reacts with metals, acids, and oxidizers. Oxidizes in the atmosphere to less hazardous materials. Half-life = 3–30 days	Not significantly corrosive as a vapor in normally expected concentrations

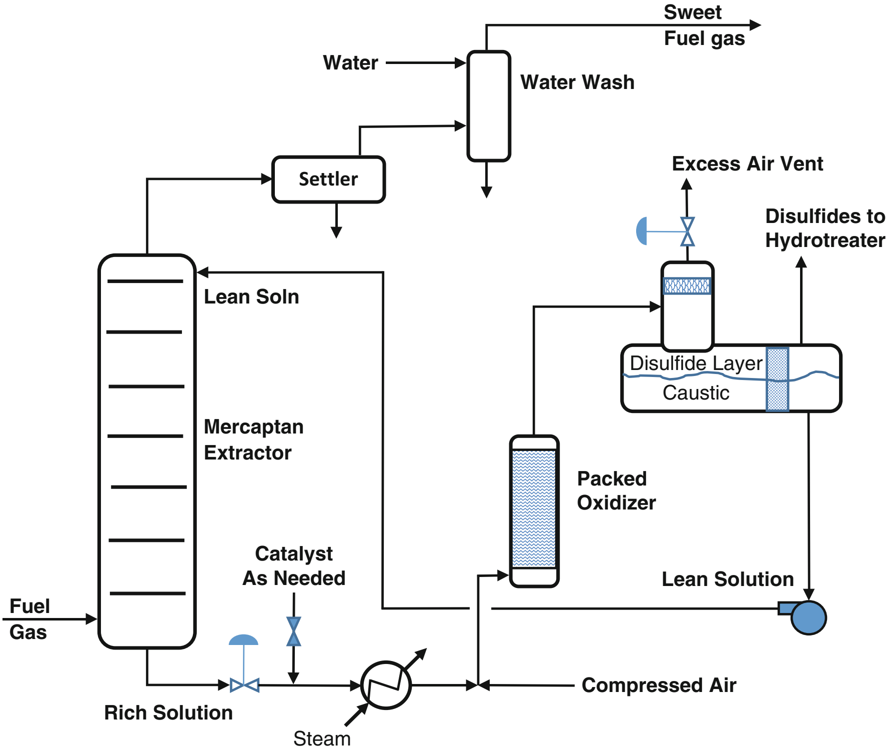


Fig. 1 Caustic removal process for fuel gas mercaptans (UOP Merox version)

$$2\,\mathrm{RSH(v)} + 2\,\mathrm{NaOH(aq)} \rightarrow 2\,\mathrm{NaSR(aq)} + 2\,\mathrm{H_2O(l)} \qquad (1)$$

The rich caustic stream is sent to a regenerator where the NaSR is then oxidized with a slight excess of air to a disulfide:

$$4\,\mathrm{NaSR(aq)} + \mathrm{O_2(aq)} + 2\,\mathrm{H_2O} \rightarrow 2\,\mathrm{RSSR(aq)} + 4\,\mathrm{NaOH(aq)} \qquad (2)$$

The disulfides (RSSR) are finally separated and sent to a hydrotreater for removal as H_2S.

The remaining mercaptans are at trace levels. These processes do not significantly remove COS.

COS Removal by Solvent or Hydrotreating

Usually, COS is present in fuel gas at low enough levels that there is no issue after H_2S and mercaptans are removed, but if there is still too much sulfur in the fuel gas, then selective solvents, absorbents, or direct hydrotreating can be used.

Some solvents that remove H_2S also remove COS. Most notable among these are physical solvents like Sulfinol. MEA, DEA, and DGA also remove some COS and other sulfides, but these solutions are degraded by the COS. A Sulfinol system, as an example, uses a concentrated mixed solvent of diisopropanolamine (DIPA) or MDEA, sulfolane (tetrahydrothiophene dioxide), and water in a scrubber/regenerator arrangement like an amine absorption system.

There are a number of direct absorbents available for COS removal. Processes using these materials come in regenerable and non-regenerable flowsheets. In some processes, all the sulfur is actually hydrotreated first to H_2S and then absorbed. Processes are offered by several vendors, including Johnson Matthey, Sud-Chemie, BASF, UOP, Alcoa, and others.

Finally, direct hydrotreating of the fuel gas followed by amine absorption is an option. In the hydrotreating step, all sulfur is converted to H_2S before absorption – similar to some of the solid sorbent options.

Fuel Oil Sulfur Control

When fuel oil is burned, the sulfur in the oil will be converted to SOx. Control of SOx emissions from fuel oil combustion can be analogous to controlling SOx from fuel gases through removal from the fuel before firing. In this case, the sulfur would have to be removed by severe hydrotreating of the fuel oil to the desired level. The cost of this often means that it is more economical to convert to fuel gas firing instead. Hence, where environmental emissions limits are tight, you will seldom find fuel oil firing of heaters. If you do need to fire low sulfur fuel oil, the handbook chapter entitled "▶ Hydrotreating in Petroleum Processing" discusses sulfur removal.

Another option for fuel oil firing of large furnaces or the FCC stack would be flue gas scrubbing. Added benefits of scrubbers are that they can help control NOx and particulate emissions. A simplified flowsheet for a flue gas scrubbing system is illustrated in Fig. 2.

In the flue gas scrubber, flue gases are contacted with a circulating slurry of limestone, caustic, or soda ash in a tower or venturi scrubbers. There is continuous makeup of chemical into the circulating stream and continuous blowdown of spent chemical. This type of system does create a significant spent slurry stream that requires disposal.

Management of Other SOx Sources

Sulfur pit vents and sulfur storage tank vents will contain SO_2 vapors. Options for managing the emissions from these sources include:

- Combining the vapors with the sulfur plant vent and routing through the stack incinerator, if the emissions limits allow.
- Routing to the front-end reaction furnace with the process air.
- Routing to a sodium bicarbonate scrubber.
- Routing to the tail gas unit ahead of the hydrogenation reactor.

Since the pit vapors will also contain H_2S, sulfur vapor, and other compounds, those materials will influence the choice.

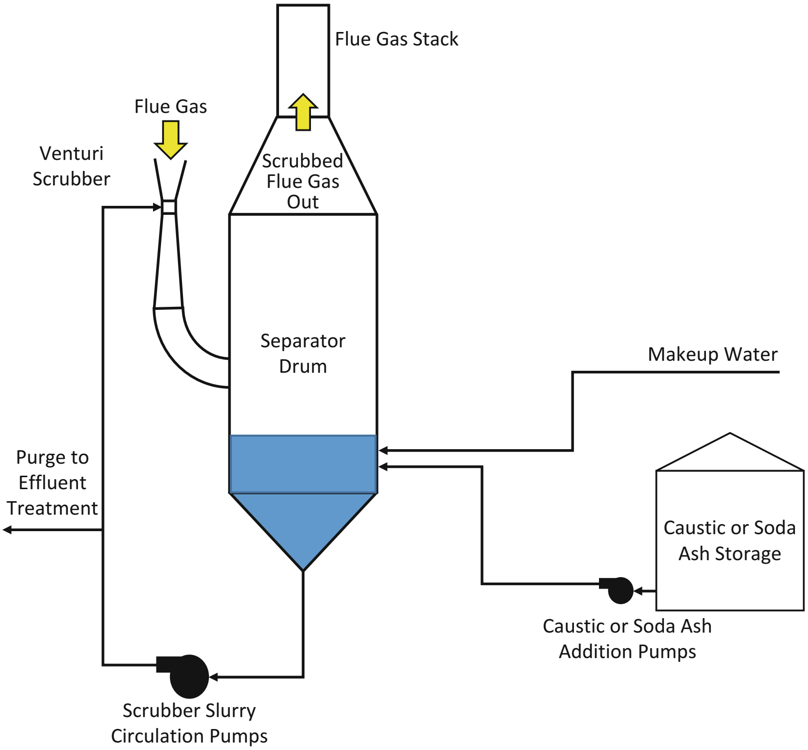


Fig. 2 A flue gas SOx scrubbing system

There are few processes that use SO_2 deliberately, so we will not address those here other than to note that fugitive SO_2 from those processes would be managed by use of proper design and operating practices to eliminate fugitives.

Iron sulfide is found throughout refineries as a product of corrosion. The FeS is normally pyrophoric, that is, it will spontaneously burn when it is dried out and exposed to air. The combustion products will include SO_2. The amount of SO_2 generated can be impressive. If the iron sulfide is in tank or other sludges, these materials can be deliberately oxidized by treating them with peroxide or another oxidizer that will make them into stable sulfates for disposal. Other solids and semisolids that can generate SO_2 if they begin burning can be kept water-wet to prevent the initiation of combustion until they can be properly disposed of.

Hydrogen Sulfide (H_2S)

The most pervasive sulfur form in a refinery after processing is normally hydrogen sulfide. Primary emissions of hydrogen sulfide are controlled by recovery of the H_2S and routing it to a sulfur recovery unit or sulfur plant. We will discuss the sulfur plant in a moment.

Because H_2S is almost everywhere in a plant, it can be released from multiple locations, among these are:

- Sewer vents
- Tank vapors and tank seals, especially on sour water tanks
- Process releases during venting or sampling
- Leaks from packings, flanges, and other pipe elements
- Compressor and pump seals
- Maintenance activities, such as blinding

Control methods for H_2S from sewer vents are discussed in the topic entitled "▶ Utilities in Petroleum Processing." If H_2S is an issue in these vents, the vapors can be routed through a canister on their way to the vent location.

For tank vapors, there are a couple of options, depending on the type of tank:

- Cone roof tanks – these can be blanketed and the blanket gas recovered and or incinerated. Some tanks have internal floating roofs, and then the floating roof options apply.
- Floating roof tanks – these use double seals to minimize fugitive emissions. In sour water tanks, the annulus can be filled with diesel or kerosene to further suppress H_2S fugitive emissions.
- Generally, it is best not to put an H_2S sour stream into an open, unblanketed, or single seal tank.

Managing process releases is primarily application of good operating practices, i.e., never open an H_2S sour line to atmosphere if there is any other choice. Always route the sour fluids to flare, sour water, a flash tank, or another enclosed system. It is safer to burn H_2S to SO_2 before emission than to let the H_2S get out.

When sampling a sour stream, in addition to personnel protection, including fresh air breathing apparatus, the venting should be minimized. If a sample requires purging for a period, design the sample purge as a closed-loop system with the sample pulled from the closed fast loop, so minimal material is vented.

Leaks from piping, valves, fitting, flanges, and other joints are managed by attention to proper fit-up and leak testing before use. It is a good practice to investigate any little whiff of H_2S that is found and eliminate the leak at the source. Control valves are often a problem. Special packing designs are available to minimize these leak points combined with routine "sniffing" of the potential leak points with a detector system (not your nose!).

Options for compressor and pump seals to prevent loss of sour process vapors continue to develop. Some of the options today are:

- Double mechanical seals, including barrier fluids
- Sealless pumps
- Purged recip compressor packing with nitrogen barrier
- Closed/controlled recip compressor distance pieces

Eventually you have to open up piping and equipment for maintenance. Many maintenance activities present opportunities for H_2S releases. Of particular concern are those activities that could expose someone to H_2S, such as initially setting isolation blinds. Every effort is usually made to eliminate all H_2S from systems, but it can still find its way to unexpected locations from which it can be released to the atmosphere. Good shutdown and maintenance practices should minimize H_2S fugitive emissions.

So this brings us to our primary tool in reducing H_2S emissions: the sulfur recovery plant.

Claus Process

The primary process used today for recovering sulfur is the Claus process.

Claus process chemistry depends on the overall Claus reaction, which makes elemental sulfur from H_2S:

$$10\,H_2S + 5\,O_2 \rightarrow 2\,H_2S + SO_2 + 7/2S_2 + 8\,H_2O \tag{3}$$

The process is diagrammed in Fig. 3.

Conceptually, the reaction is carried out in several steps:

1. Partial combustion of the H_2S to produce a 2:1 molar ratio of H_2S to SO_2. This reaction is highly exothermic. It is conducted in a high temperature, low-pressure (~21 psig/1.5 barg) reaction furnace with a stoichiometric amount of air:

$$\begin{gathered} 6\,H_2S(g) + 3\,O_2(g) \rightarrow 2\,SO_2(g) + 2\,H_2O(g) + 4\,H_2S(g) \\ (\Delta H = -4147\text{kJ/mol}) \end{gathered} \tag{4}$$

2. The H_2S and SO_2 now react to form sulfur via the Claus reaction. By the end of the reaction furnace, about two-thirds of the original H_2S has been converted to sulfur. The temperature is ~1,830 °F (~1,000 °C) at the reaction furnace outlet:

$$\begin{gathered} 2\,H_2S(g) + SO_2(g) \rightarrow 3\,S(g) + 2\,H_2O(g) \\ (\Delta H = -1166\text{kJ/mol}) \end{gathered} \tag{5}$$

3. The reaction furnace fluids are cooled in a waste heat boiler and steam generator to condense the sulfur formed. The sulfur is removed from the steam generator as liquid through a steam-jacketed seal leg or sulfur trap.
4. The remaining gases are reheated by a high pressure, superheated steam exchanger or an in-line fired reheater and then pass through a catalyst bed that is primarily alumina. The pressure is still low and the temperature is ~580 °F (~305 °C). The alumina catalyzes the Claus reaction, converting about two-thirds of the remaining H_2S/SO_2 to sulfur.
5. The reactor effluent is again cooled. The sulfur is condensed and removed. Overall, about 89 % of the original H_2S has been recovered as liquid sulfur.

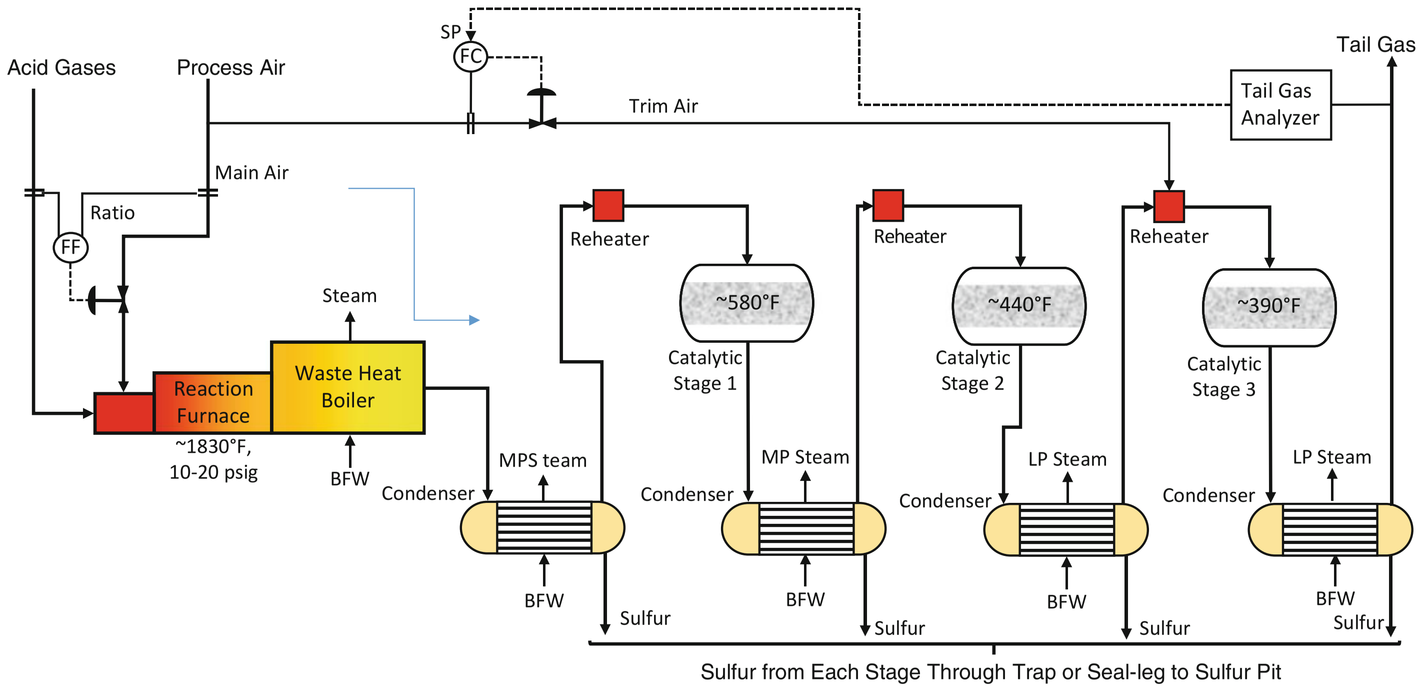


Fig. 3 A three-stage Claus plant flowsheet

6. Steps 4 and 5 are usually repeated twice more, at progressively lower temperatures – 437 & 392 °F (225 & 200 °C). The overall recovery at the end of this "3-stage Claus" configuration would be about 98–99 %. The sulfur condenser for each subsequent stage operates at slightly lower temperatures, but still in a range to keep sulfur molten.
7. The condensed, molten sulfur from the Claus stages is collected, usually in an enclosed sulfur pit, and maintained at about 285 °F (140 °C) using steam coils. The vapor space of the pit may be vented at a high point through a steam-jacketed vent or it may be swept by air or inert gas. Disposal options were discussed under SO_2 emissions. If a pit is allowed to accumulate gases, it can catch fire and must be extinguished with snuffing steam.
8. All piping along the Claus process path is maintained at about 285 °F (140 °C) – not much hotter or colder – to keep sulfur from setting up.

More than three Claus catalytic stages are of marginal value, although some plants use four stages. Usually, if recovery has to be higher, the process moves into a tail gas unit, which we will cover in the next section.

Ammonia-Burning Claus Plants

Claus plants have one other use in a refinery. The sour water collected from all the refinery units is normally steam stripped free of H_2S and ammonia in the sour water strippers (SWS). This process is detailed in section "Water and Aqueous Effluents." For the moment, it is important to know that the strippers produce a stream containing very high concentrations of ammonia and H_2S, along with water vapor, at about 170 °F and at a pressure high enough to go to the Claus furnace, maybe 30 psig (~2 barg).

The SWS gas can be introduced into the reaction furnace of the Claus unit. This is normally done by staging the injection of the SWS gas with the H_2S from the amine regenerators. The design of these systems is proprietary, but you end up with an ammonia-burning Claus plant that can deal with the ammonia as well as the sulfur.

The ammonia is destroyed in the reaction furnace. The required temperature is 2,250 °F (1,230 °C). The resulting ammonia remaining will be less than 30 ppm, which will prevent downstream deposition of ammonium salts in the cooler catalyst beds:

$$2\,NH_3(g) + 3/2O_2(g) \rightarrow N_2(g) + 3\,H_2O(g)(\text{endothermic}) \quad (6)$$

Monitoring the Claus Process

Now, what do you have to watch out for in a Claus plant?

- The feed streams to a Claus plant are extremely toxic and would be fatal with just one whiff. The acid gas from the amine regenerators will be around 85 % H_2S. The SWS gas has both H_2S and ammonia in high concentration. Personnel safety and leaks are always concerns. Generally, sulfur plants actually have the least odor in the area because the operators understand the risks and remain diligent.

- To optimize a Claus plant, control of the H_2S/SO_2 ratio is absolutely critical. There are H_2S/SO_2 analyzers available. Many units analyze the tail gas leaving the Claus unit (or in the tail gas unit) and use that result to fine-tune the air/feed ratio.
- The reaction furnace must be kept in the correct temperature range for both the Claus reaction and ammonia burning. If it is too low, conversion will be inadequate and catalyst beds and exchangers will plug. If the furnace is too hot, there will be refractory or waste heat boiler damage.
- Claus plant recoveries are affected by atmospheric pressure. Plants at high elevations will not recover quite as much sulfur as those at lower elevations because the sulfur vapor pressure has an impact on the performance of the condensers.
- Claus plants have limited turndown capability. Some plants have supplementary natural gas firing for startup or "hot-standby," but this is hard to control and generates a lot of water. There is a high probability of an air/fuel ratio error that will plug the catalyst beds with soot.
- Air/feed ratio is critical. It must be kept exactly at stoichiometric for the Claus reaction. Slight differences often mean plugged beds or equipment damage.
- Any significant amount of hydrocarbon in the feed is usually a major problem in a Claus plant. The hydrocarbons will consume a large amount of air and rob the H_2S and NH_3 of their combustion air. The air systems on Claus plants normally cannot deliver enough air to support combustion of very much hydrocarbon, so the hydrocarbons will form soot instead and plug the catalyst beds.
- So, from a monitoring standpoint:
  - Track feed rates, compositions, and conditions.
  - Calculate recovery periodically.
  - Trend the air/feed ratio.
  - Track the residual ppm sulfur in the tail gas.
  - Watch your steam generation systems carefully.
  - Watch the reaction furnace temperatures and firing pattern – keep it as close to optimum as possible.
  - Ensure the catalytic stage temperatures are in the best ranges.

Claus Tail Gas Treating Processes

The Claus tail gas after processing can often be sent to an incinerator and emitted to the atmosphere in many locations. After 3-Claus catalytic stages, the recovery would be close to 99 % of the sulfur. The balance is burned to SO_2 before discharge.

In many countries and locales, however, 99 % recovery of sulfur is still insufficient. Recovery needs to be at least 99.9 % or less than 10 vppm total sulfur compounds in the stack. The need for recovering more of the sulfur has resulted in the creation of tail gas treating technologies.

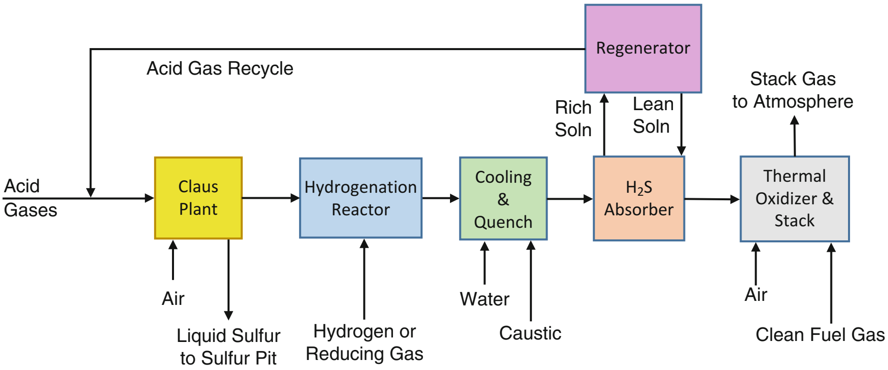


Fig. 4 Typical amine-based Claus tail gas process block flowsheet

Two approaches have been commonly taken:

- Hydrogenation of all sulfur compounds to H_2S and removal by an alkaline solution – the most common approach
- Combustion of all sulfur compounds to SO_2 and removal by an alkaline solution

A typical block flow for the most common hydrogenation + absorption approach using an amine solvent is Fig. 4. Various flavors of this process are offered on a proprietary basis by several licensors.

The gas leaving the Claus plant has a 2:1 molar ratio of H_2S:SO_2 with a few traces of other sulfur species and elemental sulfur vapor. The solvent system is intended to work on H_2S, so the first step in the tail gas unit is hydrogenation of all sulfur compounds to H_2S. The hydrogen for this step can be supplied by an external hydrogen source (hydrogen plant) or by an in-line reducing gas generator burning sub-stoichiometrically.

The tail gas is heated to about 570 °F (300 °C) and enters the hydrogenation reactor. The reactor contains a cobalt-molybdenum catalyst which promotes the reduction of all oxidized sulfur compounds to H_2S. The actual temperature in the catalyst bed can be different, depending on the catalyst choice and catalyst age. The primary reaction is

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \qquad (7)$$

The hydrogenation reactor effluent is cooled in an exchanger followed by a quench tower. In some processes, the quench tower has a caustic scrubbing section to absorb any trace SO_2 that remains, since this can degrade the absorber solution. The gas leaving the quench and cooling system will be around 100–130 °F (~80–90 °C).

The cool gases enter a trayed or packed absorber where the H_2S is scrubbed out of the gases using a lean solution. Absorber solutions that have been used include the same amines used for fuel gas scrubbing (MEA, DEA, MDEA, UCARSOL, etc.) or chemical solutions like Stretford (vanadium).

The clean absorber gas can have less than 10 ppm total sulfur compounds remaining. It is sent to a final incinerator to convert all the H_2S to SO_2 for a safer emission at the final stack. Over 99.9 % of the original sulfur is now removed.

The rich absorber solution is sent to a regenerator system. For amines and most other absorbents, the rich solution is simply steam stripped of the H_2S it absorbed, like in any amine absorber system. The H_2S released is routed back to the front end of the Claus unit to join the incoming acid gas feed.

In the rare case of a Stretford tail gas plant, the vanadium in the solution has been reduced by absorbing H_2S. It is oxidized back to its higher oxidation state using air in a large, stirred, multistage oxidizer tank. The absorbed H_2S is converted to a sulfur froth at the same time, which is skimmed off the top of the oxidizer tank.

Alternative Flowsheets

As noted above, another approach to tail gas cleanup is complete oxidation of the sulfur compounds remaining to SO_2 and subsequent absorption in caustic solution and oxidation to sulfate. These processes are also offered by licensors on a proprietary basis. The final sulfur removal in this case would be in the form of a sodium sulfate solution, which is relatively innocuous.

Tail Gas Plant Monitoring and Operation

Monitoring and operation of the tail gas system would commonly include:

- Analyzing (normally continuously) and trending the stack gas sulfur content. Problems would be immediately investigated.
- Absorber solution chemistry analysis and trending, including lean and rich solution loading, alkalinity and pH (in some cases), and the accumulation of degradation salt products.
- Reclamation or salt removal from the absorber solution when needed. There are firms and processes available who perform this service.
- Chemistry within the quench tower circulating solution – pH, alkalinity, available caustic.

Organic Sulfur Compounds

There are a number of other organic sulfur compounds handled in a petroleum processing facility. These include the mercaptans in fuel gas along with chemicals used to start up hydroprocessing and catalytic reforming units. The former have been covered adequately already. We will comment here about the sulfur chemicals used in processes.

The common sulfur chemicals found in refining processes include:

- Dimethyl disulfide (DMDS) – hydroprocessing activation, reformer startup
- Di-tert nonyl Polysulfide (DNPS) – hydroprocessing activation
- Di-tert butyl Polysulfide (TBPS) – hydroprocessing activation

These chemicals tend to be respiratory irritants in air and are skin sensitizers, but their use is limited to local areas of the refinery. From experience, note that DMDS is a very good solvent for shoes! Management is normally accomplished by ensuring no leaks occur and neutralizing any spills immediately. A 5 % bleach solution is adequate to control moderate spills of these very stinky chemicals.

In all, the potential organic sulfur fugitives and emissions, diligence in handling and addressing leaks immediately will render them non-problems.

Nitrogen Oxides (NOx, NO_2)

NOx emissions from a petroleum processing facility almost exclusively come from combustion sources, so control is focused on those sources. There are four areas that are commonly addressed:

- Elimination of nitrogen compounds, like tramp amines and ammonia, from fuel gas
- Burner design to lower NOx generation in the furnaces
- Control of excess air in the furnaces
- Selective catalytic and non-catalytic reduction of NOx that is generated (SCR and SNCR, respectively)

Fuel Gas Tramp Nitrogen Compounds

Fuel gas will have traces of amine compounds that are carried over from the amine scrubbers along with ammonia that may result from amine degradation or other sources. If these tramp nitrogen compounds reach the burners, the nitrogen will be at least partially converted to NOx.

In addition, the wet amines in the fuel gas headers promote corrosion and formation of salts, which plug burner tips and orifices. The plugged tips result in undesirable flame patterns that co-opt the low-NOx characteristics of the burners.

Control of the tramp nitrogen compounds is addressed by:

- Ensuring good knockout of amines at the scrubbers and in the fuel gas mix drum to keep the fuel gas header dry (See the utilities chapter of this handbook).
- Avoiding foaming or overloading of the amine scrubbers
- Good local knockout and other measures to keep foulants from reaching the burners within a process unit as described in the chapter entitled "▶ Utilities in Petroleum Processing"
- Attention to amine degradation and addressing accumulations of degradation products as described in the chapter "▶ Refinery Gas Treating Processes" of this handbook.
- Cleaning burner tips when fouled

The best strategy is to keep the tramp nitrogen compounds and the resulting foulants from reaching the burners.

Table 3 Impact of burner modifications on NOx production (reference: Baukal 2008)

Modification type	Approx. NOx, ppm at 3 % excess air	Est NOx emission, lb/MMBtu fired
Conventional burner	120	0.14
Staged air	70	0.08
Staged fuel	40	0.05
Internal flue gas recirculation	15	0.02
Ultra-lean premix	10	0.01

Burner Design

Emphasis on reducing NOx emission over the past several years has resulted in tremendous advancements in understanding combustion and how NOx is made within the burners of a furnace. This understanding has led to new, cleaner burner designs – primarily for gas burners. The details of the resulting burner designs are proprietary, but the general understanding has become well known.

Some key factors affecting NOx generation in a burner include:

- NOx production increases exponentially with combustion temperature.
- NOx is increased by high excess air up to a point.
- Air preheat increases NOx production.

Burner manufacturers have developed several approaches to address these issues, resulting in low-NOx and ultra-low-NOx burner designs. Burner features to reduce NOx include:

- Staging the air addition so that the initial fuel burn is in a rich environment, with the rest of the air added later in the burner.
- Staging the fuel to burn lean initially and then adding the balance of the fuel later in the burner.
- Flue gas recirculation to moderate temperatures. This can be done internal or external to the burner.
- Water or steam injection to reduce flame temperatures.
- Ultra-lean premix of fuel and air ahead of the burner.

The value of these burner modifications is seen in the NOx reduction at 3 % excess air in Table 3 with data from a John Zink paper.

Controlling Excess Air in the Furnace

Excess air has a significant impact on NOx emissions. If we look at the excess air in a furnace, the NOx emissions increase roughly linearly up to the stoichiometric air/fuel ratio – i.e., while the combustion is lean. Above this, the NOx generation continues to increase until the amount of air present cools the flame enough to reduce the NOx. This typically would occur with, perhaps, 25 % excess air (or ~5 % excess O_2). At large amounts of excess air, the NOx production drops off, but so does the furnace efficiency.

NOx control from limiting excess air must be balanced with CO emissions control, which is favored by higher excess air values. Usually the compromise means that the heaters run about 2–3 % excess oxygen (10–15 % excess air).

Selective Catalytic and Non-catalytic NOx Reduction

Ironically, the introduction of ammonia (or another easily reacted nitrogen compound like urea) into the furnace at just the right location in just the right way reduces the amount of NOx emitted. The equation that this approach promotes overall is typically

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2O \tag{8}$$

In the non-catalytic application, ammonia (anhydrous or aqueous) is injected into flue gas at high temperature. The injection occurs through a grid in the flue gas that distributes the ammonia evenly into the large flue duct. Turbulent mixing of the ammonia with the flue gas creates the conditions for the reduction reactions. Temperature for this process is in the range 1,400–2,000 °F (760–1,090 °C). This is one of the approaches that has been used for boiler and FCC NOx control. This approach can generally reduce NOx by about 40 % from an uncontrolled level. Stack NOx, relative to the above table, would be about 30–80 ppm (0.033–0.085 lb NOx/MMBtu fired).

When the emissions requirements are very low (such as those for hydrogen plants, large boilers, crude and vacuum heaters, cogeneration units, and some FCCs), selective catalytic reduction is used. In an SCR system, vaporized ammonia or urea mixed with air is injected into a grid similar to SNCR, but the injection location is selected to be within a tight temperature range. There is a short turbulent mixing zone followed by a low-pressure drop, modular grid, or baskets containing NOx reduction catalyst. This system can result in 90–97 % reduction of NO_X from the uncontrolled level. Stack NOx would be down to the 4–10 ppm range (0.006–0.015 lb/MMBtu fired).

SCR catalysts are generally available in base metal and noble metal versions. There are also zeolite catalysts for high temperatures. The base metal catalysts use a ceramic substrate, like titania with vanadium, molybdenum, or tungsten oxides as the active metal. Noble metal catalysts typically use Pt or Pd. The operating temperature for base metal catalysts is typically around 600–750 °F (315–400 °C). Precious metal catalysts are effective at lower temperatures, say <570 F (<300 °C). Zeolites work at higher temperatures, up to 1,160 °F (627 °C).

The base metal catalysts tend to be the most common in refinery applications since they are cheaper than the alternatives and fit the normal temperature windows available in flue gas ducts.

Most SCR systems cannot be started until the flue gas reaches the required temperature range. This protects against accumulation of ammonium nitrate salts

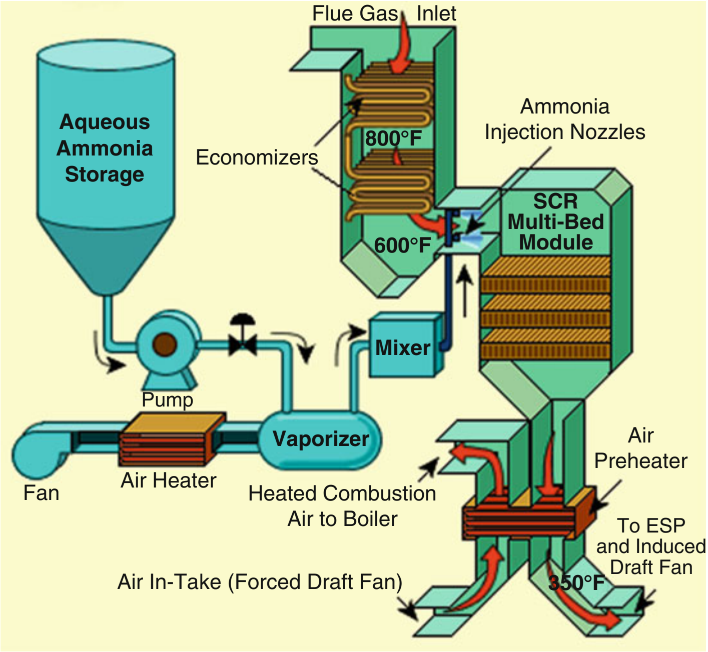


Fig. 5 A selective catalytic reduction system example (reference: United States Department of Energy)

on the exchangers downstream of the SCR. Ammonium nitrate accumulation creates the possibility of an explosion in the duct or, at the least, a significant loss of heat transfer in the downstream convection coils.

A typical SCR installation is shown in Fig. 5.

In operation of an SCR or SNCR system, the primary area of concern is the ammonia vaporizer and injection skid. If the skid fails, then NOx reduction stops, usually resulting in an immediate permit violation. The process flow in the vaporizer is simple. Atmospheric air from a fan is preheated to about 1,000 °F (537 °C) in an electric heater. Ammonia is sprayed into the hot air stream. A packed vaporizer may be used to ensure complete vaporization of the ammonia. The air/ammonia ratio in the vaporizer is carefully controlled to stay outside the explosive limits for ammonia in air. The air/ammonia mixture is sent to the ammonia injection grid. The grid may have several local meters and adjusting valves available to ensure even distribution to the grid.

The vaporizer systems have a few areas of concern:

- You are essentially mixing very hot air with a fuel in an enclosed system. An explosion is possible in the vaporizer if the air/ammonia ratio becomes explosive. These systems usually monitor the ratio and shut down if the ratio approaches the explosive range.

- Anhydrous ammonia is not a particular problem, but aqueous ammonia is corrosive to carbon steel and tends to plug the vaporizer and other systems. Aqueous ammonia must be filtered at a submicron level ahead of any metering or vaporization. All piping and tubing after filtration and before vaporization must be stainless steel.
- Packed vaporizers tend to plug. Spray-type vaporizers are more robust.
- It is advisable to have 100 % redundancy of the vaporizers and the air fans to allow for maintenance. A temporary system can also be built using anhydrous ammonia bottles and plant air, if necessary for short outages.
- The ammonia rates that must be metered are usually very tiny. The flow meters tend to plug with debris. Consider this in selection of the meters. Ultrasonic and mass meters tend to be more successful because they do not have small passages. Turbines and orifices are not usually good in this service.

NOx Emissions Monitoring and Operations

Many facilities have tight NOx emissions requirements imposed on them by permit. These require monitoring of the factors relevant to NOx. Among the more common monitoring and operating practices are:

- Continuous emissions monitoring (CEM) of the stack may be required, especially for large sources like hydrogen plants or boilers. The CEM information on NOx and CO should be watched and trended. Action should be taken on undesirable tends. Remember that you are balancing NOx against CO.
- Burner flame patterns should be examined at least every shift on all burners. Patterns that show stray flames, plugged tips, impingement, and other problems should be corrected immediately. If there is a pattern of tip fouling in a furnace, the fuel supply systems need to be reviewed for possible foulants and poor knockout facilities.
- Furnace excess oxygen needs to be kept within the correct range. Running high excess oxygen will increase NOx production and lower furnace efficiency.
- Ensure the ammonia vaporizer skid is working properly if you have an SCR or SNCR. Watch the blower/fan discharge flow and the preheated air temperature. Watch the ammonia/air ratio. Periodically check the flows to the injection grid.
- Trend the ammonia rate normalized for firing rate – this will increase as SCR catalyst ages. Your permit will often have a maximum ppm ammonia in the flue gas. When this is approached, you need to plan to replace the SCR catalyst. The usual limit is around 10 vppm. Test the flue gas periodically for the residual ammonia concentration.
- Watch your flue gas temperatures to ensure that fouling does not force the SCR into a temperature range outside optimum.

So, in short:

1. Keep your fuel gas clean.
2. Operate your burners correctly.

3. Keep your burners clean.
4. Keep your excess oxygen under control.
5. Make sure your SCR vaporizer is working.
6. Make sure your SCR catalyst is working properly at the right temperature.

Carbon Oxides (CO, CO_2)

Emissions of carbon monoxide have been regulated for many years. The emissions of carbon dioxide are only now beginning to come under regulation as part of the concerns over global warming. In this section, we will explore management of emissions for both of these gases.

Carbon Monoxide

Carbon monoxide is formed primarily by incomplete combustion of hydrocarbon fuels. In a petroleum processing facility, CO will be emitted from fired heat in several applications.

- Process heaters
- FCC regenerator
- Boilers
- Cogeneration units
- Incinerators and combustors
- Flares

The objective is complete combustion of fuel in the fired services. This will ensure efficient use of fuel while keeping CO emissions low. Some heater permits will also have CO emissions limits, including requirements for a CEM.

The flue gas from a combustion source can be analyzed using an Orsat apparatus. The Orsat provides readings for oxygen, CO, and CO_2 in a flue gas. It has largely been replaced by simpler, online, and portable analytical instruments.

Control of CO emissions parallels, and sometimes conflicts, with NOx control in these heaters. The primary control methods for CO are:

- Maintaining correct excess oxygen levels at the burners.
  - Avoid tramp air entry.
  - Keep your registers and draft under control.
  - Keep your oxygen analyzer working.
- Keeping burners clean
  - Clean up your fuel gas.
  - Clean tips as needed.
- Minimize flaring to reduce CO from the flare
- In FCCs:
  - Ensure good combustion air distribution to the regenerator.
  - If you have a CO boiler, ensure it is working properly.

Carbon Dioxide (CO_2)

In a petroleum processing plant, carbon dioxide is produced from several sources, including:

- Fired heaters, boilers, incinerators, and combustors
- Cogeneration
- Flare
- Hydrogen plant process
- FCC regenerator

Control and minimization of CO_2 emissions from these sources include:

- Fired services:
  - Maintain excess air in the required range (no tramp air).
  - Keep coils and fins in heaters clean (inside and outside).
  - Use air preheat to reduce firing rate (may increase NOx).
  - Do not heat more than necessary (e.g., do not over-treat products).
  - Maximize use of process preheat within control limits.
- Flare:
  - Minimize flaring.
  - Recover make gases for fuel use.
- Hydrogen plants:
  - Minimize excess on-purpose hydrogen production.
  - Minimize hydrogen losses to fuel gas.
  - Recover CO_2 for sale as a product.
- FCC:
  - Ensure good combustion air and catalyst distribution in the regenerator.
  - Maintain correct combustion conditions.
  - Watch heat balance and conversion.

As concerns over greenhouse gases increase, CO_2 is one of the largest concerns worldwide. Facilities are being driven to reduce CO_2 emissions and, in some cases, may also be held responsible for the emissions that result from use of their products. All you can do as a petroleum processor is to minimize your generation of CO_2 through good practices and efficiency. In more extreme cases, you may have to recover CO_2 for disposal or sequestration.

Particulate Matter (PM, PM-10)

Particulates can come from several sources within a refinery. Figure 6 illustrates the size ranges for various types of particulates. Of particular concern when discussing particular matter are particles smaller than 10 μm (PM-10). These particles can be inhaled and stay in the lungs, causing respiratory damage. They are specifically regulated in the United States.

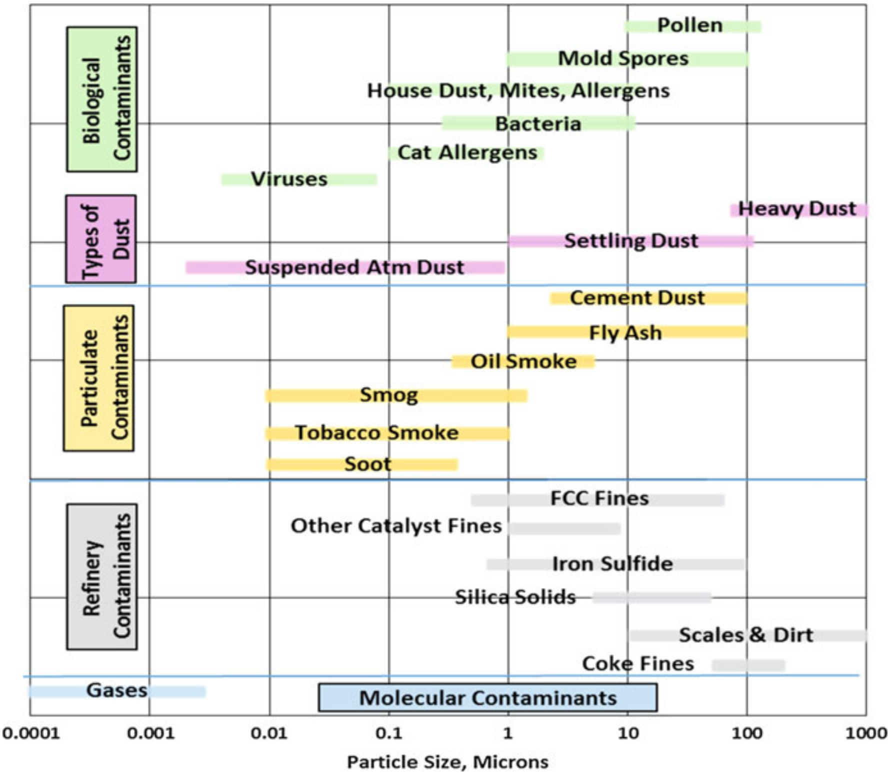


Fig. 6 Typical particulate matter size ranges

Among the more common sources are:

- Incomplete fuel combustion (<10 μm)
- FCC (0.5–80 μm)
- Catalyst and sorbent handling (1–10 μm)
- Construction activities (<10–100 μm)
- Maintenance activities (<10–100 μm)
- Decoking/soot blowing (<10 μm)
- Unpaved roads and operating areas (1–1,000 μm)

We will talk about these sources and some possible particulate control measures.

Incomplete Combustion

In burning various fuels, incomplete combustion will generate soot that can be emitted from the stack. Maintaining normal excess oxygen levels in the fired services ensures levels of soot in the stacks are controlled. In some large stacks, opacity monitoring may be used to ensure minimal PM emissions. Permits sometimes require PM emissions be tested periodically using an apparatus that takes isokinetic samples across the entire stack.

Fluid Catalytic Cracking (FCC)

In a refinery, an FCC is the biggest potential generator of PM emissions. The emission of the particulates can arise from an operating problem or from a breakdown of protection equipment, like the cyclone separators located in the critical areas of the process or the electrostatic precipitator.

There is always some carryover of small particulates from the regenerator. In most modern units, these catalyst fines are collected by cyclone separators followed by bag houses or electrostatic precipitators. The efficiency of these devices is limited. Some FCCs are driven to wet scrubbing of the FCC flue gas. This can catch the PM as well as SOx and NOx in the flue. The collected fines and solution then become an easier waste disposal issue. Failure of these systems may require shutdown for repair. Regular rapping of an electrostatic precipitator is used to keep it functioning.

A breakdown in the catalyst fines collection systems (like a precipitator ground fault), as well as certain startup and upset conditions (like a reversal), will result in large amounts of PM emitted to the atmosphere. One of the most common problems in fluid bed processes are air surges that cause a disruption of the fluidized bed. In the case of an FCC, this fluidized bed is the catalyst bed being regenerated in the regenerator. This disruption results in loss of the catalyst to the atmosphere from the regenerator exit stack. The incorporation of a CO boiler or an electrostatic precipitator does help minimize this emission, but they can be overwhelmed. Usually air surges are minimized by good flow control systems with some anti-surge system. Control of the startup and upset emissions primarily depends on moving as quickly as possible through the condition. In extreme cases, a unit may be forced to shut down instead of continuing to emit PM.

Catalyst and Sorbent Handling

Many refining catalysts and sorbents used in petroleum processing are solid extrudates, spheres, or pellets. These include hydrotreating, hydrocracking, reforming, isomerization, and Claus alumina catalysts as well as PSA adsorbents. The catalysts themselves are relatively small in size (1/20–1/8 in. nominal diameter) but are large enough not to become fugitive PM emissions.

However, the dust produced by attrition in handling the catalysts is small enough in size to become airborne. This is especially an issue during turnarounds and catalyst changes. Maximum attrition loss for catalysts is normally a specification.

FCC and other types of fluidized catalysts are small by their nature and they are abraded in service to generate dust. They easily can become fugitive PM emissions as the catalyst fines are moved around. This occurs where the fines are collected at the electrostatic precipitator or where fresh or equilibrium catalyst is transferred into the unit.

Catalyst dust may carry additional chemical health hazards, as well as PM-10 hazards. Nickel-containing catalysts are potential carcinogens because of the nickel content. FCC and other zeolite catalysts contain silica.

Control of PM from catalyst and sorbent handling can be accomplished in several ways, depending on the situation:

- Spills of fines or catalyst can be kept wet to suppress dust.
- Wet down and clean up spills immediately.
- Don't allow vehicles to drive over spilled catalyst or sorbent and crush it to powder.
- Many catalysts are handled in an inert or enclosed system using vacuum or pneumatics to move the material. These systems use cyclones and bag filters to prevent atmospheric dust.
- Personnel protection should prevent exposure of employees to the catalyst and sorbent dusts during handling. These measures would include HEPA filters as a minimum up to use of fresh air equipment.

Construction Activities

Most construction activity is going to involve earthmoving. The fugitive dust for moving soil around is sometimes difficult to control. Many construction permits require some sort of dust control.

In a petroleum processing facility, the soil may also be contaminated by chemicals from past activities when people weren't so environmentally conscious. Lead, caustic, acid, and other soil contamination may be encountered as construction activities progress. Often this material has to be completely removed for hazardous waste disposal. This generates even more potential for dust.

In some cases, construction will require removal or revamp of old equipment that may have been painted with lead-based paints or insulated with asbestos. Specific regulations may address the management of these materials. In the United States, they must generally be removed and handled by personnel or companies specifically trained and equipped for the activity. The area is usually tented and personnel wear fresh air equipment. They may need to go through decontamination after working in the area.

Aside from the specific hazardous dusts, keeping disturbed soil damp, including spraying of dust suppressants, is the normal approach to managing the PM fugitive emissions from construction. Common dust suppressants (from the Michigan Department of Natural Resources and Environment guidelines) are:

- Water
- Calcium or magnesium chloride
- Lignosulfonate products
- Emulsified asphalt or resin stabilizers
- Vegetable by-products

Use of dust suppressants is not without other environmental consequences. The impacts on groundwater need to be considered.

Maintenance Activities

The normal activities inherent in maintenance can generate fugitive PM. We have already talked about a few of these: catalyst and sorbent handling, dirt movements, and removal of lead paint or asbestos insulation.

A few other maintenance activities that should be mentioned are:

- Abrasive blasting
- Exchanger and tank cleaning
- Grinding and welding

Abrasive blasting of small parts may be done in a controlled system in the shop. These are not particularly a problem. For larger outdoor areas, PM can usually be controlled by temporarily confining the dust in the blast area using a tent. The grit itself tends to not be entrained in air, but the rust, paint, and other material being blasted off can become airborne. If dust becomes excessive from these operations, some additional thought should be put into how they are being done and how to better contain the dust. A wet spray may be needed.

Like abrasive blasting, exchanger and tank cleaning can generate fugitive PM as deposits, sludges, and other residues are removed and dry. The usual approaches to dust control include keeping the materials wet, cleaning up spills promptly, and not driving through the material and generating dust in the first place.

Grinding and welding can generate some PM. Some of the PM may contain hazardous forms of metals. The small quantity generated is not normally a general environmental problem but may present a personnel hazard in the immediate area. Attention to good industrial hygiene practices in these activities should be adequate to manage fugitive dust.

Decoking and Soot Blowing

These could be classified as maintenance activities, but they are specifically listed here. Decoking is the removal of coke and other deposits on the process (inside) of fired heater tubes. Soot blowing is the removal of carbon or soot deposits on the outside of heater tubes. Both activities can generate fugitive PM, as well as other emissions.

At one time, steam-air decoking was the common approach to the removal of process-side tube deposits. In this approach, steam was run through the tubes at high velocity to spall the solids off the tube walls. The spalled solids were collected in a knockout drum vented to atmosphere. Dust from the drum could escape. After spalling, air was introduced with the steam to burn out remaining deposits, generating more potential for PM emissions.

Today, spalling may be done online with the spalled material retained in the process. This is especially common in cokers where the spalled material is collected along with the coke.

Another approach that has become common in process-side tube cleaning is "pigging" where fairly large balls or other-shaped devices are pushed through the tube to physically abrade the deposits off the tubes. The removed material is then collected in a system that controls the PM emissions.

In soot blowing, the soot collected on the firebox sides of furnace tubes is literally blown off the tubes using air or, more commonly, steam. The soot thus removed leaves the furnace with the flue gas. This soot will also contain heavy metals present in the fuel and deposited on the tubes. Management of PM from soot blowing depends on the removal of the soot from the flue gas. Wet scrubbing, filtration, or other flue gas treatments on a furnace will catch the soot. Since soot is primarily the result of fuel oil burning, firing a furnace on fuel gas and eliminating the fuel oil would also eliminate soot blowing PM emissions. Soot blowing is not allowed in many jurisdictions.

Unpaved Roads and Operating Areas

In many facilities, the roads outside the main operating areas, and many operating areas themselves, are not paved. The exposed soil can become fugitive dust as wind or vehicle traffic picks it up.

Use of dust suppressants (see the list above) and keeping the exposed soil damp can greatly reduce fugitive dusts.

In tank dikes, sleeper ways, and below pipe racks, it is also possible to chip and seal or oil the areas. In the chip-and-seal approach, gravel is laid down in a layer a couple of inches thick and then sprayed with tar or asphalt to seal it. This forms a hard crust over the ground that resists dust generation. Oiling an exposed area just means spraying it with tar or asphalt to seal the ground directly. Local environmental practices for air or groundwater protection may limit the chip-and-seal or oiling options. The seal must be renewed about every 10 years by re-spraying the area with tar.

Of course, exposed areas can always be paved to eliminate PM generation.

Volatile Organic Carbon (VOC)

The major sources of atmospheric pollution by VOC emission in refinery include:

- Relief and vent valves open to atmosphere
- Control valve, flange, seal, and packing leaks
- Storage tanks
- Rail and road tanker filling facilities
- Ship loading and unloading facilities (jetty area)
- Water effluent treatment facilities and sewers

Attention to control of these sources continues to push toward more monitoring, more controls, and better operating practices. The following discussion will address some of the key VOC emissions issues.

Relief and Vent Valves

Relief and vent valves normally discharge to a closed relief header which is routed to flare system. However, in some cases, because of the location of the relief and/or vent valve and the quantity of the discharge material, the valve(s) are open to atmosphere. A typical example is crude distillation unit relief. These are located at the top of the distillation towers, about 200 ft. (60+ m) above grade. Steam injection facilities may be installed at the valve discharge to facilitate atomization and dispersion. Nevertheless when these valves do open, there will be some considerable VOC emission to atmosphere. Upset events that would cause these valves to discharge are extremely rare and do not usually warrant the extensive costs of increased flare header and flare design that would be necessary to cater for these valve discharges. Still, many refineries are making the necessary changes to include these valves in the flare systems.

A multiple fatality explosion event at Texas City in the United States has prompted several refiners to review the use of unfired vent stacks and US regulators to more tightly review these VOC sources. Most refiners are eliminating any unfired vents. The trend is to route all hydrocarbon or VOC vents to the relief and recovery system or flare.

Control Valve, Flange, Seal, and Packing Leaks

Leaks from control (and other valves), pump seals, packing, and flanged joints are related entirely to the refinery's maintenance policy and program.

In the United States and other locations, there are required leak monitoring programs that involved "sniffing" all the flanges, packings, seals, and other potential leak points on a regular basis, usually quarterly, with a leak detection instrument. The sniffing may be done using a combustible gas detector or may even use a portable mass spectrometer. Fugitive VOCs identified above specific levels require repair of the identified leak point within specific, defined time frames and proof that the repair was made. The repair may be as simple as tightening a packing follower or may involve clamping and injecting an exchanger channel-to-shell flange.

Seal leaks of VOCs from rotating equipment are often controlled through the use of double or tandem seals, often with barrier fluids, with appropriate maintenance programs for these seal systems. In some parts of the United States, a leak of as little as a drop or less per minute of a VOC from a rotating equipment seal may require repair actions that may include shutdown of the equipment.

Storage Tank Emissions

Perhaps the biggest sources of VOCs from a refinery and its operation are the storage tanks. Emission occurs during the tank filling, particularly in the case of fixed roof tanks and LPG bullets and spheres, or by evaporation of tank contents.

The emissions from floating roof tanks are generally low, and the function of a properly installed roof and seals should minimize the emission from these sources. Highly volatile liquids should not normally be contained in floating roof tanks, but there are occasions when high vapor pressure material may find its way into a tank. These upsets need to be dealt with promptly when they occur to avoid damage to the roof as well as the VOC emission. The seals need to be inspected and repaired regularly. These emissions controls are discussed further in the off-sites section of this handbook: "▶ Off-Site Facilities for Petroleum Processing."

Many of today's refineries have installed closed inert gas blanketing for fixed roof tanks containing high vapor pressure hydrocarbons using nitrogen or natural gas. Blanketing is sometimes required in intermediate tanks whose contents are feed to processes which need to avoid oxygen contamination or contact of the feed. Extension of this inert gas to all fixed roof tanks as a blanket can prevent the emission of VOC during their movements. These systems are also discussed in the off-sites section of this handbook.

Tanks containing low vapor pressure materials (say <2–3 psi RVP) are not generally a VOC emission problem, so do not usually have inert gas blankets.

The storage of LPG also has potential for emitting VOCs to the atmosphere. One method used to combat this is to float the make/break valves of the spheres and bullets on the refinery fuel gas main header.

In highly regulated areas, the VOC controls may extend to smaller storage tanks or sumps. Often VOCs from the small tanks or sumps can be managed by connection to carbon canisters through a flame arrestor.

Rail and Road Tanker Filling Facilities

Spills from truck and railcar loading facilities have always been a problem. Most spills occur when filling the vessels. Most loading facilities today have automatic shutoff on the loading arm nozzles in the event of failure, very similar to those commonly used in public filling stations. These use a level-sensitive device to close the filling valve at a prescribed filling level in the tank or on excessive flow rate. The other source of VOC emission is a poorly designed slops/recovered oil system that allows the draining of bottoms from road tankers and railcars. Such a system should allow for steam-out facilities on vessels carrying heavy petroleum cuts. Vents on this system should be routed to the flare header.

Ship Loading and Unloading Facilities (Jetty Area)

The jetty along with ship loading and unloading is also a potential source of VOC emissions. Again, as in the case of the tank farm and product loading facilities, the most vulnerable product in this respect is the handling of the light hydrocarbon streams. As the ships or barges are filled, the vented vapors will contain VOCs. The vapors should be routed to an incineration system through a flame arrestor to ensure the displaced vapors are combusted to eliminate VOCs.

In the loading of LPG, a flash recycle system has been found to be effective. In this system, the LPG flashes as it first enters the ship's empty tank at close to atmospheric pressure and temperature. This flashed vapor is routed, under pressure control, to a compressor and cooler system, where it is liquefied and returned to the LPG feed stream. The system continues to operate throughout the loading activity, acting as the loading relief system.

Water Effluent Treatment Facilities and Sewers

The sewer and wastewaters collected from a petroleum processing facility will contain hydrocarbons, some of which will flash in the system to generate VOCs.

This is especially notable if any light ends or naphtha is drained or spills into the sewer.

The methods for control of fugitive VOCs from sewer and wastewater treating systems are addressed in detail in the utilities and off-sites discussions of this handbook ("▶ Utilities in Petroleum Processing" and "▶ Off-Site Facilities for Petroleum Processing." The approaches generally involve sealing sewers and sumps with vents through flame arrestors to hydrocarbon collection systems, such as canisters. Oil water basins may be covered by membranes, with VOC vapors collected and recovered. API separators are often covered for vapor collection or may have floating roof covers with skimming and seals similar to a floating roof sour water tank.

A dissolved air floatation unit (or DAF) may be a particularly difficult source of VOC emissions because the process involves deliberately bubbling air through an oily water. Ideally, you want to separate any volatile hydrocarbons from wastewater before it is routed to a DAF.

Aerobic digestion in a trickle bed, activated sludge, or other bio unit has the potential for creating VOC fugitives. Light hydrocarbons should be eliminated from the wastewater before it is routed to a "bug" unit. The bio unit is usually the last processing unit in the water effluent treatment system.

There is further discussion of effluent water treatment later in this chapter.

Ozone

Ozone is not normally directly emitted by the refinery. It is primarily the product of the atmospheric reactions of other air pollutants. NOx catalyzes the formation of ozone in the lower atmosphere through the reaction path:

$$O_2 + \text{UV light}(< 240\,\text{nm}) \longleftrightarrow 2\,O \tag{9}$$

$$O_2 + O + NO_x \longleftrightarrow O_3 + NO_x \tag{10}$$

VOCs can also contribute to ozone generation.

Control of ozone from a refinery generally comes down to control of the compounds that contribute to its formation, which we have already addressed.

One additional, but uncommon, ozone source in a refinery can be disinfection of water using ozone directly. It is a strong disinfectant and can replace chlorine or bleach, but the cost is usually higher to generate ozone and it offers no residual disinfectant action. When used, ozone is generated and used immediately. Fugitive ozone does not survive long in the air, so it is not really an emissions concern, except in the immediate area of use.

Ammonia (NH_3)

Ammonia can usually be emitted as a fugitive gas:

- Where ammonia is handled
- As a residual from NOx reduction equipment

- Through sour water leaks
- From the hydrogen plant degasifier vent

In the air, ammonia is relatively quickly removed by formation of ammonium salts and by rain, with some pH implications.

Ammonia supply systems for SCRs, SNCRs, and other uses in a refinery offer the chance to leakage and emissions of ammonia. Attention to maintenance and operations of these systems will prevent any significant releases. Methods to manage ammonia releases from a storage and distribution system are detailed in the section of this handbook concerning "▶ Utilities in Petroleum Processing."

When used in NOx reduction processes, a slight excess of ammonia is normally added. The residual should normally be less than 10 vppm in the flue gas. Still, 10 ppm in a large flue gas stream can represent a significant amount of ammonia. Control of this ammonia emission centers around control of the NOx removal process so the minimum amount of ammonia is used. Refer to the discussion of NOx reduction above.

Sour water contains ammonia in significant concentrations. The ammonia is tied up as a bisulfide, normally. As a result, the ammonia emitted is usually low. The most significant risk of ammonia emission from sour water would be in storage tanks where good tank sealing practices, as discussed in the chapter on "▶ Off-Site Facilities for Petroleum Processing," would minimize losses to atmosphere. If the ammonia reaches the sulfur recovery plant, it will be destroyed in the Claus reaction furnace or an oxidizer, so it is not emitted.

A hydrogen plant makes ammonia in trace quantities. This is especially true in plants running a low steam/carbon ratio. The ammonia ends up in the shift condensate and is emitted when the condensate is stripped in the degasifier/deaerator. The amount emitted is generally below regulatory interest, but newer plants running very low steam/carbon ratios can make a significant amount of ammonia. In these units, prevention of ammonia emissions entails either sending the degasifier off-gas to the hydrogen plant SMR furnace to be combusted or the degasifier may be pressurized with the off-gas plus steam sent to the SMR process side.

For most petroleum processing facilities, ammonia would not be a major problem emission.

Methanol (CH_3OH)

Methanol often gets lumped with VOC emissions, so most control methods for methanol are similar to those of VOCs.

One exception is in hydrogen plants where methanol can be made in significant quantities in low temperature shift reactors. In these cases, the methanol ends up in the shift condensate, which is routed to the degasifier for reuse. The methods noted above for control of fugitive ammonia from hydrogen plants also effectively capture and destroy methanol to prevent its emission. It is also possible to use special low methanol shift catalysts to reduce the process make of methanol.

As with ammonia, methanol is generally not an emissions problem for most refiners.

Water and Aqueous Effluents

In this section, we will discuss the aqueous or water-based refinery streams and their dispositions. The basic aqueous waste stream origins were highlighted initially in Table 1 for reference. Now we will explore these wastes and their management in greater depth.

The discussion is divided into a description of the pollutants in aqueous wastes, the processes that generate the wastes, and the treatment of the various aqueous waste streams. Recycle opportunities are highlighted where these are feasible as a means of waste reduction.

Pollutants in Aqueous Waste Streams

The potential pollutants in refinery aqueous streams are conveniently listed in greater detail, with some typical rates and pollutants, in Table 4, from a US EPA report.

A number of laws and regulations populate the regulatory landscape controlling the allowable contaminants in water effluents and permit requirements. A sampling of the key, applicable regulations includes:

- US laws and amendments:
  - EPA regulations:
    - Clean Water Act (CWA)
      - Permit requirements, including National Pollutant Discharghe Elimination System (NPDES) permits
      - Storm Water Pollution Prevention Plans (SWPPP)
      - Spill Prevention, Control, and Countermeasures (SPCC) plans
    - Clean Air Act (CAA) and amendments (CAAA, 1990)
      - Title V permitting
      - New Source Performance Standards (NSPS)
      - National Emission Standards for Hazardous Air Pollutants (NESHAP, especially benzene, relates to water)
    - Resource Conservation and Recovery Act (RCRA)
    - Emergency Planning and Community Right-To-Know Act (EPCRA)
      - Notifications of local emergency agencies
      - Release notifications
      - MSDS and inventory reporting requirements
      - Requirement for annual toxic release inventory reporting
    - Safe Drinking Water Act (SDWA)
      - Regulation of drinking water
      - Regulation of underground water injection
  - Numerous state and regional laws and regulations, over and above state regulations

Table 4 Some of the aqueous wastewater streams and the potential pollutants from a refinery (Source: "Leavitt et al. (2004))

Process	Wastewater description (possible pollutants)	Wastewater flow rate (gallon/barrel of crude petroleum)	Percentage of total wastewater flow rate
Distillation	Sour water (hydrogen sulfide, ammonia, suspended solids chlorides, mercaptans, and phenol)	26.0	44 %
Fluid catalytic crackling	Sour water (hydrogen, sulfide, ammonia, suspended solids, oil phenols, and cyanides)	15.0	26 %
Catalytic reforming	Sour water (hydrogen, sulfide, ammonia, suspended solids, mercaptans, oil)[a]	6.0	10 %
Alkylation	Spent potassium hydroxide stream (hydrofluoric acid)	2.6	4 %
Crude desalting	Desalting wastewater (salts, metals, solids, hydrogen sulfide, ammonia, and phenol)	2.1	4 %
Thermal crackling/ visbreaking	Sour water (hydrogen, Sulfide, ammonia, suspended solids, dissolved solids, and phenol)	2.0	3 %
Catalytic hydrocracking	Sour water (hydrogen sulfide, ammonia, solid suspended solids)	2.0	2 %
Coking[b]	Sour water (hydrogen, sulfide, ammonia) and suspended solids	1.0	2 %
Isomerization	Sour water (hydrogen sulfide and ammonia) and caustic, wash water (calcium chloride or other chloride salts)	1.0	2 %
Additive production: ethers, manufacture	Pretreatment wash water (nitrogen contaminants)	<1.0	
Catalytic hydrotreating	Sour water (hydrogen, sulfide, ammonia, suspended solids, and phenol)	1.0	2 %
Chemical treating: sweetening/ Merox process		[c]	
Sulfur removal/ Claus process	Sour water (hydrogen sulfide and ammonia)	<1.0	
Lubricating oil manufacture	Stream stripping wastewater (oil and solvents) and solvent recovery wastewater (oil and propane)	<1.0	
Total		58.7	100 %

US DOE. *Water Use in Industries of the Future: Petroleum Industry*. July 2003

[a] Additional pollutants identified in EPA's *Industry Sector Notebook: Petroleum Refining*, September 1995

[b] Fluid coking produces little or no effluents

[c] Little or no wastewater generated

- Several European Union directives are applicable to wastewater; members of the Union implement these individually. Among the requirements are:
  - Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) – registration and evaluations
  - European Pollutant Release and Transfer Register (E-PRTR) – reporting
  - Industrial Emissions Directive (IED) – reduction requirements
  - Water Framework Directive (WFD) – obligation of member countries to achieve water quality and reduce effluents
  - Groundwater Directive (GWD) – similar to WFD applicable to groundwater
  - Environmental Quality Standards Directive (EQSD) – specific limits for priority substances, obligations to inventory and reduce losses
  - QA/QC Directive – monitoring standards
  - Marine Strategy Framework Directive (MSFD) – similar to WFD for marine environment
- Similar regulatory structures apply throughout most of the world. Some regions are less restrictive.

In general, the regulations target the most undesirable types of pollutants in aqueous waste streams:

- Those that deplete the dissolved oxygen content of the waterways into which they discharge
- Those contaminants that are toxic to almost all forms of life, such as arsenic, cyanide, mercury, selenium, and the like
- Those contaminants that impart undesirable tastes and odors to streams and other waterways into which they discharge

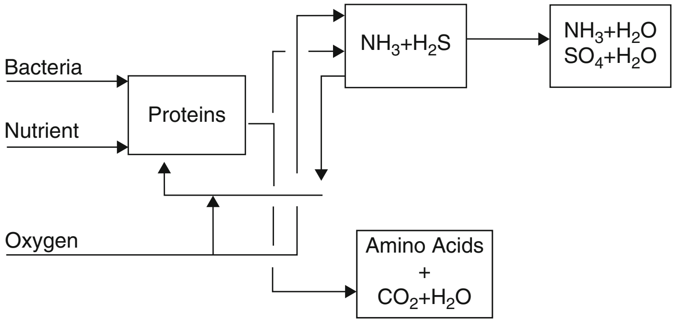
A description and discussion on these contaminants are expressed in the following paragraphs.

Impacts of Contaminants on Oxygen Balance in Natural Waterways

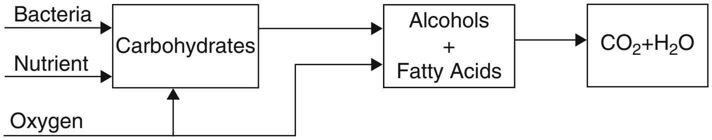
Natural waterways have a complex and delicate oxygen balance. The water contains an amount of dissolved oxygen which has an equilibrium of between 14 ppm in winter and 7 ppm in summer. Aquatic life (fish and tadpoles) continually consumes oxygen from the water, but aquatic plants produce oxygen naturally maintaining the balance required to sustain fish life.

Any oxidizable contaminant introduced into the natural waterways consumes the dissolved oxygen to be oxidized. The dissolved oxygen will be depleted below the saturation point and will be replenished only by re-aeration. The relative rate of replenishment to its saturation level will depend on a time factor related to the stream distance or the stream flow rate.

Oxygen depletion occurs by the introduction of one or more of the following contaminants into the waterway:



Protein Biochemical Oxidation.



Carbohydrate Biochemical Oxidation.

Fig. 7 Typical BOD chemistry

- Natural pollution by surface runoff rainwater, or melting snow, in the form of soluble salts leached from the earth – consider paved and parking areas
- Natural pollution caused by decay of organic plants from swamps or other sources
- Human and animal life excretion – consider sanitary sewer systems
- Chemical pollution from reducing agents in industrial plant wastes. Such as sulfides, nitrites, ferrous salts, etc.
- Biochemical pollution from such industrial wastes as phenols, hydrocarbons, carbohydrates, and the like

The degree of oxygen depletion from the pollution sources described above may be catalogued by the following terms:

BOD – biological oxygen demand
COD – chemical oxygen demand
IOD – immediate oxygen demand

Biological Oxygen Demand (BOD)

Since all natural waterways will contain bacteria and nutrients, almost any waste compound introduced into the waterway will initiate biochemical reactions. These reactions will consume some of the dissolved oxygen in the water. This is illustrated in Fig. 7.

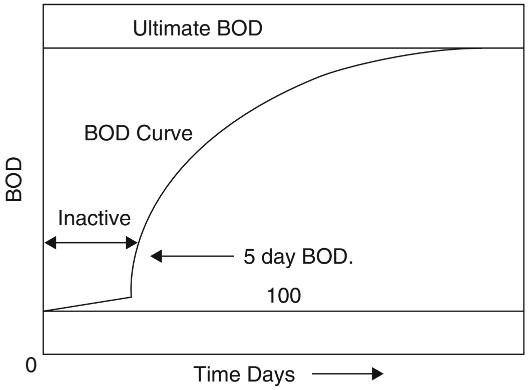


Fig. 8 Lab determination of 5-day BOD versus ultimate BOD

The depletion of oxygen due to biological pollution is not very rapid. It follows the laws of a first-order reaction. Because of this, the effect of BOD is measured in the laboratory on a 5-day basis and has been universally adopted as the measure of pollution effect.

The "ultimate" BOD is a measure of the total oxygen consumed when the biological reaction proceeds to near completion. The "5 day" BOD is believed to be approximately the ultimate. Figure 8 illustrates how the "5 day" BOD relates to the ultimate BOD.

In summary BOD measures organic wastes that are biologically oxidizable.

Chemical Oxygen Demand (COD)

The COD is a measure of the oxygen depletion due to organic and inorganic wastes which are chemically oxidizable. There are several laboratory methods accepted to measure the oxygen depletion effect of this pollution. The two most widely accepted are the "4 h permanganate" method or the "2 h dichromate" method. Although there is no generalized correlation between BOD and COD, usually the COD will be larger than the BOD. The following table illustrates how different wastes exhibit a different relationship between COD and BOD (Table 5).

Immediate Oxygen Demand (IOD)

Oxygen consumption by reducing chemicals, such as sulfides and nitrates, is typified by the following equations:

$$\begin{array}{c} S^{2-} + 2O_2 \rightarrow SO_4^{2-} \\ NO_2^- + \frac{1}{2}O_2 \rightarrow NO_3^- \end{array} \tag{11, 12}$$

These types of inorganic oxidation reactions are very rapid and create what is measured in the laboratory as immediate oxygen demand (IOD). If waste contaminants contain these inorganic oxidizers, the "5 day" BOD test will include the consumption of the oxygen due to IOD also. A separate test to determine IOD must be made and this result subtracted from the "5 day" BOD to arrive at the true BOD result.

Table 5 Relationship between BOD and COD

Source	Pollutants	BOD "5 day"	COD "2 h dichromate"
Brewery	Carbohydrates, proteins	550	–
Coal gas	Phenols, cyanides, thiocyanates, thiosulphates	6,500	16,400
Laundry	Carbohydrates, soaps	1,600	2,700
Pulp mill	Carbohydrates, lignins, sulfates	25,000	76,000
Domestic sewage	Solids, oil and grease, proteins, carbohydrates	350	300
Petroleum refinery (sour water)	Phenols, hydrocarbons, sulfides	850	1,500
Petroleum refinery	Phenols, sulfides, hydrocarbons, mercaptans, chlorides	125	2,600

Toxic Pollutants Common to Oil Refining

Toxic pollutants that are of greatest concern in untreated refinery aqueous wastes include:

Hydrocarbons, Oil, and Grease

Heavy oil and other hydrocarbons are the most problematic pollution to be found in refinery water effluent. All refineries exercise the most stringent methods to control and remove these undesirable pollutants. Indeed, in many cases, the treated effluent streams leaving the refinery may well be purer than incoming potable water used in the processes.

Aromatics are a particular problem and are specifically regulated to very low ppb levels in effluents. Benzene is specifically targeted by both water and air regulations.

Phenols

These chemicals are often formed in refinery processes such as catalytic and thermal crackers. They are highly toxic to aquatic life in concentrations of 1–10 ppm. Apart from their toxicity, phenols also impart an unpleasant taste and odor to drinking water in the range of 50–100 ppb. In concentrations of 200 ppm and higher, these chemicals can also deactivate biological water treatment plants such as trickle filters and activated sludge units. This could include a downstream publicly owned treatment works (POTW) that received refinery effluent water.

Caustic Soda and Derivatives

Solutions containing sodium hydroxide (NaOH) and related chemicals (like soda ash) are used in a number of refinery processes and maintenance activities. Inevitably some of these chemicals enter the refinery's wastewater system. Most of these contaminants are toxic to living organisms, even in low concentrations. The spent caustic (compounds leaving the process) such as sodium sulfide can be even more injurious.

Aqueous Solutions of Ammonium Salts

The most common of these are ammonium sulfide (NH_4SH) and ammonium chloride (NH_4Cl). Both these salts are present in effluent water from the crude distillation unit overhead accumulator; from the cracking processes, and from hydroprocessing units (hydrocrackers and hydrotreaters). Other ammonium salts are also present in hydrocracking and deep oil hydrotreating sour waters and from processing of some alternative feeds and renewable stocks.

Acids in Aqueous Effluents

The most common of the acids in wastewater are from the alkylation processes, which use either hydrofluoric acid or sulfuric acid. In the reforming and isomerization processes, hydrochloric acid is also used as a catalyst promoter. In some older processes (e.g., Edeleanu), sulfur dioxide is used to remove aromatics. Sulfuric acid is also used at cooling towers and other locations as an additive, where spills may reach the water treatment system. The most common acidic effluent form is dilute sulfuric acid.

Ketones, Furfural, and Urea

These compounds are used in the refining of lube oils. MEK and urea are used in some dewaxing processes. Furfural is used in some extraction processes for finished lube oil stock. All of these compounds are toxic.

Selenium and Metals

The recent years have seen an increase in the regulations to control toxic metals in effluents. Specific emphasis has been placed on selenium in refining because of its bioaccumulation effects. Selenium occurs naturally in crude oil at very low concentrations (0.03–1.4 ppm). When oil, especially distillate, is refined, the sour water produced in processes like hydrotreating contains enough selenium to require separate treatment to reduce the selenium to ppb levels in the refinery effluent.

Treating Refinery Aqueous Wastes

The treatment options for aqueous wastes from oil refineries fall into three general categories:

- In-plant treatment – these are onsite processes, usually sour water strippers, spent caustic oxidizers, and spent caustic neutralizers
- The API separator, or similar oil/water separating device
- Secondary treatment, which includes chemical coagulation, activated sludge processes, trickle filters, air flotation, and aerators

Most energy refineries contain the first two of the above categories. Some refineries also have secondary treatment, especially if they discharge effluent directly to a stream or body of water.

We will explore some specific treatments in more detail in this section, including:

- Sour water strippers
- Spent caustic disposal
  - Neutralization
  - Oxidation
- Oil/water separation
  - API separator
  - Corrugated plate interceptors
- Storm surge ponds
- Other processes
  - Oxidation ponds
  - Air floatation/dissolved air floatation (DAF)

Sour Water Strippers

Sour water stripping is one of the most common treating processes. Its purpose is to remove the pollutant gases included in the sour waters produced in the facility. The primary sour water pollutants are ammonia, ammonium salts, and hydrogen sulfide. The sour water stripper is often located in the sulfur recovery area of the refinery, because the stripper off-gas is usually routed to the sulfur recovery unit for disposal.

Feed to the stripper may include effluent water from the crude unit overhead condensers, water phase from the desalters, condensed water from the vacuum unit's hot well, and all the water condensate and wash waters from the hydroprocessing units.

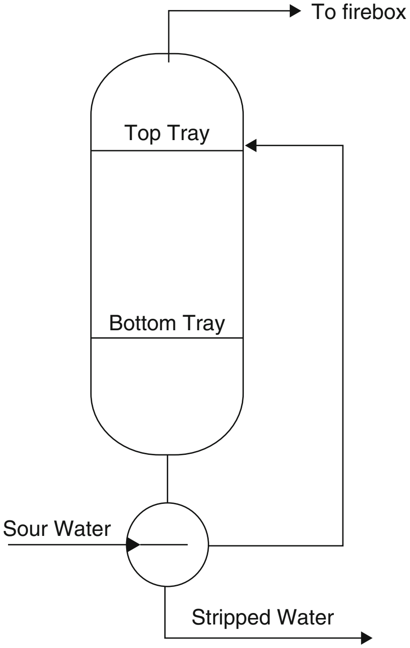
A sour water stripper is usually a trayed tower (with about 20 trays) with no reflux or a similar tower with an overhead reflux stream. Figure 9 shows a simple stripper tower with no reflux and Fig. 10 shows a stripper with an overhead condenser and reflux. In many refineries, there are two or more sour water strippers (SWS) that feed different water streams:

- Sour water containing phenols (AKA phenolic sour water)
- Sour water without phenols (AKA non-phenolic sour water)
- Dedicated hydroprocessing unit wash water stripper

Separation of the streams helps minimize waste, especially a dedicated hydroprocessing wash water stripper. With a separate hydroprocessing wash water stripper, the stripped water can usually be reused in the units if it meets certain quality limits and has not collected nonvolatile salts.

These types of sour water strippers lend themselves to tray-by-tray mass and heat transfer calculations for design. The sour water feed is introduced on the top tray of the tower while steam, usually at a rate of 0.5–1.5 lbs/gal of feed, is introduced below the bottom tray. The steam is usually generated by reboiling the bottoms from the tower.

Fig. 9 Sour water stripper with no reflux



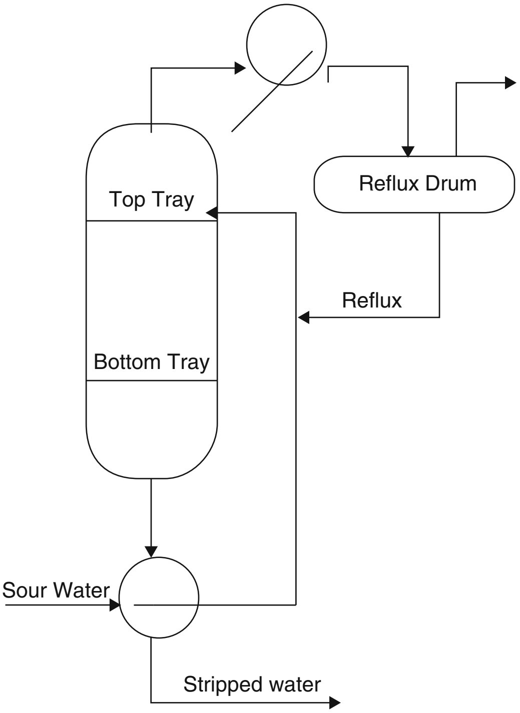


Fig. 10 Sour water stripper with reflux

In the case of a tower with reflux, the reflux enters the tower with the fresh feed. The design of both towers takes advantage of the equilibrium relationships of NH_3 and H_2S in aqueous solutions. A series of graphs giving these relationships is included in Appendix 1 of this chapter as Figs. 20, 21, 22, 23, 24, 25, 26, 27, 28, and 29.

An example of the design for a sour water stripper with no reflux is given in Appendix 2 of this chapter.

Selenium Removal from Stripped Sour Water

Selenium in a refinery normally ends up in the sour water. The selenium in the wastewater may be present in many forms: e.g., selenide, selenite, selenate, and selenocyanate. These are potential environmental hazards. Normally, selenium is removed from oil refinery wastewater or stripped sour water by proprietary chemical treatments that promote precipitation and/or adsorption followed by separation techniques. Some biological agents are also useful in facilitating selenium removal.

Spent Caustic Disposal

Another major aqueous effluents from oil refining are the spent caustic streams from hydrogen sulfide and phenol removal. Refiners usually have the following options in the disposal of these streams. In order of preference, these can be listed as follows:

- Phenolic spent caustic:
  - Disposal by sales
  - Disposal by dumping at sea
  - Neutralizing with acid
  - Neutralizing with flue gas
- Sulfidic spent caustic:
  - Disposal by sales
  - Oxidation with air and steam
  - Neutralization with acid and stripping
  - Neutralization with flue gas and stripping

Both the phenolic and sulfidic spent caustics may have a commercial value in industrial areas and where transportation costs make sales an attractive economic option. In the case of the phenolic spent caustic, processors recover, separate, and purify various cresylic acid fractions for commercial use and sales. In the case of the sulfidic spent caustic, this can be sold as sodium sulfide with some additional processing.

Neutralizing Phenolic Spent Caustic

As listed above, phenolic spent caustic can be neutralized using acid or flue gas. When neutralized the mixture separates into two liquid phases. The upper phase contains the acid oils, while the lower phase is an aqueous solution of sodium sulfate or sodium carbonate. The neutralization using either acid or flue gas can be accomplished in either batch or continuous operations.

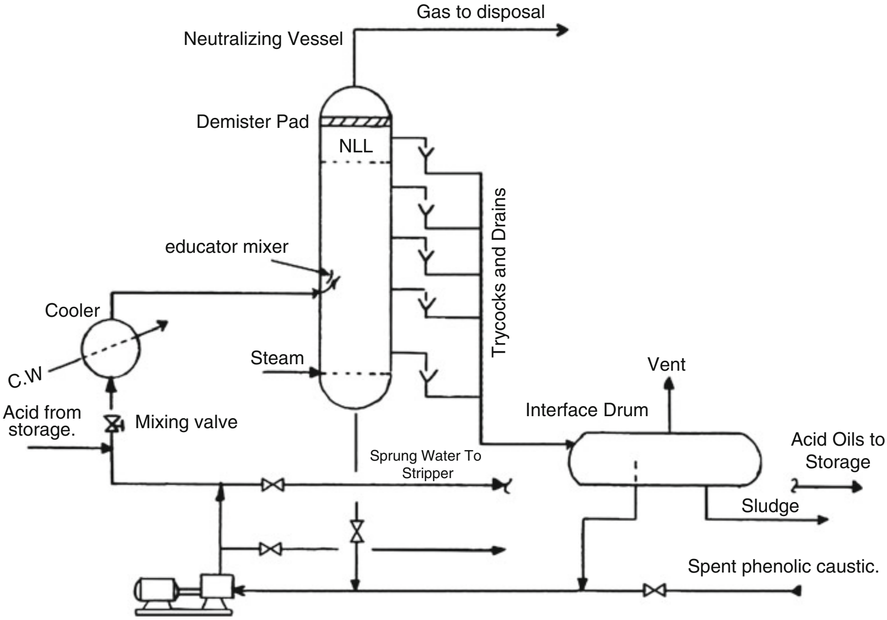


Fig. 11 Batch neutralization of spent caustic with acid

Batch neutralization, using acid, is considered to be the preferable route in this case. Flue gas neutralization, although practical and commercially used in many installations, is more complex in design than the acid application and does not lend itself readily to batch operation. It may require, in some instances, large piping, switch valves, and a blower.

A diagram of a phenolic caustic batch neutralizer is shown in Fig. 11.

The process is fairly simple involving the following steps:

1. Charging the spent caustic batch into the neutralizer vessel.
2. Addition and thorough mixing of the acid neutralizer into the batch. This has to be accomplished slowly and carefully to avoid lowering the pH of the batch too far. A pH of between 4 and 5 will be required to free the phenols completely.
3. A settling period is necessary to allow the sprung acids to separate from the sprung water.
4. Pumping out and disposal of the sprung water.
5. Sprung acid is steam stripped to remove any residual H_2S and light mercaptans.
6. Pump out the interface material which will be included in the next spent caustic batch.
7. Finally pumping out of the sprung acid.

The neutralization step is exothermic, giving out around 125 Btu/lb of sprung acid. As the objective of the process is to produce a phenol-free sprung water for disposal, the system temperature should be kept as low as possible until the sprung water is removed. For example, the solubility of phenol in pure water at 120 °F is about 11 w%, while its solubility at 100 °F is 8.5 w%. For this reason, steam stripping should not begin until the sprung water has been removed. Routing the sprung water to the sour water stripper ensures the removal of any entrained H_2S in that stream.

Mixing of the acid/spent caustic is usually achieved using a mixing valve at the inlet of the neutralizer. An educator or a jet nozzle inlet to the vessel itself would ensure complete mixing if this is required.

Spent Caustic Oxidation

Spent caustic cannot be steam stripped to remove the sulfides contained in it due to the H_2S removal process in which the caustic was used. This is because sodium sulfide does not hydrolyze even when heated. Acids could be used to neutralize the spent caustic, which would release gaseous H_2S. This could be a costly procedure and could cause a potential air pollution problem, although some sour water strippers are designed to dispose of caustic in this manner using waste acid.

The alkaline sulfide can be economically oxidized to form thiosulfates and sulfates. This is the process most commonly used in refineries where only sulfides are the pollutants in the spent caustic and the release of gaseous H_2S is a problem. The oxidation process can also be used in the presence of ammonium sulfide in the stream. The process has not been applied to wastes containing a higher percentage of phenols, because the phenols interfere with the oxidation process.

The oxidation options are described in the following, more detailed discussion.

Oxidation of Sulfides to Thiosulfates

The oxidation of Na_2S or $(NH_4)_2S$ to the corresponding thiosulfates may be expressed in ionic terms as follows:

$$\begin{array}{lllllllllll} & 2S^{2-} & + & 2O_2 & + & H_2O & \rightarrow & S_2O_3^{2-} & + & 2OH^- \\ \text{lb} & 2(32) & & 2(32) & & 18 & & 112 & & 2(17) \\ H_f & 2(-10) & & 2(0) & & +68 & & +154 & & 2(+55) \end{array} \tag{13}$$

where H_f is the theoretical heat of formation in kcals/gm-mole in dilute solution. The plus sign denotes heat evolved, while the minus sign denotes heat absorbed.

Similarly the oxidation of NaSH or NH_4SH to the corresponding thiosulfate can be expressed as follows:

$$\begin{array}{llllllll} & 2SH^- & + & 2O_2 & \rightarrow & S_2O_3^{2-} & + & H_2O \\ \text{lb} & 2(33) & & 2(32) & & 112 & & 18 \\ H_f & 2(+3) & & 2(0) & & +154 & & +68 \end{array} \tag{14}$$

In both cases, the theoretical oxygen required is 1 lb/lb of S, and the theoretical air required would be 4.33 lbs/lb of S. The theoretical heat of reaction in both cases is 216 kcals/gm-mole of S_2O_3 or 6,100 Btu evolved per lb of sulfur.

Figure 12 shows a typical oxidizing unit.

Briefly, the oxidizer unit consists of an oxidizing tower and an overhead separator. The sour water feed enters the oxidizing tower, after preheating by exchange with the hot oxidizer overhead effluent. Heating steam and air are injected into the sour water feed stream before entering the oxidizer tower. The steam flow is controlled by the temperature of the inlet mixture, while the air is flow controlled to meet the reactor condition premise.

The oxidizing tower itself is divided into three sections, with mixing nozzles connecting the inlet to each section. The reactants (air and the sour water feed) enter the base of the oxidizer, also through a mixing nozzle, and flow upwards through the sections of the tower. The oxidized effluent leaves the top of the tower to be cooled and partially condensed by exchange with the sour water feed. The cooled effluent enters a separator, operating under pressure control. The vent gases leave through the pressure controller to flare or other suitable disposal equipment (such as a heater firebox).

The oil phase of the effluent is skimmed off as a side stream, while the water phase, after settling, leaves the bottom of the separator as the oxidized effluent.

High temperature and low pressures tend to vaporize some of the water in the top section of the oxidizer. This results in more sulfides being stripped out into the vapor phase. Thus, it is recommended that the oxidizer top pressure be at least 25–40 psi above the vapor pressure of the water at the oxidizer top temperature. Typical design criteria for these oxidizing units are given in Table 6.

Oxidation of Mercaptans

If caustic soda has been used to remove H_2S, there will almost certainly be mercaptans present in the sour stream. Caustic soda will also react with and remove these from a process stream. In treating these light streams from sour crudes, the mercaptan content of the spent caustic stream could be as high as 3,000 ppm of sodium mercaptide sulfide. The greater part of the mercaptides will be oxidized to hydrocarbon disulfides according to the equation

$$2\,\mathrm{RSNa} + \tfrac{1}{2}\mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{RSSR} + 2\,\mathrm{NaOH}. \qquad (15)$$

Almost all the mercaptides will be oxidized in a concurrent flow reactor. However, some of the mercaptides will be partially hydrolyzed, and it can be assumed that there will be a certain amount of free mercaptan present in accordance with the equilibrium:

$$\mathrm{RSNa} + \mathrm{H_2O} \leftrightarrow \mathrm{RSH} + \mathrm{NaOH}. \qquad (16)$$

The free mercaptan formed by this reaction will be stripped out of solution and leave the reactor in the overhead vapor phase. Now, if the separator is operating at 62 psia and 125 °F, the vapor pressure of water at 125 °F is 2 psia, and then the partial pressure acting to condense the overhead vapor is 60 psia. Methyl mercaptan may condense under these conditions, but the heavier mercaptans and the disulfide

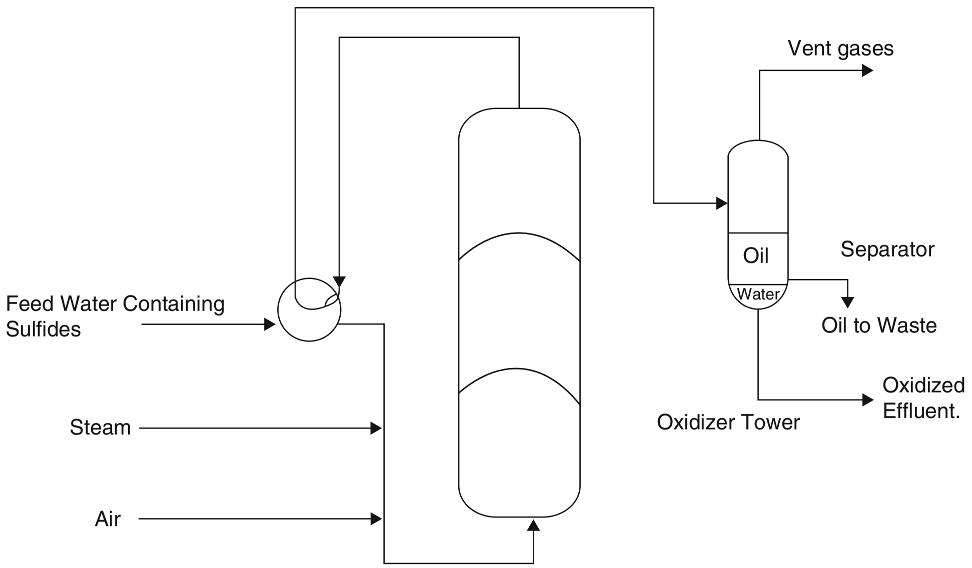


Fig. 12 Schematic of an oxidizer plant

Table 6 Typical design criteria for sulfide oxidizers

Temperature at bottom, °F	165–225
Pressure at bottom, psia	75–100
Inlet air (lbs/gal)/(1,000 ppm S)	0.05–0.075
Inlet air (lb/lb S)	1.4–2.1
Superficial air (ft/s)	0.08–0.1
Sulfide oxidation rate (lbs/h)/cuft	0.35

certainly will condense. The disulfides are immiscible in aqueous alkaline effluent and will form the upper oil layer, to be skimmed off for disposal. The mercaptans that are condensed will form mercaptides with the NaOH present. This will really occur in the feed/effluent exchanger when the reformed mercaptides are still in contact with the reactor air supply. Most of the mercaptides, if not all, will be oxidized to disulfides again.

The theoretical oxygen requirement for oxidizing mercaptides to disulfides is 0.25 lb per pound of mercaptide sulfur, and the theoretical air requirement is 1.09 lb per pound of sulfur. For convenience, the following value of the theoretical amount in this case can be taken as

$$1\,\text{Theory} = 0.0091(\text{lb air/gal})/(1{,}000\,\text{ppm RSH} - \text{S}) \tag{17}$$

Oxidation of Sulfide to Sulfate

The oxidation of sulfides to thiosulfides only reduces the ultimate oxygen demand of the sulfides from two pounds of oxygen per pound of sulfides to one pound per pound of sulfide. The oxidation to thiosulfate will remove the short term or immediate oxygen demand. Thiosulfate limits are not usually stipulated in water pollution regulations, while sulfides are always stipulated.

In those cases where thiosulfates are a regulated limit, it will be necessary to convert the thiosulfate to the sulfate. The chemistry relating to this may be written as follows:

$$S^{2-} + 2\,O_2 \rightarrow SO_4^{2-} \tag{18}$$

The above equation applies equally to aqueous ammonium sulfide and to sodium sulfides.

The theoretical oxygen requirement is 2 lb per pound of S, and the theoretical air requirement is 8.66 lb per pound of S. The theoretical heat of reaction is 12,700 Btu evolved/lb of S. That is, one theory of air is

$$0.072(\text{lb air/gal})/(1{,}000\,\text{ppm S}) \tag{19}$$

Table 7 compares those units oxidizing to thiosulfates to those oxidizing to sulfates. Although many units processing the sulfides to sulfates do not use a catalyst, they convert the sulfide to a mixture of thiosulfates and sulfate.

Table 7 Comparison of sulfide oxidation processes

	Oxidizing to thiosulfate only	Partial oxidizing to sulfate	Total oxidizing to sulfate
Anions produced			
SO_4^{2-} %	Nil	46	100
$S_2O_3^{2-}$ %	100	54	Nil
% Sulfide oxidized to			
SO_4^{2-}	Nil	34	100
$S_2O_3^{2-}$	100	66	Nil
Sulfide oxidation rate (lbs/h)/cuft	0.33	0.033	0.035
Air rate in theories			
Oxidation to $S_2O_3^{2-}$	2.05	1.55	6.53
Oxidation to actual anions	2.05	1.17	3.27
Air/water flow	Concurrent	Countercurrent	Countercurrent
Catalyst used	None	None	$CuCl_2$

To convert the sulfide completely to the sulfate, a copper chloride catalyst is used to accelerate the reaction rate. The reaction rate of this conversion is quite slow without the catalyst.

Oil/Water Separation

Most aqueous effluents from a refinery will contain oil. This oil content has to be reduced to less than about 10 ppm before it can be deposited into a river, lake, or ocean. Publicly owned treatment works (POTWs) will have similar requirements for what they will accept for processing to avoid causing problems in their systems.

The oil contamination sources are from multiple areas, including process water rundown, paved area drainage, storm catch pots, tanker ballast pump-out, and tank farm diked areas. All the water from these sources is treated in oil separation processes. The most important of these oil/water separation processes is the API separator.

There are also proprietary corrugated plate interceptors available, which operate on similar principles to the API separator. These contain slanted packs of multiple, parallel, corrugated metal plates, which enhance water separation.

Here we will primarily focus on the common API separator in the discussion.

The API Oil/Water Separator

The design of an API separator is based on the difference in specific gravity of oil and water in accordance with the general laws of settling. The applicable laws are represented by the following equations:

$$
\begin{aligned}
V &= 8.3 \times 10^5 \times \frac{d^2 \Delta S}{\eta} \quad \text{(Stokes' Law)} \\
V &= 1.04 \times 10^4 \times \frac{d^{1.14} \times \Delta S^{0.71}}{S_c^{0.29} \times \mu^{0.43}} \quad \text{(Intermediate Law)} \\
V &= 2.05 \times 10^3 \times \left[\frac{d \times \Delta S}{S_c}\right]^{1/2} \quad \text{(Newton's Law)}
\end{aligned}
\qquad (19, 20, 21)
$$

where:

V = settling rate in inches per min
d = droplet diameter in inches
ΔS = specific gravity differential between the two phases
η, μ = viscosity of the continuous phase (water in this case) in centipoise
S_c = continuous phase specific gravity

When the Reynold's number is <2.0, use Stokes' law. When the Re number is between 2 and 500, use the intermediate law. When the Re number is >500, use Newton's law:

$$\text{The Re number in this case is given as} \frac{10.7 \times d V S_{\mathrm{c}}}{\eta} \qquad (22)$$

As a guide, the droplet size of the oil in water can be taken (as a minimum) as 0.008 in., when the oil specific gravity is 0.850 or lighter, and as 0.005 in., when the gravity of oil is greater than 0.850.

The above laws for settling in oil refining processes usually apply to the hydrocarbon being the continuous phase with water (the heavier phase) being the one that settles out. In the case of the API separator, the reverse is true. That is, the continuous phase is water and the lighter oil phase is the one that is separated to be disposed as the product skimmed from the surface. In the design of this system, Stokes' law is used to reflect the rate at which the oil rises to the surface through the water. This modified Stokes' law may be written as

$$V_{\mathrm{r}} = 6.69 \times 10^4 \frac{d^2 \Delta S}{\eta} \qquad (23)$$

where:

V_r = rising rate of the oil phase in feet/min
d = droplet diameter in inches
ΔS = difference in specific gravity of the phases
η = viscosity of the continuous phase (water) in centipoises

An example of the application of this equation in the design of an API separator is given in Appendix 3 of this current chapter.

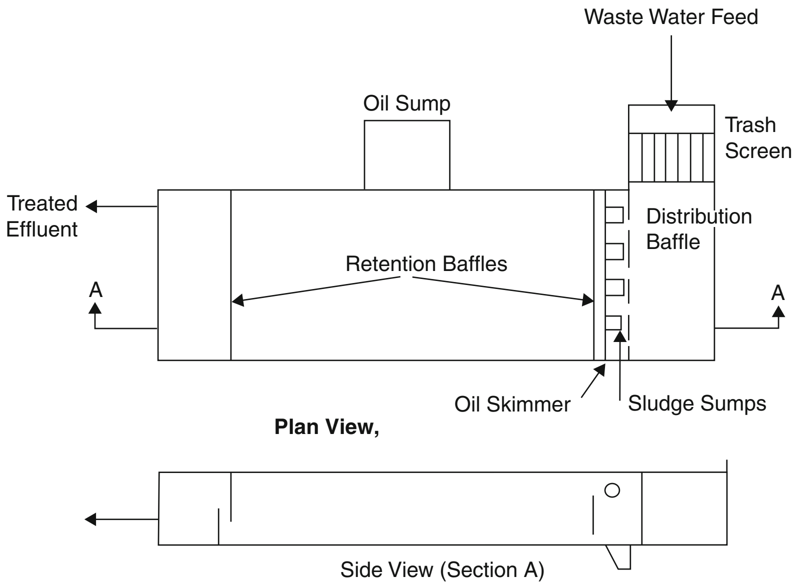


Fig. 13 Schematic diagram of a typical API separator

The oil phase from the API separator is removed using specially designed skim pipes through an oil sump.

A simplified diagram of a typical API separator is given in Fig. 13.

Ancillary equipment used in the design and operation of the API separator are described in the following items.

Oil Skim Pipes

As a good part of the oil will separate from the water on leaving the inlet flume, two oil retention baffles with skim pipes are provided. One is located ahead of the flow baffle and the other ahead of the overflow weir. The distance between these baffles will be the function "L" as calculated in Appendix 3. The API manual recommends 10 in. diameter skim pipes where the horizontal run is less than 40 ft. Larger diameter skim pipes will be installed in greater horizontal runs.

The Oil Sump

The oil recovery sump is located at one edge, usually midway along the horizontal run. The size of the sump is based on the oil content of the inlet stream to the separator plus four times that amount as water delivered by the skim pipes. For example, if the inlet stream contains 200 ppm by volume of oil and the water outlet contains 50 ppm, then the oil removal from the separator will be 150 ppm or 0.015 v%, which, in the case of the specification given in Appendix 3, will equate to

$$0.00015 \times 600 \times 1{,}440 = 130\text{gals/day}. \qquad (24)$$

Use the API recommendation to add to this figure four times the 130 gal per day for the amount of water contained with the skimmed oil delivered by the skim pipes. Then the total liquid to the sump will be 650 gal/day.

For ease of operation a sump size is often based on a predicted weekly accumulation which amounts to 4,550 gal in this example. Assume the sump cross-sectional area is 144 sqft (12 × 12 ft.) then the liquid depth to NLL should be 4,550/(7.48 × 144) = 4.2 ft. and the HLL can be set at 5 ft. To ensure adequate gravity head for the oil removed by the skim pipes, the bottom of the sump will be 8 ft. below the NLL of the separator.

The Sump Pump

The sump pump will be a standard vertical pump with a capacity to pump out the entire sump in about 1 h or less. Normally refineries pump the sump oil to the "Bottom Settling Tanks" of the refinery. These are tanks used to store the bottoms of crude oil tanks which usually contain high water and sediment content not suitable for the normal process plants. The contents are allowed to sit for some time and are then returned as feed to the normal refinery processes via recovered oil or slops. The bottom settling (water) from these tanks is routed back to the API separator.

Oil Retention Baffles

API recommends that oil retention baffles have a depth below the level in the separator that is 60–80 % of the liquid level. Further the baffle should extend 1 f. above the normal liquid level of the separator.

Distribution Baffles

An important feature in the design of the API separator is the means of distributing the influent evenly. API recommends either "V"-shaped (V-notched) baffles or pipes with multiple holes installed at the inlet of the separator to be used for this purpose. It is also recommended that the open area between slots be 3–7 % of the chamber cross-sectional area.

Sludge Sumps

Sludge sumps are located immediately downstream of the distribution baffles. API recommends that these sumps should be at least 30 in. deep – meaning, at least 30 in. below the floor of the separator. The sludge pump suction is to extend to within 6 in. of the sump bottom and the suction line would be 3 in. diameter. Normally the sludge bottom will be four square inches in cross-sectional area (or 2 in. square). API also recommends that these sumps slope a minimum of 1.7 in. vertically to 1.0 in. horizontal. In the example design in Appendix 3, if we chose 18 × 18 in. sumps sloping to 2 × 2 in. bottoms, we would have a slope of 1.9:1, which would meet the API recommendation. Such a layout could accommodate six sumps.

Trash Rack

API recommends that a trash rack, made up of series of parallel, 3/8 in. rods on 1.5 in. centers, be installed as a trash trap at the separator inlet.

Flight Scrapers

Many API separators have flight scrapers. These are baffles on a moving chain that follow a circuit: moving along the bottom of the API separator bay scraping sludge accumulations toward the sludge sumps then moving backwards down the bay at the top level pushing the oil into the first set of skimmers. The scrapers themselves are usually about 2 in. by 8 in. slats made of heart redwood or fiber-reinforced plastic spaced about 2–3 f. apart.

Storm Surge Ponds

These ponds are installed to provide storage for maximum rainfall conditions. There are several forms of these surge ponds, some requiring pumps, some located upstream of the API separator, and some downstream of the separator.

In most cases the storm drain system is directed to the storm surge pond. Thus, in a storm, the excess rainfall is held in this pond and fed to the API separator over a period of time, at a rate that will not exceed the separator's capability to handle the water effectively. In this way, the refinery ensures that any oily water will not bypass the separator under the worst condition.

The surge pond(s) must be sized to handle the maximum rainfall expected. Normally, the size is based on a 100-year precipitation event, but some facilities design for more. Understanding the precipitation event definitions is critical in selecting the sizing basis. The definitions depend heavily on application of probability theory. The pond(s) must be capable of accepting flow from all the catch basins and open culverts that form part of the refinery drainage system.

Surge ponds are constructed with a shallow depth over a large surface area. The ponds are usually clay-lined to limit loss to groundwater. In some areas, they may be lined or double lined with thick, impermeable (e.g., UV-stabilized polyethylene) membranes to prevent groundwater contamination. They may have a pump-out sump or other provisions for water transfer.

Surge pond elevations are usually only slightly above the API separator, but near the low point of the refinery. Thus, even when the pond is full of water, it will not "back up" into the process area drains. In some cases, where it is not possible to locate the ponds at the lowest elevation, people have installed intermediate lift sumps with multiple vertical lift pumps on uninterruptable power or steam to move water into the ponds at high rate in a large precipitation event.

Refer to the topic "Utilities in Petroleum Processing" in this handbook for more discussion of sewers and how they interact with storm water basins.

Other Refinery Water Effluent Treatment Processes

Oxidation Ponds

Oxidation ponds are usually used as a secondary effluent cleanup after the API separator. There are three types of oxidation ponds:

- *Aerobic* – where the oxidation of the water utilizes oxygen from the atmosphere plus oxygen produced by photosynthesis
- *Anaerobic* – where oxidation of the wastes does not utilize oxygen
- *Aerated* – where oxidation of the wastes utilizes oxygen introduced from the atmosphere by mechanical aeration

Looking at the more common aerobic oxidation ponds, consider a shallow pond containing bacteria and algae. The bacteria will utilize oxygen to biochemically oxidize the incoming water. In so doing, they will produce H_2O, CO_2, and, perhaps, NH_3. The algae will use sunlight plus the H_2O and CO_2 to produce oxygen. Oxygen in turn produces additional bacteria and algae growth. Aerobic oxidation ponds will often contain aerators to ensure an oxygen supply and keep the ponds from "going anaerobic," which tends to be more odorous.

The aerobic cycle is shown in Fig. 14.

Air Flotation and Dissolved Air Flotation (DAF)

The purpose of the air flotation process is the clarification of wastewater by the removal of suspended solids and oil. This is achieved by dissolving air in wastewater under pressure and then releasing it at atmospheric pressure. The released air forms bubbles which adhere to the solid matter and oil in the wastewater. The bubbles cause the adhered matter to float up to the surface of the water as a froth.

The dissolved air in the water also achieves a reduction in the oxygen demand of the effluent stream. Figure 15 illustrates the principle elements of a typical air flotation process.

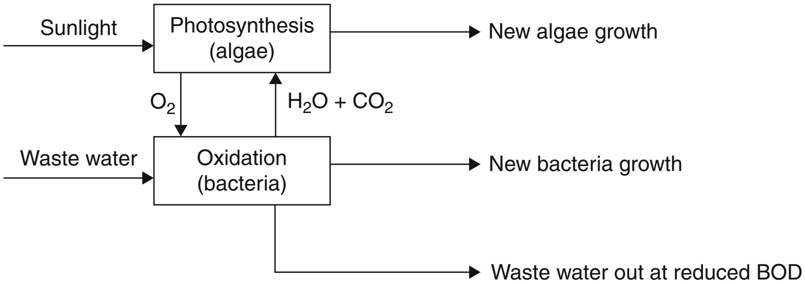


Fig. 14 Aerobic cycle in oxidation ponds

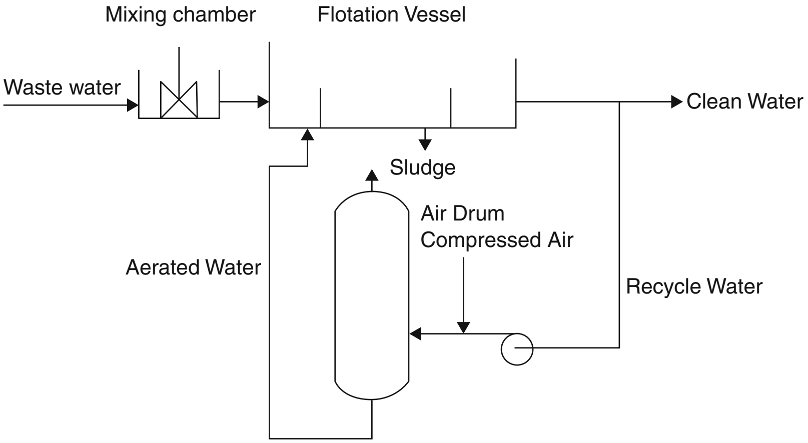


Fig. 15 A typical air flotation process

Table 8 Design criteria for a typical recycle air flotation unit

Recycle rate	50 % of raw feed rate
Air drum pressure	35–55 psig
Air drum retention time	2 min of recycle flow (from liquid level to drum bottom)
Flotation tank retention	15–20 min of total flow (raw feed plus recycle)
Flotation tank rise rate	3.0 gal/min of total flow per sqft of liquid surface
pH	7.5–8.5
Flocculating chemical	25 ppm of alum in total flow
Air rate	0.25–0.5 scf/100 gal of total flow
Flotation tank liquid depth	6–8 f. (to meet requirements above)

The process shown is the preferred recycle type. The process can also be designed for a once-through operation. The typical design criteria for the recycle process are given in Table 8.

Referring to Fig. 15, the flocculating chemical and pH control chemical are mixed in the mixing tank with the raw water feed before the feed enters the flotation vessel.

The processes described in this section have been those found in oil refining most often. Indeed, of the processes described above, most refineries only use the API separator and the surge ponds to meet the oil/water separation required.

Solid Wastes

We have discussed air emissions and water emissions management from petroleum processing facilities. Now the discussion turns to solid wastes generated by a refinery.

There are several types of solids generated in processing petroleum. Not all are "solids" in the normal sense of the word. Some are semisolids or near liquids, but we will treat them here as solids for the discussion.

Some typical solid wastes generated in a refinery are listed in Table 9 along with some of their characteristics and disposal options. Some are considered and defined as hazardous, while others are relatively innocuous. All must be dealt with appropriately.

The table lists some of the options for disposal of the different types of wastes. The actual disposition, however, will be heavily influenced by the applicable regulations from many different governing authorities. An acceptable disposal method in one jurisdiction may not be acceptable in another location.

Solid Waste Disposal Regulations

As with all environmental issues, there is a complex web of cross-connected regulations that define what you can and cannot do with a solid waste in a particular locale. Some of the applicable regulations in the United States and the European Union are listed below:

- United States
  - Resource Conservation and Recovery Act (1970).
    Lists specific wastes defined as hazardous (F & K wastes, for instance)
    Established "characteristic" hazardous waste definitions
    Universal wastes defined – e.g., batteries, pesticides, mercury-containing equipment, and light bulbs/lamps
  - Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (1980).
  - Hazardous and Solid Waste Amendments (HSWA) (1984).
  - Federal Facility Compliance Act (1992).
  - Land Disposal Program Flexibility Act (1996).
  - Used Oil Recycling Act (1980).
  - Solid Waste Disposal Act Amendments (1980).
  - Superfund Amendments and Reauthorization Act (SARA) (1986) – CERCLA reauthorization and strengthening.
  - Ocean Dumping Ban Act (1988) – bans ocean dumping of wastes.
  - RCRA Cleanup Reforms I & II (1999, 2001).
  - Used Oil Management Standards (2003).
  - Emergency Planning and Community Right-To-Know Act (EPCRA) (1980).
  - RCRA Expanded Public Participation Rule (1996).
  - Pollution Prevention Act (1990).
  - Hazardous Waste Combustors; Revised Standards; Final Rule – Part 1 (1998).
  - Numerous state and local regulations also govern solid wastes, hazardous and non-hazardous. Many encourage reclamation and recycle over disposal in a landfill.

Table 9 A survey of refinery "solid" wastes

Type of waste	Source(s)	Hazardous? (RCRA designation)	Typical disposition options
Defined hazardous wastes under US regulations (RCRA)			
Primary oil/water/solids separator sludges	Miscellaneous sources	Yes (F037)	Coker injection, combustion, wet oxidation
Secondary oil/water/solids sludges	Miscellaneous sources	Yes (F038)	Coker injection, combustion
Dissolved air flotation (DAF) float	Water effluent treatment DAF unit	Yes (K048)	Coker injection, combustion
Slop oil	Refinery-wide sources	Yes (K049)	Recycle, coker injection, combustion
Heat exchanger bundle cleaning sludge	Maintenance or within a unit	Yes (K050)	Landfill, encapsulation, combustion
API separator sludge	Water effluent treatment	Yes (K051)	Coker injection, combustion
Tank bottoms (leaded)	Leaded gasoline tanks	Yes (K052)	Combustion, wet oxidation
Crude oil storage tank sediment	Crude tanks	Yes (K169)	Coker injection, combustion
Clarified slurry oil tank sediment/filter solids	FCC or tankage	Yes (K170)	Combustion
Spent hydrotreating catalyst	Hydrotreaters, hydrocrackers	Yes (K171)	Regeneration and reuse, reclamation, landfill
Spent hydrorefining catalyst	Hydrotreaters, hydrocrackers, other units	Yes (K172)	Regeneration and reuse, reclamation, landfill
Other types of "solid" refinery wastes			
Oily sludges	Tank bottoms, biotreatment, interceptors, wastewater treatment, contaminated soils, desalters	Probable (some classified above)	Coker injection, combustion, wet oxidation
Oily solids	Contaminated soils, oil spill debris, filter clay acid, tar, rags, filters, packing, lagging, activated carbon	Possible	Combustion, landfill
Drums and containers	Miscellaneous sources	Possible	Recycle, landfill
Spent catalysts (non-listed)	FCC, cat poly, reformers, etc.	Not normally	Reclamation, landfill

(*continued*)

Table 9 (continued)

Type of waste	Source(s)	Hazardous? (RCRA designation)	Typical disposition options
Non-oily materials	Resins, BFW sludges, dessicants, adsorbents, neutral alky sludges, flue gas desulfurization wastes	Not normally	Reclamation, landfill
Radioactive wastes	Catalysts (NORM), lab, level instruments	Possible	Reclamation, landfill, encapsulation
Scales	Leaded and unleaded deposits, rust	Possible	Landfill, encapsulation
Construction and demolition debris	Scrap metal, concrete, asphalt, soil, asbestos, mineral fibers, plastic, wood	Some (asbestos, mineral fibers)	Landfill, encapsulation
Lab wastes	Laboratory	Possible	Reclamation, landfill
Pyrophoric wastes	Iron sulfide-containing scales, certain spent catalysts	Probable	Reclamation, combustion, landfill
Mixed wastes	Domestic refuse, vegetation	Not normally	Landfill, composting
Waste oils – not listed above	Spent lube oil, cutting oil, transformer oil, recovered oils, engine oil, slops	Possible	Reclamation, combustion

- European Union
  - Council Directive 75/439/EEC – disposal of waste
  - Council Directive 75/442/EEC – wastes
  - Council Directive 91/689/EEC – hazardous waste
  - Council Regulation (EEC) No 259/93 – shipments of waste within, into, and out of the European Community
  - Council Directive 94/67/EC – incineration of hazardous waste
  - Council Decision 97/640/EC – control of transboundary movements of hazardous wastes and their disposal
  - Council Directive 1999/31/EC – landfill of waste
  - Council Decision 2000/33/EC – criteria and procedures for acceptance of waste at landfills
  - Commission Decision 2000/532/EC – lists of wastes and categories, incineration
  - Regulation (EC) No 2150/2002 – waste statistics

The regulatory thrusts have moved from controlling disposal toward encouraging waste reduction, reuse, and reclamation over simple disposal.

Some Definitions

We have used several terms without definition so far. Here we will review a couple of the important definitions and considerations in solid waste management.

Hazardous Waste

A hazardous waste is normally defined as a spent material which may pose a substantial risk to public health or the environment. In the United States, the EPA defines some refinery wastes specifically as hazardous. These are highlighted by a designation like the F or K numbers in Table 9 and are called "listed hazardous wastes."

Other wastes are deemed hazardous by their characteristics, as determined by specific tests:

- Ignitability (i.e., flammable) – in air – may be pyrophoric or self-heating
- Reactivity – with other materials or air
- Corrosivity – acids or caustics
- Toxicity – to animals or other life

Jurisdictions outside the United States have generally taken similar approaches for waste classification.

Non-hazardous Waste

The definition of non-hazardous solid wastes in the United States is included in RCRA, Subtitle D. The definition actually includes some hazardous wastes that were exempted from the regulations (e.g., small quantity household hazardous wastes). Oil and gas exploration and production wastes are also exempted. Subtitle D mostly applies to things like garbage, appliances, scrap metal, construction materials, some POTW sludges, and drinking water treatment plant sludges.

Waste Minimization and Reduction

This is the practice of reducing the amount of net waste produced from a facility through changes to the process, raw materials, or disposition of spent materials. It may mean:

- Redesign and operation of a process to reduce by-products or wastes – e.g., minimizing offgrade product through good operation practices
- Reuse of waste from one process in another process, can be internal or external – e.g., cascading slightly spent caustic to other users or reprocessing offgrade products
- Recycling of waste – e.g., sending API separator sludge to the coker or sending slops/recovered oil back to the crude unit as feed
- Reclamation of usable materials from a facility waste – e.g., reclaiming Co, Ni, and Mo from spent catalysts

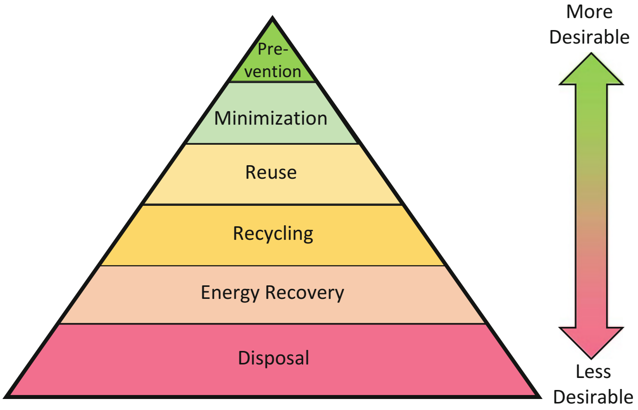


Fig. 16 The waste minimization pyramid concept

- Recovery of heat from sludges and waste oils – e.g., incinerating sludges to generate steam

The concept of waste minimization is illustrated by the pyramid in Fig. 16. The least desirable disposition is by disposal in a landfill for most solid wastes.

Solid Waste Management Techniques and Practices

Many techniques and practices have been developed for management and minimization of solid wastes. We will only list a few of the common approaches here, along with some comments and examples.

Waste Minimization Techniques (from CONCAWE Report No. 6/03)

- Reduction at the source:
  - Process selection and design – e.g., consider another technology for trace sulfur removal instead of caustic treating; cascade caustic solutions among units
  - Process/equipment modifications – e.g., closed-loop sampling systems, mechanical seals on pumps, selection of chemicals for better operations
  - Alternative treatments – e.g., regeneration and reuse of hydrotreating catalysts, hydrotreat lube oils instead of acid treating
- Recycle and reuse of wastes:
  - Internal to facility – e.g., re-running off-spec products or recovered oil, reuse of spent caustic in less demanding applications (like crude unit corrosion control)
  - External to facility – e.g., catalyst metals reclamation, FCC catalyst use as road aggregate, cresylic acid recovery from spent caustic

- Use materials efficiently:
  - Good catalyst activation and conditioning to extend life
  - Not over-treating products
  - Not using more chemical than optimum
- Good housekeeping:
  - Avoid/limit spills – e.g., proper handling of materials to eliminate leaks and losses, tank farm dike design to contain spills, quality spill prevention and containment plan.
  - Limit the need for cleaning – e.g., use antifoulants in service to minimize exchanger cleaning; spray-neutralizing with soda ash rather than flooding reactors; dewatering sludges before disposal (avoid "treating" them, however).
  - Prevent solids from entering the sewer system – e.g., keep dirt, plants, and trash from accumulating in facilities, like in sleeper ways; control the pH of drainings to sewer; segregate storm and process sewers.
- Waste handling:
  - Segregate wastes – e.g., do not mix hazardous and non-hazardous wastes (it all becomes hazardous).
  - Pretreat if possible to reduce volume or render non-hazardous.
- Minimize caustic wastes:
  - Use alternatives of high efficiency caustic contacting.
  - Reuse caustic in refinery.
  - Sell caustic to others for reuse.
  - Manage through the effluent system.
  - Several alternatives are discussed in this chapter under wastewater disposal.
- Do not put a non-hazardous material in a hazardous material storage area, lest it get contaminated or inadvertently disposed of at a higher classification than needed. As a corollary, do not classify a material as more hazardous than it is "just to be safe." Ensure a material is correctly classified with the information you have at the time. It can be reclassified later.

Storage Facilities

The wastes, especially hazardous wastes, awaiting disposal require adequate, environmentally acceptable storage facilities. Here are a few storage considerations:

- Specific permitting is usually required for a facility to be allowed to treat and/or store hazardous wastes beyond a specific time frame. In the United States, hazardous wastes must be out of a facility within 90 days of its generation, unless the facility has a treatment and long-term storage permit. Other countries have similar storage time limits. Most refineries do not have these permits. There are provisions for small, satellite hazardous waste accumulation locations in a facility for up to 1 year – such as for waste lube oil accumulation drums.

- It is a good practice to ensure all containers, whether holding hazardous or non-hazardous materials, are labeled with the contents and hazards. In the United States, an unlabeled container is an immediate violation. Labeling is easy enough to do, so there is no sense in incurring this penalty. Ensure all containers are labeled with material, generation date, hazards (as you know them), and other pertinent data. You may need to change these labels based on any test results.
- The hazardous waste storage area normally must be segregated from other storage, with storm and other runoff collected and managed separately from general plant runoff. If the runoff is not contaminated by anything in storage, it can usually be pumped into the plant sewer system, but if it becomes contaminated, it will have to be disposed of separately.
- Often, the haz-waste storage area must be double contained, with an impermeable membrane under it to prevent groundwater contamination.
- Materials in the haz-waste storage area should be in drums, flow-bins, bags, or other sealed containers. If the materials are pyrophoric or self-heating, they should be sealed under an inert gas blanket and monitored for temperature rises.
- The haz-waste area should have adequate firefighting with hazmat handling PPE and materials immediately available to manage any problems.
- Keep all the wastes in the haz-waste area separated by type and specific waste.

Disposal Practices

- Ensure your selected disposal location is licensed and qualified to dispose of the materials you send them. Often facilities are vetted by a company group or team specifically charged with ensuring the quality of disposal facilities to be used. The facilities should be periodically re-reviewed to maintain their qualifications.
- The vetting practices should include hazardous waste testing labs and transportation companies. We depend on these vendors a great deal. Transportation of a solid waste actually presents the greatest risk of something going wrong of all the handling steps for wastes.
- When a hazardous material is sent for reclamation or disposal, be sure you get confirmation in writing that the required disposition has, in fact, occurred. In the regulatory structures, you retain liability for a waste until it is properly disposed of. Many companies have been surprised when they find out that wastes they thought had been destroyed were just stored (or worse, dumped) by someone. The company ends up paying for the cleanup and disposal twice (at the least).

Noise Pollution

Noise Problems and Typical In-Plant/Community Noise Standards

Noise has been widely recognized as a major industrial/environmental problem in most processing plants because of the risk of hearing loss involved when workers are exposed to high noise levels. Occasionally, the noise levels affect the general public: recent focus has been placed on flaring and the resulting noise in communities, as well as the resulting emissions.

The high noise levels in process plants can be attributed to a great number of sources. Major noise sources are compressors, fans, pumps, motors, furnaces, control valves, steam and gas turbines, and piping systems. The noise-generating mechanism for each piece of equipment is complex, but, in most cases, the noise levels can be reduced to desired limits through the implementation of proper noise control measures.

With increasing awareness of the noise problem and its effect on the general public, regulations on noise standards have been adapted in many countries throughout the world. In the United States, the Occupational Safety and Health Act (OSHA) of 1970 (29 CFR 1910.95) and the Noise Control Act of 1972 and later amendments have served as basic guidelines for noise control requirements. OSHA contains maximum permissible sound pressure levels for each daily time of exposure. These guidelines are presented in Table 10 and serve as a basis for in-plant noise criteria for any process plant constructed in the United States.

Conversely, community noise criteria are more variable and depend on a number of factors, including local ordinances, existing noise levels, and the site of the plant with respect to the community. Some typical community noise limits are shown in Table 11.

The art of acoustics and noise control is beyond the scope of this book. Only the most important concepts necessary for an analysis of process plant noise will be considered. The classification of different areas of the community in terms of environmental noise zones is usually determined by the regulatory authorities, based upon the assessment of community noise survey data.

In the United States, the Noise Control Act of 1972, administered by the Environmental Protection Agency, was intended to establish federal noise emission standards. This act serves a broader scope by coordinating all noise control efforts. It places the primary responsibility for noise control on the states. Please refer to current and local regulations.

Table 10 OSHA noise exposure limits

Duration per day, hr	Sound level, DBA
8	90
6	92
4	95
3	97
2	100
1.5	102
1	105
0.5	110
0.5 or less	115

Table 11 Some typical community noise limits

		Noise levels, DBA		
		Noise zone classification		
Receiving land use category	Time period	Rural suburban	Suburban	Urban
One and two family residential	10 pm–7 am	40	45	50
	7 am–10 pm	50	55	60
Multiple dwelling residential	10 pm–7 am	45	50	55
	7 am–10 pm	50	55	60
Limited commercial some dwellings	10 pm–7 am		55	
	7 am–10 pm		60	
Commercial	10 pm–7 am		60	
	7 am–10 pm		65	
Light industrial, heavy industrial	Any time		70	
			75	

Fundamentals of Acoustics and Noise Control

Several factors contribute to this problem:

1. *Sound pressure level:*
   Sound is a fluctuation in the pressure of the atmosphere at a given point. Sound pressure level is expressed as a ratio of the particular sound pressure and a reference sound pressure:

$$\mathrm{SPL} = 10 \log \frac{p^2}{P_{\mathrm{ref}}^2} \tag{25}$$

   where:
   SPL = sound pressure level in dB (decibels)
   p_2 = mean-square amplitude of the pressure variation
   $P_{\mathrm{ref}} = 2 \times 10^{-5}$ N/m^2
2. *Sound power level:*
   Sound power level is defined as the ratio of the particular sound power and the reference power:

$$\mathrm{PWL} = 10 \log \frac{W}{W_{\mathrm{ref}}} \tag{26}$$

   where:
   W = sound power (rate of acoustic energy flow) in acoustic watts
   $W_{\mathrm{ref}} = 10^{-12}$ W
   The relationship between SPL and PWL is

$$\mathrm{SPL} = \mathrm{PWL} + K \tag{27}$$

where:
K = a constant dependent upon geometry and other aspects of the situation

3. *Wavelength:*
   Consideration of the wavelength is important to noise control. It is defined as

$$\lambda = \frac{C}{f} \tag{28}$$

   where:
   λ = wavelength in feet
   C = speed of sound in feet per second
   f = frequency, cycles per second (Hz)

4. *Octave band:*
   An octave refers to a doubling of frequency. Generally, the audible frequency range consists of ten preferred octave bands with following center frequencies: 31.5, 63, 125, 250, 500, 1,000, 2,000, 4,000, 8,000, and 16,000.

5. *A-weighted sound pressure level (dBA):*
   Most noise regulations set the maximum allowable noise limits based on the use of the "A" weighting network which provides a popular means of rating noise. This network is designed to account for the response of the human ear. The other "B" and "C" weighting networks are no longer in common use. Table 12 shows the A-weighting network band corrections for each octave band to convert the sound pressure level (dB) to an A-weighted sound pressure level (dBA).

6. *Adding decibels:*
   The noise levels expressed in decibels cannot be added arithmetically, but the addition should be performed on the basis of energy addition. Therefore, the combined dB level is determined by

$$\mathrm{dB_{total}} = 10\log\sum_{i}^{N} 10\,\mathrm{dB_i}/10 \tag{29}$$

   where:

Table 12 A-weighting network band correction

Octave band (Hz)	Band correction (dB)
63	−25
125	−16
250	−9
500	−3
1,000	−0
2,000	+1
4,000	+1
8,000	−1

dB_{total} = the combined dB level
dB_i = the individual dB level
N = the total number of dB levels

7. *Sound fields:*

   A sound field is a description of the relationship between the PWL of the source and the SPL at different points in the surrounding space.

   (a) *Idealized sound field:*

   The sound field for an idealized sound sources which can be considered as a very small, uniformly pulsating sphere is given by the following equation:

$$\mathrm{SPL} = \mathrm{PWL} - 20\log\ r + K\ \ \mathrm{dB} \tag{30}$$

where:

r = distance from source to measurement point
K = a constant

   (b) *Non-idealized sound fields:*

   i. *Outdoor:*

   The sound field of a directional source radiating over a plane (hemispherical radiation) is given by

$$\mathrm{SPL} = \mathrm{PWL} + 10\log\frac{Q}{\mathrm{r}^2} + 2.5\,\mathrm{dB} \tag{31}$$

where:

Q = directivity factor in the direction of interest
r = distance from source in feet

   ii. *Enclosed space:*

   If source is radiating in an enclosed space, the field equation becomes

$$\mathrm{SPL} = \mathrm{PWL} + 10\log\left(\frac{Q}{4\mathrm{r}^2} + \frac{4}{R}\right) + 10.5\,\mathrm{dB} \tag{32}$$

where:

R = room constant in square feet

8. *Directivity:*

   The directivity factor may be defined as the ratio of the mean-square sound pressure at a given distance in a particular direction to the value which would exist if the source were non-directional. The directivity index is defined by

$$DI = 10\log\ Q \tag{33}$$

   where:

   Q = directivity factor in the direction of interest

   Some typical directivity indices are shown in Table 13.

9. *Sound propagation:*

Table 13 Some typical directivity indices

Location	*Q*	*DI*
Near a single plane surface	2	3 dB
Near the intersection of 2 plane surfaces	4	6 dB
Near a corner formed by 3 plane surfaces	8	9 dB

The propagation of sound waves can be affected by a number of factors. The factors important to noise control consist of sound absorption, transmission loss, barriers, atmospheric, and terrain effects.

(a) *Sound absorption:*

Sound waves traveling in an enclosed space are affected by the absorptive quality of the incident surface. The amount of absorption is expressed as

$$R = \frac{S \cdot ab}{1 - ab} \tag{34}$$

where:

R = room constant in sqft.
S = total interior surface area in square feet
ab = average absorption coefficient

(b) *Transmission loss:*

The sound isolating capability of a wall is defined as

$$TL = 10 \log \frac{1}{\tau} \, \text{dB} \tag{35}$$

where:

τ = transmission coefficient (ratio of transmitted sound intensity to incident sound intensity)

(c) *Barriers:*

Appreciable sound attenuation can often be obtained by interposing a barrier or acoustical shield between the source and receiver. The sound attenuation of a barrier is given approximately by

$$B = 10 \log \frac{20H^2}{\lambda r} \tag{36}$$

where:

B = reduction of the sound pressure level at a given frequency
H = effective barrier height
r = distance from source to barrier
λ = wavelength of sound at the frequency being considered

(d) *Atmospheric and terrain effects:*

Table 14 Molecular effects T = 72 °F; RH = 50 %

Frequency (Hz)	Attenuation (dB per 1,000 ft)
500	1
1,000	2
2,000	3
4,000	8
8,000	15

> The propagation of sound outdoors at long distances may be significantly influenced by atmospheric and terrain effects. Sound propagated through the atmosphere is subject to small energy losses due to molecular effects. This loss is dependent upon air temperature and relative humidity. The molecular effects for 72 °F and 50 % RH are shown in Table 14.

The other effects resulting in noise reduction include attenuation due to substantial vegetation, the effects of uneven terrain and tall buildings, and the effects of wind and temperature gradients. These effects are more complex and, in most cases, can be neglected in a process plant noise analysis.

Coping with Noise in the Design Phase

Because of local, state, and/or federal noise regulations which establish the maximum noise reception limits, permission to build or expand any significant industrial facility may be dependent on predicting that the reception limits set by the controlling agency will not be exceeded.

Consequently, noise control engineering must be commenced early in the design stage. A typical noise control program adopted by some major engineering companies is shown in Fig. 17:

(a) *Plant noise design targets*:
Design criteria should be developed early in the design stage, with considerations given to federal, state, and local laws, company standards, proximity and type of adjacent communities, as well as anticipated community growth patterns.

(b) *Development of mechanical equipment and control valve noise criteria*:
Criteria for individual items of equipment will be developed to meet plant noise design objectives and will be made part of inquiry specifications for all noise-generating equipment.

(c) *Preparation of preliminary noise contour map*:
Noise reception levels will be predicted using the engineering company's in-house estimate data bank and noise prediction computer programs.

(d) *Preparation of noise control budget*:
A budget is prepared which identifies funds necessary to implement noise control measures.

(e) *Plot plan assistance:*

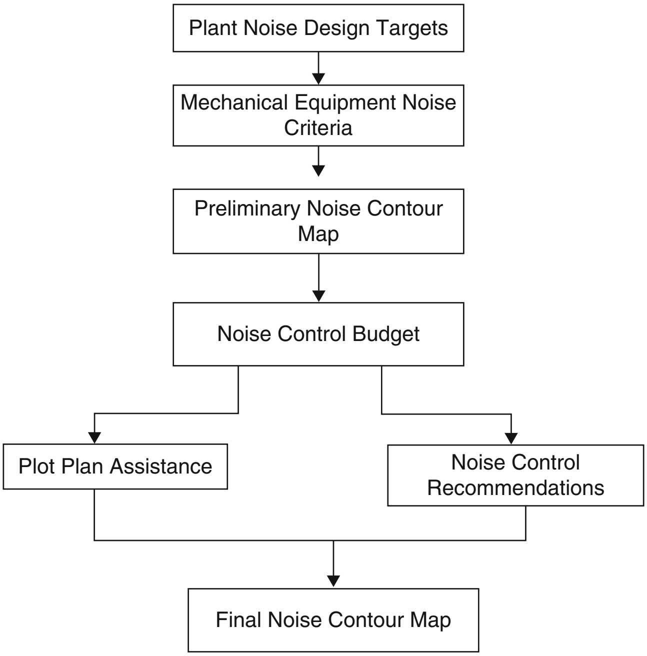


Fig. 17 A typical noise control program flowchart

Equipment location can be optimized based on projected noise levels which will minimize the need of attenuation treatment.

(f) *Noise control recommendations:*
Recommendations for noise attenuation are prepared based on the contribution of all major equipment to the composite noise level of a given plant area. It may be necessary to apply special coatings, insulations, or acoustical lagging (e.g., lead or heavy PVC) to meet the required noise levels.

(g) *Preparation of final noise contour map:*
After final noise level data have been obtained, the plot plan has been finalized, and any noise control measures have been implemented, a noise contour map can be prepared. The noise contour map identifies that the plant noise design objectives have been met. This contour map is normally prepared using the company's own modeling program. Alternatively a proprietary program can be leased from an appropriate software company.

An effective noise control program requires an analysis in the early stage of plant design, when no equipment has been purchased. The most efficient and economical approach to noise control is to include noise control features as an integral part of equipment design through equipment specifications. An optimal plot plan arrangement can also minimize the need for attenuation treatment by strategically locating noisy equipment or positioning process areas or known noise sources at maximum distances from sensitive areas.

The task of predicting noise levels to be used in the design phase can be overwhelming without the aid of the computer. A typical project may involve hundreds of thousands of noise sources, and attempting to do the noise level predictions by hand is almost impossible. Normally a computer program is used to predict the community/in-plant noise levels. The features of this type of program are discussed in the next section.

A Typical Community/In-Plant Noise Program

The noise pollution cycle is one of emission, propagation, and reception. A computer program is usually developed to simulate the noise propagation from several types of noise sources with different configurations. Here we will describe the necessary capabilities of such a program and its application to plant design.

1. *Capabilities:*
   The computer program calculates sound pressure levels generated by single or multiple noise sources at specified grid points or special receptors. This program should utilize a simple algorithm to simulate the propagation of four different source models. These models include point, line, discrete points on a line, and plane sources.
2. *The mathematical model:*
   The basic equation used in the program is

$$\mathrm{SPL} = \mathrm{PWL} + 10\log[F(\mathrm{R})] + DI + K - AE \tag{37}$$

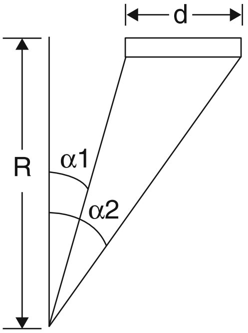
where:
SPL = sound pressure at any receptor in dB
PWL = source sound power level in dB
10 log[F (R)] = distance attenuation factor for various types of source which will be defined in the following paragraphs in dB
DI = directivity index in dB
K = characteristic resistance of air in dB
AE = total excess attenuation factor (molecular absorption, ground absorption, screening effect, barrier effect, etc.) in dB

- *Distance attenuation* F(R):
  (A) *For a point source:*

$$F(R) = \frac{1}{R^2} \tag{38}$$

where:

Fig. 18 Continuous line source



R = distance between source and receptor

(B) *For a continuous line source:*

$$F(R) = \frac{\alpha_2 - \alpha_1}{R_{\mathrm{Od}}} \tag{39}$$

All terms are defined in Fig. 18.

(C) *For discrete sources on a line:*

$$F(R) = \sum_{n=1}^{N} \frac{1}{R_n^2} \tag{40}$$

where:

N = the number of sources on the line

R = the distance between receptor and each source

(D) *For a plane source:*

$$F(R) = 1/A \int_{-L/2}^{L/2} \int_{-L/2}^{L/2} R\, dxdy \tag{41}$$

where:

R = distance from the receptor to a differential area *dxdy* on the plane

All terms are defined on Fig. 19.

- *Excess attenuation A:*

  Excess attenuation due to ground and molecular absorption can be entered as input data. When these data are not entered, the default values shown in Table 15 should be used. In-plant shielding corrections may be included in the ground absorption correction. Corrections due to the effect of wind, temperature gradients, rain, sleet, and barriers can be added later.

3. *Input data requirements:*

   The requirements for each noise source are basically the source sound power spectrum, the source location, and the desired noise level prediction model. Additionally, excess attenuation factors including molecular and ground absorption data can be input if available.

Fig. 19 Plane source

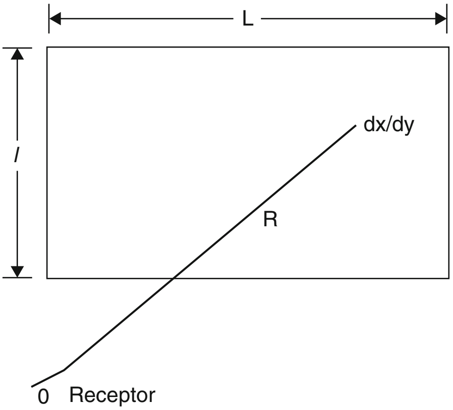


Table 15 Default values for excess attenuation

Frequency, Hz	Ground absorption, dB	Molecular absorption, dB/1,000 ft
63	0	0
125		0
250		0.3
500		1.0
1,000		2.0
2,000		3.0
4,000		6.0
8,000		11.0

4. *Output:*
   In the program described here, all the input data would be summarized and the calculation results will be available electronically or in hard copy. The calculated octave band sound pressure level, overall sound pressure levels, and A-weighted sound pressure levels will be tabulated for all the special receptors specified. The calculated A-weighted sound pressure levels for all grid points will also be listed. A contour map can be produced.
5. *Applications:*
   The community/in-plant noise program described here can be used to perform the following applications:
   - Estimating the net noise impact due to a prospective industrial activity
   - Checking plant design for compliance with noise regulations
   - Establishing noise emission levels and plant design necessary to comply with the applicable environmental regulations

As with other computer programs, the accuracy of computer-calculated noise levels depends on the accuracy of the input data as well as the application of the model selected for a particular noise source.

Environmental Discussion Conclusion

Complete compliance with environmental regulations today is part of the right to operate a petroleum processing facility. Some refiners have found themselves on the wrong side of the regulations, sometimes resulting in shutdown until they comply. Some regulations contain provisions under which criminal prosecution is possible.

Good, diligent, comprehensive design and operating practices along with awareness of the requirements will keep a plant operating cleanly and efficiently.

Appendix 1 Partial Pressures of H_2S and NH_3 Over Aqueous Solutions of H_2S and NH_3

This appendix includes Figs. 20, 21, 22, 23, 24, 25, 26, 27, 28, and 29 for partial pressures of H_2S and ammonia over aqueous solutions of H_2S and NH_3. The figures are in the next few pages. Refer to Appendix 2 for the interpretation and use of these charts.

Appendix 2 Example of the Design of a Sour Water Stripper with No Reflux

Specifications

Feed: The tower is to be designed to handle 200 gpm (at 100 °F) of sour water containing 10,000 ppm of H_2S and 7,500 ppm of NH_3 (by weight).

Unit: The unit shall be a trayed column using sieve trays (efficiency of 0.5) with no reflux.

Steam rate: Refinery 50 psig saturated steam shall be used at a rate of 1.3 lbs/gpm of feed.

Tower pressure and temperature: The vapors leaving the tower top shall have sufficient pressure to enter a “rat-tail” burner in a nearby heater. The tower top pressure shall be 20 psia. The feed entering the top tray shall be preheated to a temperature of 200 °F. The total tower pressure drop shall be 2 psi.

Stripped water specification: The tower shall be designed and operated to remove 99.0 % of the H_2S in the feed and 95 % of the NH_3.

The Design

Assume the stripping will be accomplished using four theoretical trays. Then at an efficiency of 0.5, the number of actual trays will be eight. The pressure drop per tray will be 0.25 (i.e., 2 psi/8 trays).

Calculate Feed Mass Per Hour

Water at 100 °F has a specific volume of 0.1207 gal/lb.

Then 200 gpm of water $= \frac{200 \times 60}{0.1207} = 99,420 \text{lbs/hr}.$

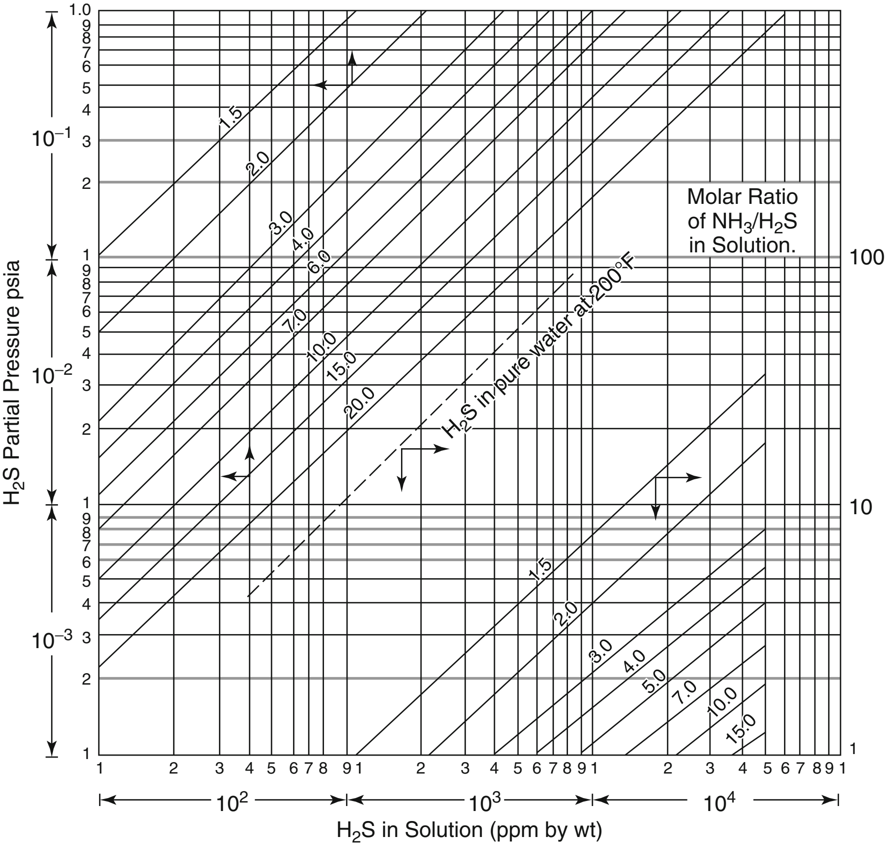


Fig. 20 Partial pressure of H_2S over aqueous solutions of H_2S and NH_3 at 200 °F

The feed will be as follows:

	lbs/h	Moles/h	
Water	99,420	5,523.3	
NH_3	745.65	43.86	(7,500 ppm by wt)
H_2S	994.2	29.24	(10,000 ppm by wt)

Calculate Stripping Steam

Tower bottom pressure will be 20 psia + (8 × 0.25) = 22 psia.

From steam tables, tower bottom temperature will be water at 22 psia = 233 °F.

Feed temperature = 200 °F.

Then steam used for heating = 99,420(33/924) = 3,550 lbs/h.

And steam used for stripping = 15,550–3,550 = 12,000 lbs/h.

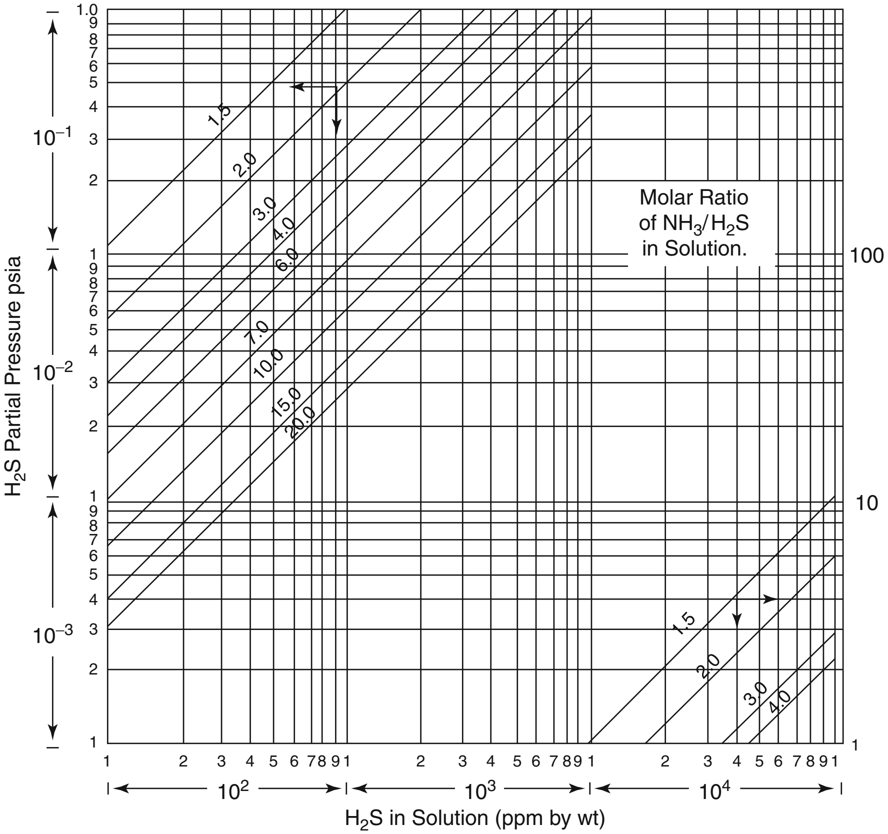


Fig. 21 Partial pressure of H_2S over aqueous solutions of H_2S and NH_3 at 210 °F

Calculate Stripped Water Quantity and Composition

Stripped water shall contain feed water plus condensate. 99,420 + 3,550 = 102,970 lbs/h.

NH_3 in stripped water shall be 5 % of total = 37.28 lbs/h = 2.19 moles/h = 361 ppm by wt.

H_2S in stripped water shall be 1 % of total = 9.94 lbs/h = 0.29 moles/h = 100 ppm by wt.

Calculate the Overhead Vapor Partial Pressures

Overhead vapor leaving the tower V_o will be as follows:

	Moles/h	lbs/h	PP psia
NH_3	41.67	708	1.13
H_2S	28.95	984	0.78
Steam	667	12,000	18.09
Total	737.62	13,692	20.00

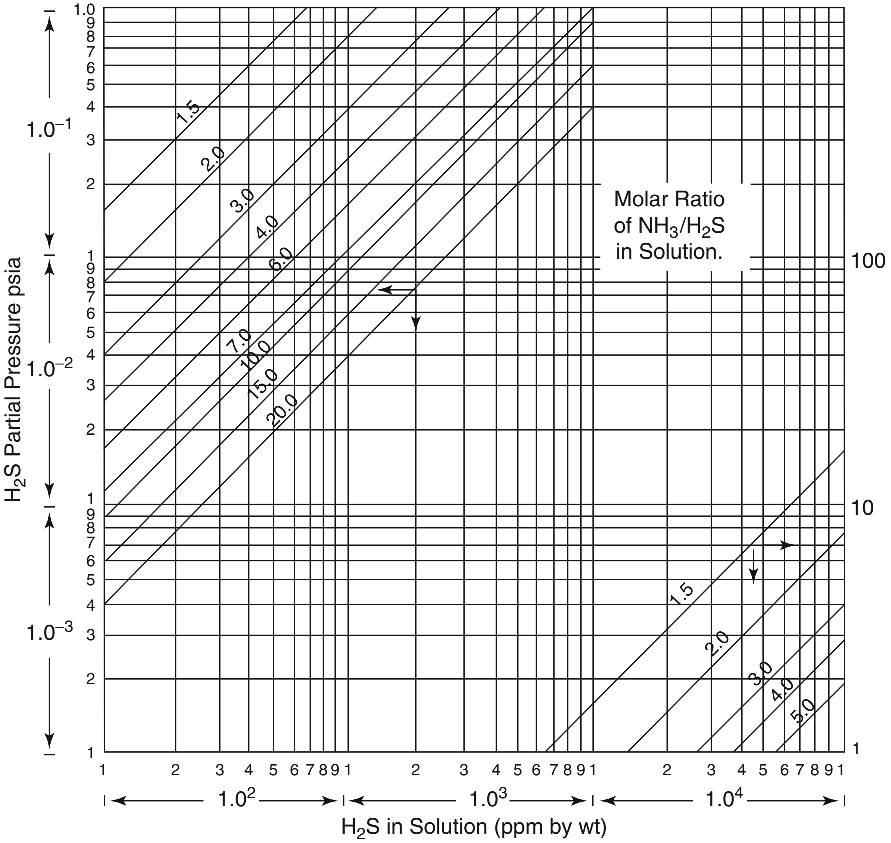
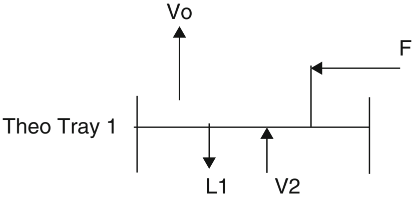


Fig. 22 Partial pressure of H_2S over aqueous solutions of H_2S and NH_3 at 220 °F

Temperature of top theoretical tray is steam at a saturation pressure of 18.09 psia = 223 ° F.

Top Tray Calculation



Assume a ratio of NH_3/H_2S as 3.8 moles, that is, (17/34) × 3.8 = 1.9 by wt.

From Appendix 1, Fig. 28, NH_3 at a partial pressure of 1.13 will be 4,600 ppm by wt and H_2S ppm by wt will be 4,600/1.9 = 2,421 ppm.

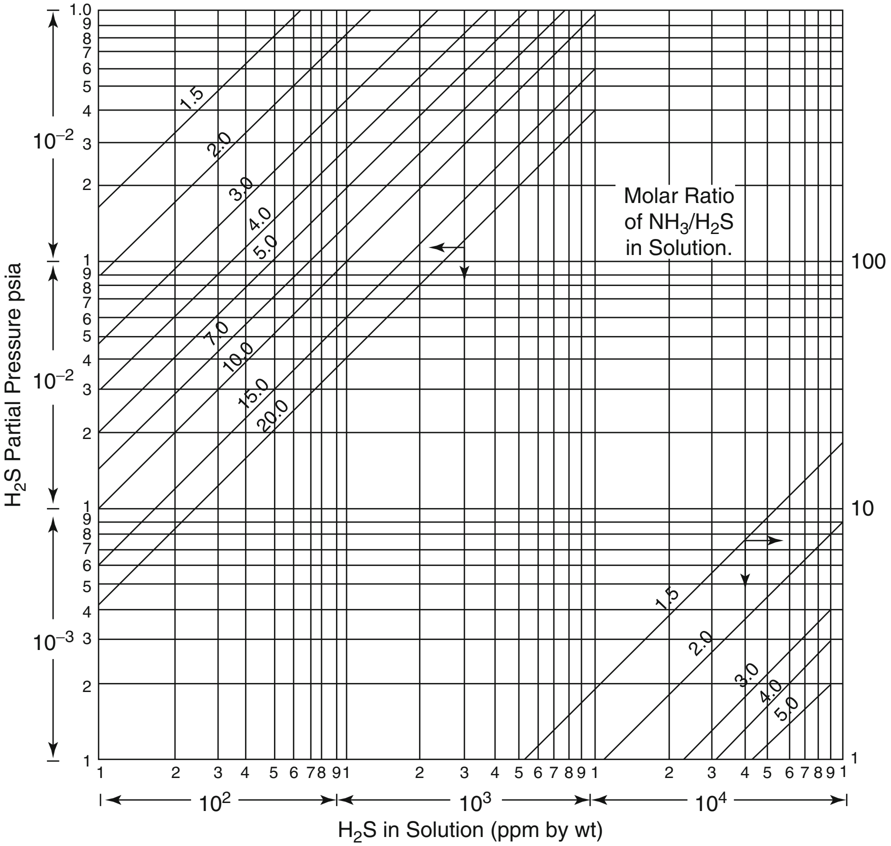


Fig. 23 Partial pressure of H_2S over aqueous solutions of H_2S and NH_3 at 225 °F

From Fig. 23 partial pressure of $H_2S = 0.75$ which is acceptably close to 0.78, which was established.

Note: Should the partial pressure of H_2S be substantially different to that for V_o, then a different ratio of the two components would have to be chosen and the calculation repeated.

Calculate Liquid from Top Tray L_1

	ppm	lbs/h	Moles/h
NH_3	4,600	457	26.9
H_2S	2,421	241	7.08

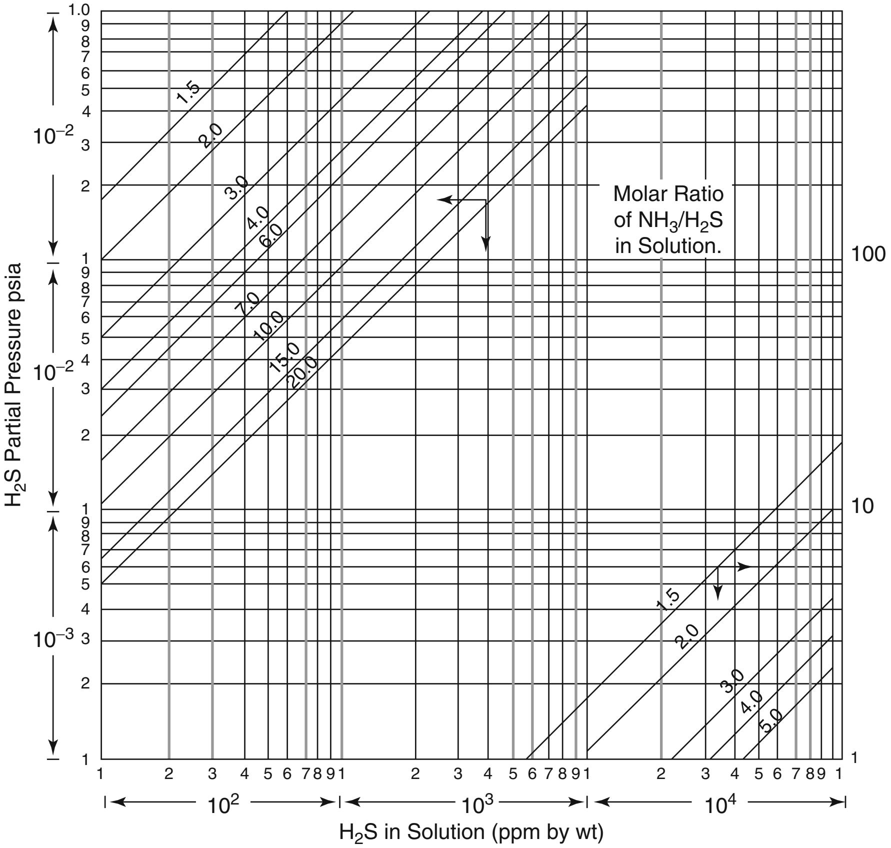


Fig. 24 Partial pressure of H_2S over aqueous solutions of H_2S and NH_3 at 230 °F

Calculate Vapor from Theo Tray 2 V_2

Moles vapor for NH_3 and H_2S will be those moles in $V_o + L_1 - F$

Pressure on Theo 2 will be (1/0.5) = 2 actual trays at 0.25 psi pressure drop = 20 psia + 0.5 = 20.5 psia.

	Moles/h	PP psia	Notes
NH_3	24.71	0.73	
H_2S	6.79	0.2	
Steam	667	19.57	
Total	698.5	20.5	Tray temp (from steam tables = 226 °F)

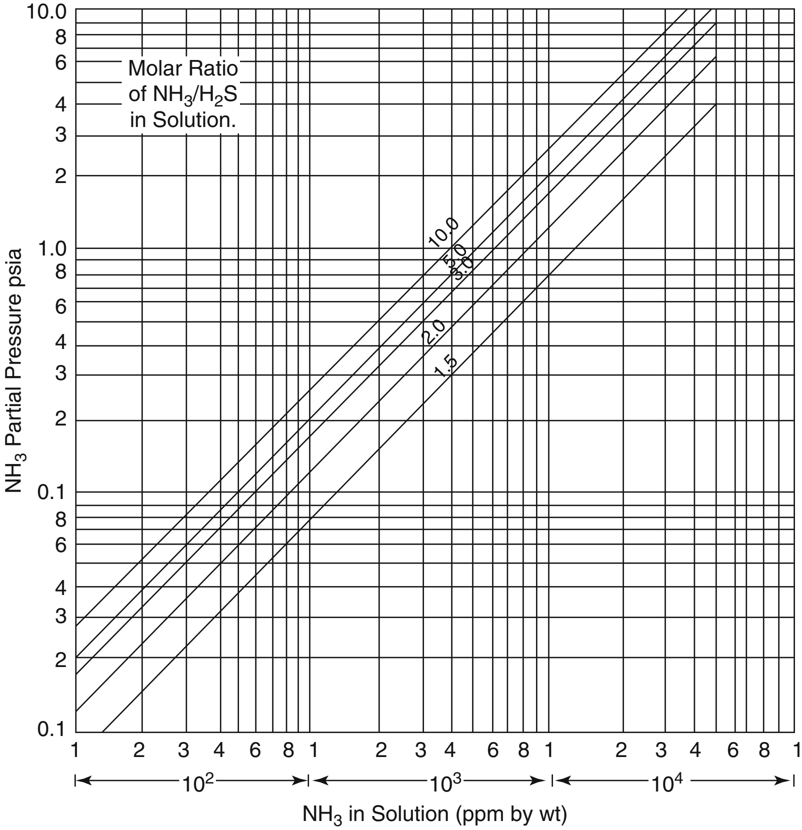
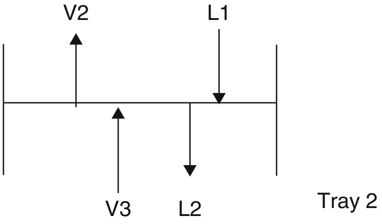


Fig. 25 Partial pressure of NH_3 over aqueous solutions of H_2S and NH_3 at 200 °F



Calculate Balance Over Theoretical Tray 2

Assume NH_3/H_2S ratio is 5.0 molar and 2.5 ppm by weight.

NH_3 at a PP of 0.73 and 5.0 molar ratio = 2,400 ppm by wt (from Appendix 1, Fig. 29).

H_2S ppm is 2,400/2.5 = 960.

From Fig. 24, H_2S ppm = 0.19, which is a satisfactory match.

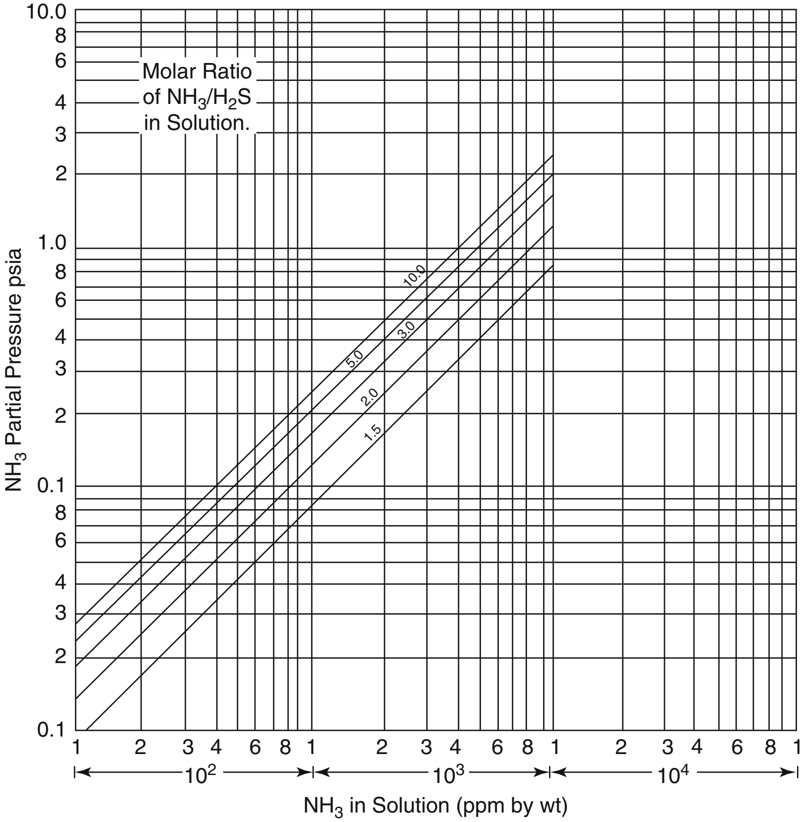


Fig. 26 Partial pressure of NH_3 over aqueous solutions of H_2S and NH_3 at 210 °F

Liquid from Tray 2. L_2

	ppm	lbs/h	Moles/h
NH_3	2,400	278.4	16.37
H_2S	960	95.5	2.81

Vapor from Tray 3 V_3

Total tray pressure = 21 psia and temperature is 231 °F:

$$\text{Vapor from tray 3} = V_2 + L_2 - L_1$$

	Moles/h	PP psia
NH_3	14.18	0.44
H_2S	2.52	0.08

(*continued*)

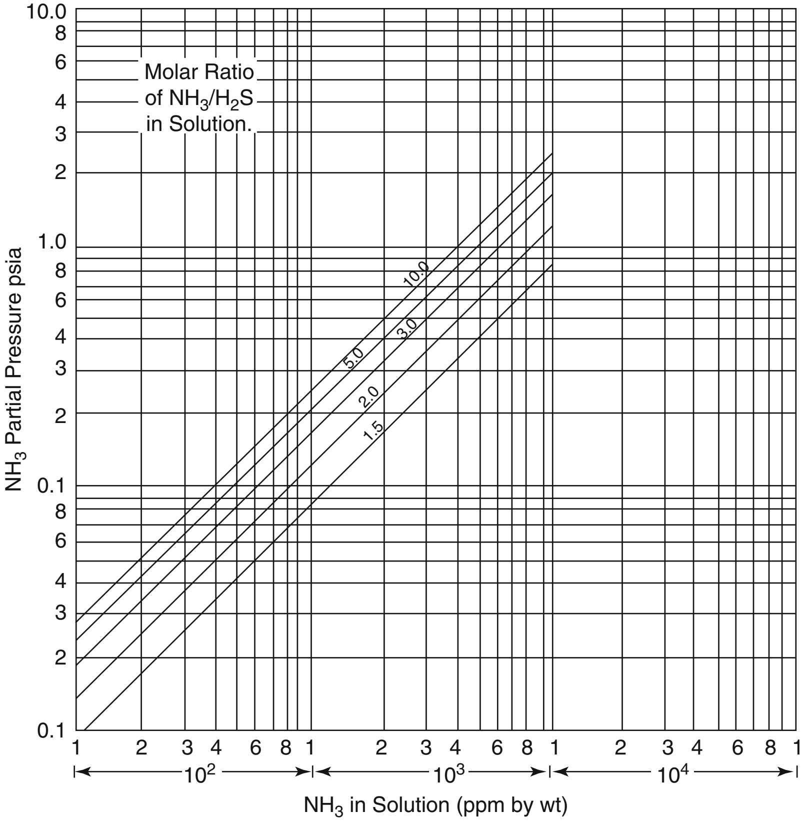
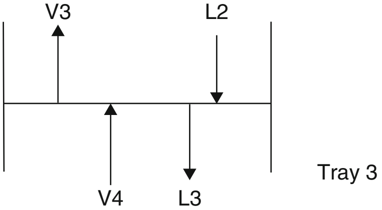


Fig. 27 Partial pressure of NH_3 over aqueous solutions of H_2S and NH_3 at 220 °F

	Moles/h	PP psia
Steam	667	20.52
Total	683.7	21.00

Calculate Balance Over Theoretical Tray 3



Assume NH_3/H_2S ratio is 6.5 molar and 3.25 by weight.

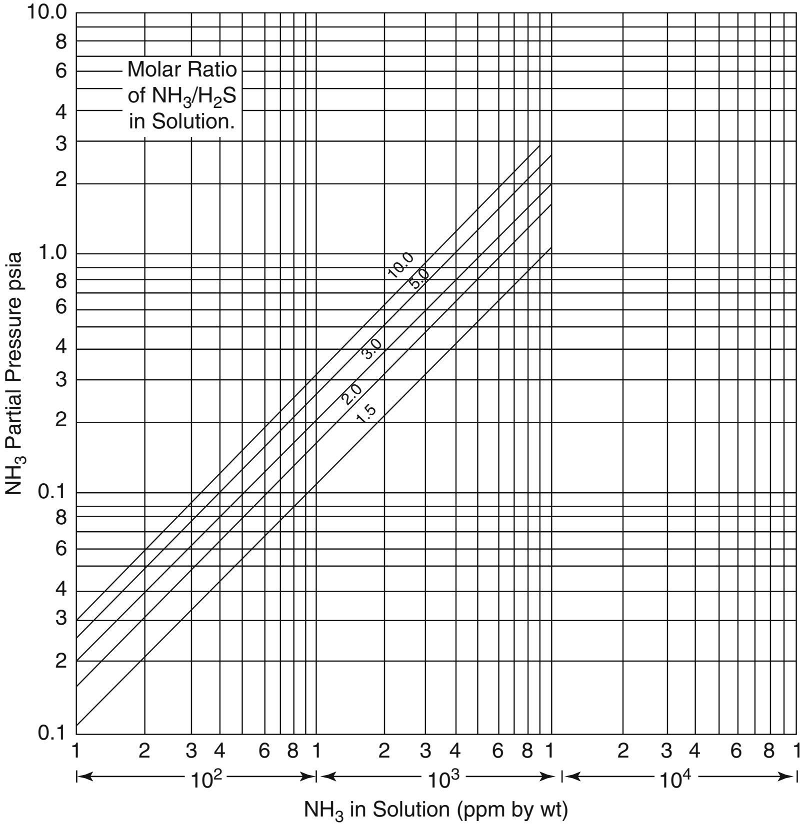


Fig. 28 Partial pressure of NH_3 over aqueous solutions of H_2S and NH_3 at 225 °F

NH_3 ppm from Fig. 29 = 1,600 ppm by weight.

H_2S is 493 ppm from Fig. 25. PP of H_2S is 0.085, which is a satisfactory match.

Liquid from Theoretical Tray 3, L_3

	ppm	lbs/h	moles/h
NH_3	1,600	159.1	9.35
H_2S	493	49	1.3

Vapor from Theoretical Tray 4, V_4

Tray pressure 21.5 psia temperature 232 °F

$$V_4 = V_3 + L_3 - L_2$$

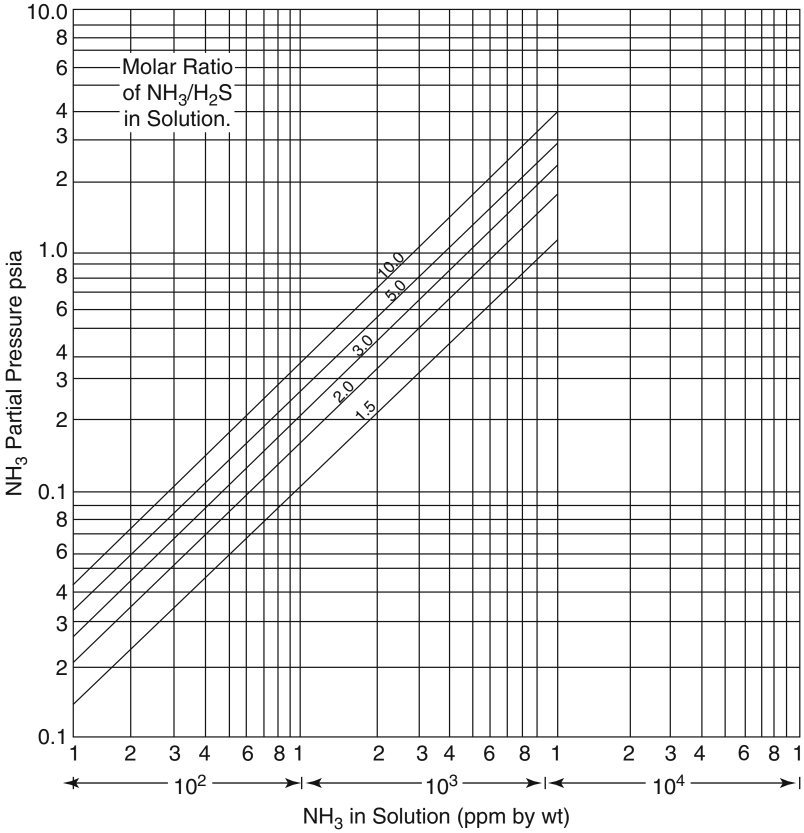
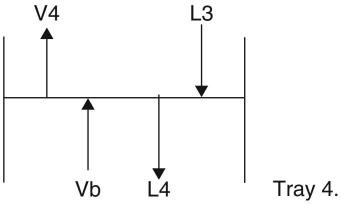


Fig. 29 Partial pressure of NH_3 over aqueous solutions of H_2S and NH_3 at 230 °F

	Moles/h	PP psia
NH_3	7.16	0.23
H_2S	1.01	0.032
Steam	667	21.24
Total	675.17	21.5

Calculate Balance Over Theoretical Tray 4



Assume NH_3/H_2S ratio is 6.6 molar and 3.3 by weight.

NH_3 ppm from Fig. 29 is 610.

H_2S ppm is 185. PP psia of H_2S from Fig. 25 is 0.032, which is a satisfactory match.

Liquid from Theoretical Tray 4, L_4

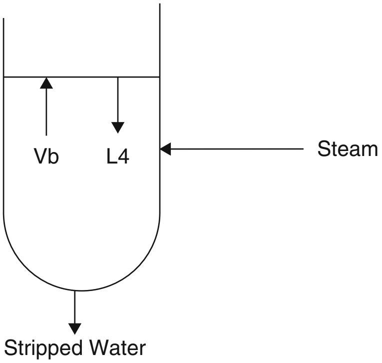
	ppm	lbs/h	Moles/h
NH_3	610	60.6	3.57
H_2S	184.8	18.4	0.54

Vapor from Tower Bottom V_b

Pressure 22 psia temperature 233 °F

$V_b = V_4 + L_4 - L_3$

	Moles/h	PP psia
NH_3	1.38	0.045
H_2S	0.25	0.008
Steam	667	21.947
Total	668.83	22.0



Calculate the Bottom of the Tower

Assume NH_3/H_2S ratio is 7.0 molar and 3.5 by weight.

NH_3 ppm from Fig. 29 is 180.

H_2S ppm is 51.4. PP psia of H_2S from Fig. 25 is 0.008 (extrapolated), which is a satisfactory match.

Contaminants in stripped liquid product:

	ppm	lbs/h
NH_3	180	17.9
H_2S	51	5.1

Conclusion

The tower will handle 200 gpm of sour water and remove 97.6 % weight of NH_3 and 99.49 % weight of H_2S using eight actual trays and a steam rate of 1.3 lbs/h per gpm of feed. Feed will be preheated to 200 °F by heat exchange with tower bottoms before entering on the top tray of the tower.

Appendix 3 Example Design of an API Separator

Specification

We are asked to design an oil/water separator to handle the normal quoted rainfall and process waste from a 4,500 BPSD hydro-skimming refinery. The quantity of inflow to the separator is estimated to be 600 gpm. The normal rundown temperature for this stream is taken as 100 °F. The design of the separator shall be in accordance with the appropriate section of the *API Manual* – sixth edition. The following data shall be used in the design:

Specific gravity of water	0.995
Specific gravity of the oil	0.890
Viscosity of water	0.7 cP
Diameter of the oil globules	0.006 in

The oil shall be removed from the separator by means of oil skimming pipes and an oil sump designed to meet the oil influent content of 400 ppm by volume.

The Design

The rising rate of the oil is calculated from the equation

$$V_{\mathrm{r}} = 6.69 \times 10^4 \times \frac{d^2 \Delta S}{\mu}$$

where:

V_r = rising rate of oil in ft/min.
d = diameter of oil globule in inches = 0.006 inches
ΔS = difference in the SGs of oil and water phases = 0.105
μ = viscosity of the water phase in centipoise = 0.7

Then

$$\begin{aligned} V_{\mathrm{r}} &= \frac{6.69 \times 0.36 \times 0.105}{0.7} \\ &= 0.361 \mathrm{ft/min.} \end{aligned}$$

V_h = the horizontal velocity of the effluent = 15 × V_r but not to exceed 3 ft/min; so use 3 ft/min for the design.

$$\text{Volumetric rate of flow} = Q = \tfrac{600}{7.48} = 80\text{cuft/min}$$

$$\text{Minimum cross sectional area of flow} = \tfrac{80}{3} = 26.7\,\text{sqft say}\,27\,\text{sqft.}$$

API recommends the following limits:

Depth – 3–6 ft.
Width – 6–20 ft
Ratio of depth to width – 0.3–0.5
Width of section = 27/3 = 9 f. which meets the API recommended depth to width ratio.

Calculating the effective separation length of unit:

The API manual gives the following factors to include in the determination of the unit's length.
Turbulence factor $F_t = 1.22$
Short circuit factor $F_s = 1.2$
The length is then calculated by the expression

$$\begin{aligned} L &= (F_t + F_s)(V_H/V_r) \times \text{depth.} \\ &= 2.42 \times 8.31 \times 3 \\ &= 60\,\text{ft.} \end{aligned}$$

This 60 f. is the length between the oil retention baffles (see Fig. 13).

Recommendations regarding the types and sizes of the internal equipment are found in the appropriate section of the API manual. A brief description of these is given in the text of this chapter.

References

J.S. Alshammari et al., Solid waste management in petroleum refineries. Am J Environ Sci **4**(4), 353–361 (2008). Suez Canal University, 2008

M.R. Beychok, *Aqueous Wastes from Petroleum and Petrochemical Plants* (Wiley, New York, 1967)

M. Beychok, Image: Claus sulfur recovery.png; Wikimedia Commons, 2 Mar 2012. Accessed Feb 2014

C.E. Baukal (John Zink Co. LLC, 2008), Article: NOx 101: a primer on controlling this highly regulated pollutant, Process Heating reprint, Feb 2008. Accessed Feb 2014

CAI-Asia, Fact sheet: Sulfur dioxide (SO_2) standards in Asia, Clean Air Initiative for Asian Cities, CAI-Asia Fact Sheet No. 4, Aug 2010, http://cleanairinitiative.org/portal/sites/default/files/documents/4_SO2_Standards_in_Asia_Factsheet_26_Aug_2010.pdf. Accessed Feb 2014

D.A. Dando, D.E. Martin (CONCAWE, 2003), Report 6/03: A guide for reduction and disposal of waste from oil refineries and marketing installations, Brussels, Nov 2003, https://www.concawe.eu/content/default.asp?PageID=569. Accessed Feb 2014

K. den Haan, Presentation to Japan Petroleum Energy Center conference: Water in EU: legislation & the refining industry's response (CONCAWE, 2011), http://www.pecj.or.jp/japanese/overseas/conference/pdf/conference11-12.pdf. Accessed Feb 2014

W.L. Echt (Union Carbide Corp.) and C.J. Wendt (The Ralph M. Parsons Co.), Paper: Reduce sulfur emissions from Claus sulfur recovery unit tail gas treaters, presentation to AIChE National Meeting, 1993

Fuelling Europe's Future website, Item: Fuelling Europe's future: impact of EU legislation (2013), http://www.fuellingeuropesfuture.eu/en/refining-in-europe/economics-of-refining/demand-trends. Accessed Feb 2014

GPSA, *Book: Engineering Data Book,* 10th edn. (Gas Processors Suppliers Association, Tulsa, 1987)

T. Huntsman (ed.), S. Watson, et al., Article: Study compares COS-removal processes (Pearl Development Co., 2003), www.ogj.com, 101, 36. 22 Sep 2003

India Environment Portal, Article: Effluent and emission standards for oil refineries: guidelines 8 May 2008, www.indiaenvironmentportal.org. Accessed Feb 2014

IPIECA Operations Best Practice Series, Best practice entitled: Petroleum refining water/wastewater use and management (2010), http://www.ipieca.org/publication/petroleum-refining-waterwastewater-use-and-management. Accessed Feb 2014

IPIECA, Publication: Refinery air emissions management: Guidance for the oil and gas industry, IPIECA (2012), http://www.ipieca.org/publication/refinery-air-emissions-management. Accessed Feb 2014

M. Leavitt et al. (EPA, 2004), Technical support document for the 2004 effluent guidelines program plan, Section 7, U.S. Environmental Protection Agency, Office of Water, EPA-821-R-04-014, Aug 2004. Accessed Feb 2014

Matheson Tri-Gas, Inc., MSDS: ethyl mercaptan (2009), Accessed Feb 2014

Michigan Department of Resources and Environment, Guidance document: Guidelines for selecting dust suppressants to control dust and prevent soil erosion, Feb 2010. Accessed Feb 2014

M. Mihet et al., Low temperature hydrogen selective catalytic reduction of NO on Pd/Al_2O_3. Rev Roum Chim **56**(6), 659–665 (2011). Academia Română, 2011

W.L. Nelson, *Petroleum Refinery Engineering*, 4th edn. (McGraw-Hill Book Co., New York, 1969)

P.K. Niccum et al. (KBR, 2002), Paper: FCC flue gas emission control options, Paper AM-02-27, NPRA 2002 Annual Meeting. 17–19 Mar 2002

Praxair, Inc. MSDS: carbon dioxide, Jul 2007. Accessed Feb 2014

M. Quinlan, A. Hati (KBR, 2010), Article: Processing NH_3 acid gas in a sulphur recovery unit, Apr 2010, www.digitalrefining.com Accessed Feb 2014

M. Rameshni, Paper: Selection criteria for Claus tail gas treating processes (WorleyParsons, Approx. 2008), http://www.worleyparsons.com/CSG/Hydrocarbons/SpecialtyCapabilities/Documents/Selection_Criteria_for_Claus_Tail_Gas_Treating_Processes.pdf. Accessed Feb 2014

Sciencelab.com, MSDS: methyl alcohol, 21 May 2013. Accessed Feb 2014

D. Seligsohn, Article: China's new regional air quality regulations: a win-win for local air quality and the climate (China FAQs, 2013), www.chinafaqs.org, 14 Nov 2013. Accessed Feb 2014

Shell Global Solutions, Fact sheet: Sulfinol-M (2012). Accessed Feb 2014

Tanner Industries, Inc., MSDS: aqua ammonia, Feb 2006. Accessed Feb 2014

The Lubrizol Corp., MSDS: Sulfrzol 54. 4 Jan 2013

U.S. EPA, Reference document (Draft): Hazardous waste listings: a user-friendly reference document, U.S. Environmental Protection Agency, Mar 2008, http://www.epa.gov/osw/hazard/refdocs.htm. Accessed Feb 2014

U.S. EPA, Public outreach presentation: Addressing air emissions from the petroleum refinery sector: risk and technology review and new source performance standard rulemaking, U.S. Environmental Protection Agency (2011), http://www.epa.gov/apti/video/10182011Webinar/101811webinar.pdf. Accessed Feb 2014

U.S. EPA Fact sheet: Sulfur dioxide: health, U.S. Environmental Protection Agency, 28 Jun 2013, http://www.epa.gov/airquality/sulfurdioxide/health.html. Accessed Feb 2014

Wikimedia Commons, Image: Airborne particulate size chart.jpg, 30 Sep 2010. Accessed Feb 2014

Wikipedia and Wikimedia images. Multiple items accessed Feb 2014

Wikipedia, Article: Selective catalytic reduction, 6 Jan 2014. Accessed Feb 2014

Wikipedia, Article: Selective non-catalytic reduction, 15 Mar 2013. Accessed Feb 2014

Wikipedia, Article: Merox, www.wikipedia.org, 15 Oct 2013. Accessed Feb 2014

WorleyParsons, White paper: Options for handling vent gases in sulfur plants, http://www.colteng.com/CSG/Hydrocarbons/SpecialtyCapabilities/Documents/Options_for_Handling_Vent_Gases_in_Sulfur.pdf. Accessed Feb 2014

Part IV

Safety Systems

Safety Systems for Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_20

Abstract

The processing of petroleum can be an inherently hazardous activity. The processes we use are handling a flammable material. They use strong, often hazardous, chemicals and employ high pressures and temperatures to convert the oil into finished products. All these factors present safety risks for both personnel and those living near a process facility. Still, the industry experiences very few incidents while processing millions of barrels of oil each day. Refineries place a high value on safety. This chapter discusses four key areas which contribute toward safety performance: personal protective equipment and systems, Process Safety Management (PSM), pressure safety, and temperature safety. A relief valve sizing example is presented.

Keywords

Refinery • Safety • PPE • Process safety management • PSM • Relief • Runaway • Facility siting

Petroleum Processing Safety

The processing of petroleum can be an inherently hazardous activity. The processes we use are handling a flammable material. They use strong, often hazardous, chemicals and employ high pressures and temperatures to convert the oil into finished products. All these factors present safety risks for both personnel and those living near a process facility.

In spite of the possible risks, very few significant incidents occur as the industry processes millions of barrels of oil each day. It is, in fact, statistically one of the safest industries in which to work in. The total personnel incident rate (recordable incidents per 100,000 man-hours) was 0.9 in 2012 for refining and 0.4 for petrochemicals. Few industries approach these low values. Most that do are light industries, like retail sales and electronic product manufacturing. All industries together had an incident rate of 3.7 in 2012.

This is not to say that incidents do not happen. Because of the materials present, extreme conditions, and huge volumes involved in petroleum processing, when an incident does occur, it is usually large and garners a lot of media and regulatory attention.

The petroleum industry's excellent safety history is not by "accident." A great deal of focus is placed on plant safety from design through operations to final shutdown. The focus is on ensuring that petroleum processing facilities are safe places to work and that the public is protected from harm resulting from any incidents in the facilities.

In this chapter, we will focus on several areas of safety:

- Personal protective equipment and systems
- Process safety management
- Pressure safety
- Temperature safety

Additional safety discussions are included in many areas of this handbook. These include the topics entitled:

"▶ Process Controls in Petroleum Processing"
"▶ Environmental Control and Engineering in Petroleum Processing"
"▶ Hazardous Materials in Petroleum Processing"
"▶ Fire Prevention and Firefighting in Petroleum Processing"

We will start with a general discussion of personnel protection practices.

Personal Protective Equipment and Systems

One of the primary and immediate focuses of safety in a facility is personnel safety. You must be able to protect your people from harm.

The facility design, equipment codes and standards, process design, control systems, and many other practices all work together to provide basic layers of protection for people working in a plant. These, however, can only go so far in protecting the workers. The use of personal protective equipment (PPE) provides an additional layer of protection.

In most facilities, the following are the minimum PPE required for a person entering a process area:

- Hard hat
- Flame-retardant outer clothing (like Nomex®) – long sleeves
- Safety glasses, usually with side shields
- Work boots, usually steel or safety toe

There are specific, applicable regulations that define the performance requirements for each of these PPE items. Companies often go above and beyond the regulations in their local specifications. Hard hats, in the USA, for instance, are specified by ANSI Z89.1-2009. Safety glasses normally must meet the OSHA specification ANSI Z87.1-2010.

In addition, specific PPE may be required in certain areas of the plant or during certain activities. Examples include:

- Hearing protection (earplug and/or muffs) in high-noise areas
- Gloves for general work or impermeable gloves for chemicals
- Goggles and face shield in chemical handling areas
- Personal monitors for H_2S, CO, and other hazardous substances potentially in an area
- Acid suits in acid handling areas
- Full PVC or neoprene suit with supplied air for HF acid
- Fresh air breathing apparatus for potential exposure to hazardous atmospheres or O_2 deficiency
- Respirators of various kinds (dust, chemical, etc.) appropriate to a potential hazard
- Fire suits for intense fires or high radiant heat areas
- Turnout gear for firefighting
- Man-down monitors
- Radios

Plants also contain a number of systems designed to protect workers from harm in the event of a problem. Included in these systems are the following:

- Safety showers and eyewashes (see the topic "▶ Utilities in Petroleum Processing")
- Firefighting systems (see the topic "▶ Fire Prevention and Firefighting in Petroleum Processing") – including deluges and water curtains
- Blast-resistant buildings and shelters
- Emergency shutdown buttons at safe distances from equipment
- Alarm notification systems
- Area public address systems
- Emergency breathing air stations and SCBAs throughout units
- Unit log in/log out system for anyone entering an operating area
- Installed area monitors with alarms for hazardous atmospheres like H_2S or CO
- Operator training
- Fire and emergency response plans and systems

This heavy focus on personnel protection is reflected in the low industry incident rates.

The tracking of personnel incident rates is important to comply with regulations; but what makes the difference between just tracking and developing improvements in personnel safety are (1) analyzing the data for trends and (2) taking action on undesirable trends. You can get ahead of the game by gathering data on "near misses," where an incident came close to occurring or could have happened under slightly different conditions. There will normally be many related near misses for each type of incident. Identifying and discussing those near misses with your workers can help build awareness and influence attitudes toward safety that will prevent future incidents. You have to have the information and get it to the workers to be effective, however.

Entire books can be written (and have been written) on improving personnel safety. You must always be mindful and proactive in protecting the workers to operate safely.

Process Safety Management

For many years, the focus of safety in industry has been on the protection of workers from generally recognized hazards and the programs focused on how the employee interacted with the facility and processes. This emphasis worked up to a point, greatly improving personal safety. In the processing industry, however, the actual chemical and physical processes employed can also create significant safety risks. Under a traditional safety program approach, the process received limited attention.

This situation changed in the 1980s and 1990s, after a series of major process safety incidents resulted in multiple fatalities, both inside and outside processing plants. Recognizing the risks, there was new emphasis placed on process safety management (PSM), in addition to the traditional "people"-based approaches to safety.

Specific requirements for PSM have been incorporated into legislation and regulation throughout the world. Here, we will discuss the US version of PSM as it applies to refineries in a general way. We will go into a little more depth on some specific aspects of the regulations where necessary.

Elements of PSM

The key elements of the US federal regulations on process safety management are in the Occupational Safety and Health Administration (OSHA) 1910.119 along with several guidelines OSHA has developed. There are similar regulations promulgated in many other countries, in addition to local (state, province, etc.) governments.

There are 14 key elements to a required PSM program. The remarks below indicate the general nature of the PSM elements. Comments and considerations in complying with the PSM program elements are offered, but these are not part of the regulations. This is not intended as a legal document, so reviewing and complying with the applicable regulations is left to the reader.

1. *Process safety information* – This is a compilation of written information about:
    (a) Highly hazardous chemicals used in the process – toxicity, PEL, physical data, reactivity, corrosivity, thermal and chemical stability, and hazards of mixing with other substances

   (b) Process technology – up-to-date block flow diagram or PFD, process chemistry and properties, maximum intended inventory, safe upper and lower operating conditions, and consequences of deviations (including safety and health consequences)
   (c) Process equipment – materials of construction, P&ID or MFD, electrical classification, relief system design and design basis, ventilation design, codes and standards used, compliance with recognized and generally accepted good engineering practices (RAGAGEP), heat and material balances, and dedicated safety systems
2. *Process hazard analysis* (*PHA*) – This essentially requires completion of a PHA using one of the approved techniques, for each process unit. The PHA must be periodically reviewed and updated based on new learnings. A PHA is a detailed study of each process or unit to identify potential process hazards and evaluate the adequacy of safeguards to prevent incidents and releases. It is conducted by a team with the appropriate engineering and operating knowledge of the process being reviewed. A PHA must address:
   (a) Process hazards
   (b) Previous incidents – to benefit from learnings
   (c) Engineering and administrative controls
   (d) Consequences of failure of the controls
   (e) Facility siting – much more emphasis following an industry multiple fatality incident
   (f) Human factor considerations
   (g) Evaluation of effects of failures on personnel and off-site

   The results of a PHA are normally contained in a report summarizing all things that were evaluated and the conclusions. These reports can be hundreds of pages long and very detailed. Problems found and recommendations made must be resolved in a timely manner. Usually the time frame depends on the potential severity of the risk. The results must be communicated to employees and contractors.

   Methods employed for PHAs include:
   - Hazard and operability reviews (HazOp)
   - Layers of protection analysis (LOPA)
   - What-ifs
   - Checklists
   - Failure modes and effects analysis (FMEA)

   Each company defines its own approach to meeting the PHA requirement, including the risk matrix or allowable risk profile for a PHA. OSHA offers some guidelines. API has also provided guidance in API Recommended Practice 750.
3. *Operating procedures* – Procedures must address specific hazards of the process, along with defining the operating limits for each phase of unit operations (start-up, shutdown, normal operations, etc.). The procedures should indicate the required PPE, precautions, and emergency procedures in the event of a problem. There must be procedures for the safety systems. These all need to be

in writing. The detail in the operating procedures varies from company to company, even site to site within a company.

Sometimes writing good procedures to cover all these requirements and ensure an operator will be thinking about the right things at the right times becomes difficult. By nature, procedures are a series of sequential steps. In practice, plants are started up, operated, and shutdown by multiple parallel steps. The challenge is to coordinate among several parallel steps – easier said than done.

4. *Training* – There is no substitute for the operator or staff knowing what they are doing and how to do it. This is where training plays a critical role in PSM. The training must include the procedures, equipment, operating limits, and, especially, safety systems. It is usually periodically refreshed. Each process change requires retraining on the changes. This must all be documented. Practices to comply with the regulatory requirements vary in accomplishing the objectives.
5. *Contractors* – This element of PSM requires that visitors and contractors to a facility be made aware of the process hazards and the work procedures that apply in that plant. The extent of training may vary, depending on what the contractor or visitor is doing in the plant. Someone who will not be physically working on the equipment does not need to know how to get a hot work or vessel entry permit, for instance; but they still need to know the process hazards that may be around when they enter a unit, what to do if they hear an alarm siren, and that they have to check in at the control room before entering. Conversely, a welder entering a unit will need much more complete training, including how to get a hot work permit and what to do if an alarm sounds.
6. *Mechanical integrity* – This element of PSM focuses on maintaining the process equipment in good operating condition. It would include the maintenance and inspection programs, as well as spare parts. Safety systems may require additional, periodic proof-testing to verify if they will function when needed.
7. *Hot work* – The regulations require that there be specific, appropriate hot work procedures before welding or any potentially sparking-type operation is performed in a process area. Many refiners extend this to other permitting procedures.
8. *Management of change* (*MOC*) – Facilities are seldom static collections of equipment and process fluids. There are ongoing improvements and changes for many reasons. The MOC provisions require that each change in a unit, which is not a direct like-in-kind replacement, be evaluated for the potential process hazards it might cause. Essentially, the change has to undergo a form of PHA, the procedures and process safety information must be updated, the impacts addressed, the operators trained, and all the other myriad details of the change fully integrated into the PSM system.

The definition of a change is something people struggle with. Many refiners say any change is a “change” for purposes of MOC. Others would classify more changes as “like in kind” by not including changes where, say, replacement equipment satisfies the same process intent as the original equipment.

Each company must reach its own consensus on what is and is not a change for purposes of MOC.

Within a company, the MOC process itself can be very onerous and time consuming. Consideration to streamlining the process, without compromising the value and validity of process safety, is usually worthwhile.

9. *Incident investigation* – There is a requirement that serious incidents and near misses be investigated in a timely manner. To make the best use of this element, investigations should be documented and the lessons taught should be conveyed to plant personnel to improve their knowledge and understanding. The objective here is to prevent future incidents of the same type. In some very serious incidents, a company may be required to make the learnings known to other companies in the industry. This is important in maintaining a safe industry overall – not everyone should have to make the same mistake to learn the lessons.

   The incidents will usually have corrective actions, with time deadlines for follow-up. These must be documented and completed.
10. *Compliance audits* – There must be a program of regular auditing of compliance with the PSM elements. The audits include PSI information, operating procedure certifications, current PHAs, etc. Quality of the PSM program, materials, and compliance is audited. Companies perform these audits internally for their own edification and improvements more frequently than OSHA audits. There will be an OSHA audit scheduled on a less frequent basis. Penalties can be assessed by OSHA as a result of gaps in the PSM program identified in their audits.
11. *Trade secrets* – It is recognized that some of the process information required to operate a plant safely is proprietary (i.e., a trade secret). The fact something is in this category cannot be used as a reason for not sharing the information with operators, engineers, maintenance personnel, and contractors who could be affected by it and need to know the risks. Employees and contractors are usually bound by confidentiality agreements to not divulge such information to outside companies or competitors. Usually, there are ways to provide the information needed for safe activities while protecting the trade secret owner's intellectual property (IP). Involving the IP owner in how the information is disclosed may be helpful.
12. *Employee participation* – It is a requirement of the PSM regulations that the employees be involved in the PSM program. Usually, participation by the operators and maintenance personnel, as well as the technical staff, is valuable in PHAs, incident investigations, near miss reporting, PSI verification, PSSRs, and other areas. This also helps with the training requirements.
13. *Pre-start-up safety review* (*PSSR*) – A PSSR is required for new facilities or "changes." The PSSR verifies if the facilities are constructed correctly, the procedures to operate them are in place, and the required training related to the facilities has been completed. Basically, the PSSR confirms the changed plant is ready to operate safely. A PSSR is normally conducted by a team which includes technical and operations personnel. The team physically examines the

new or changed facilities, essentially punch-listing them. They ensure all aspects of PSM that must be completed before start-up are, in fact, done. Only after agreement of the PSSR team can the changed facilities be used.

14. *Emergency planning and response* – Using PHAs and the related information as a guide, this element requires that a plant have an appropriate emergency plan and response plan in place. These plans are often integrated and/or coordinated with local public emergency services groups. Often, if there are other processing facilities in an area, there are mutual aid agreements among the different facilities. The important thing is that there must be a plan to address process emergencies and you must be ready and capable of implementing the plan.

Foundational Needs for PSM

Now, to ensure that the PSM elements work and that you actually get value from it (not just meet a regulation), there are two foundational elements that need to be in place but may not necessarily be required by regulation:

- There must be a management commitment to develop, operate, and maintain the PSM system. Failure to have a demonstrated commitment from management in this area can result in gaps that can lead to citations.
- There must be a system available for appropriately sharing and managing the documentation developed by the PSM system. Current, correct information must be easy to get when needed.

Pressure Safety

A major requirement in the design and engineering of a plant or system is to ensure safe equipment operation. Much of the effort in this respect is directed to determining the pressure limits of equipment and to protect that equipment from dangerous overpressure conditions. Pressure relief valves are normally used for this protection service, although under certain conditions, bursting disks (rupture disks) may be used. This section describes the various types of relief valves and a procedure for calculating the correct orifice size of the valve and the valve selection. There is also software available (including some from relief valve vendors) to perform these calculations.

Determination of Relief Cases

The cost of providing facilities to relieve all possible emergencies simultaneously can be high. Every emergency arises from a specific scenario. The simultaneous occurrence of two or more emergencies or contingencies is not common; however, problems, such as utility failures, must be considered on a plant- or area-wide basis and may create simultaneous relief requirements that set relief system sizes and back pressures. Electrical power failures are notorious for causing large relief loads.

Unless a failure can cascade into multiple types of failure, an emergency which can arise from two or more types of failure (e.g., the simultaneous failure of a control valve and cooling water) is not usually considered when sizing safety equipment.

Each unit or piece of pressure equipment must be studied individually and every contingency must be evaluated. The safety equipment for an individual unit is then sized to handle the largest load resulting from the controlling contingency. If a certain emergency would involve more than one unit, then all must be considered as an entity. The equipment judged to be involved in any one emergency is termed “single risk.” The single risk which results in the largest load on the safety facilities in any system is termed “largest single risk” and forms the design basis for the equipment.

Note that the emergency which results in the largest single risk on the overall basis may be different from the emergency(ies) which form the basis for individual pieces of equipment.

Several contingencies must be evaluated when considering the relief load for an individual piece of equipment. The minimum scenarios to consider (as applicable) are the following:

- Fire (external)
- Blocked discharge:
  - On the process side flow(s)
  - Include cases for liquid, vapor, or mixed phase
- Electrical power failure:
  - May be local or refinery-wide event
  - May be total or partial
  - Increases superimposed back pressure on a relief device
  - May cascade into instrument air, steam, and other utility failures
  - Often sets the relief sizing and flare size
  - May be necessary to look hard at timing of different reliefs
  - May require emergency depressuring of some units (e.g., hydrocrackers), which would impose a large back pressure
- Coolant failure:
  - Especially critical on towers
- Reflux failure (towers)
- Other failures to consider:
  - Mal-operation
  - Temperature runaway – depressuring
  - Mechanical failure of equipment (e.g., reboiler steam valve fails to open)
  - Abnormal heat input
  - Split exchanger tube
  - Automatic control failure

- Instrument air failure
- Valve left open
- Steam-out
- Thermal (blocked-in line or equipment)
- Any other type of failure that can create a relief condition

Be sure you consider *all* the credible failure scenarios in sizing the relief systems and devices.

Definitions

The terms used and the descriptions given in this item are based on data given in two API publications. These are API RP-520 and RP-521. References are also made to Part 1 ANSI Proposed Standard, "Terminology for Pressure Relief Devices," and to ASME PTC 25.2. These publications are the safety standards commonly in current use. The following definition of terms used in the design of safety systems helps to understand the design and criteria of safety systems.

Accumulation	Accumulation is the pressure increase over the maximum allowable working pressure of the vessel during discharge through the pressure relief device expressed as a percent of that pressure or in psi or bar.
Atmospheric discharge	Atmospheric discharge is the release of vapors and gases from pressure relief and de-pressurizing devices to the atmosphere.
Back pressure	Back pressure is the pressure existing at the outlet of the pressure relief device due to pressure in the discharge system at the time the device must relieve. This is sometimes imposed by relief or venting of other devices simultaneously.
Balanced safety relief valves	A balanced safety relief valve incorporates means for minimizing the effect of back pressure on the performance characteristics – opening pressure, closing pressure, lift, and relieving capacity.
Blowdown	As used here, blowdown is the difference between the set pressure and the resealing pressure of a pressure

	relief valve, expressed as a percent of the set pressure or in psi or bar.
Burst pressure	Burst pressure is the value of inlet static pressure at which a rupture disk device functions.
Conventional safety relief valve	A conventional safety relief valve is a closed bonnet pressure relief valve that has the bonnet vented to the discharge side of the valve. The performance characteristics (opening pressure, closing pressure, lift, and relieving capacity) are directly affected by changes of the back pressure on the valve.
Design pressure	Design pressure is the pressure used in the design of a vessel to determine the minimum permissible thickness or physical characteristics of the different parts of a vessel.
Flare	A flare is a means for safe disposal of waste gases by combustion. With an *elevated flare*, the combustion is carried out at the top of a pipe or stack where the burner and igniter are located. A *ground flare* is similarly equipped except that combustion is carried out at or near ground level. A *burn pit* differs from a flare in that it is normally designed to handle both liquids and vapors. Flare systems are described and discussed more fully later in the handbook chapter entitled "▶ Off-Site Facilities for Petroleum Processing".
Lift	Lift is the actual travel of the disk away from closed position when the valve is relieving.
Overpressure	Overpressure is the pressure increase over the set pressure of the primary relieving device; it would be termed *accumulation* when the relieving device is set at the maximum allowable working pressure of the vessel. *Note*: When the set pressure of the

	first (primary) pressure relief valve to open is less than the maximum allowable working pressure of the vessel, the overpressure may be greater than 10 % of the set pressure of that valve.
Pilot-operated pressure relief valve	A pilot-operated pressure relief valve is one that has the major flow device combined with and controlled by a self-actuated auxiliary pressure relief valve. This type of valve does not utilize an external source of energy. These are usually used where the operating pressures are very high or the set pressure is close to operating pressure (within about 5 %).
Pressure relief valve	Pressure relief valve (PRV) is a generic term applied to relief valves (RV), safety valves (SV), pressure safety valves (PSV), or safety relief valves (SRV).
Relieving conditions	Relieving conditions pertain to pressure relief device inlet pressure and temperature at a specific overpressure. The relieving pressure is equal to the valve set pressure (or rupture disk burst pressure) plus the overpressure. The temperature of the flowing fluid at relieving conditions may be higher or lower than the operating temperature.
Rupture disk (RD or PSE)	A relief device that consists of a thin metal plate or disk designed to burst or fail when a specific pressure differential is imposed on the disk. Once the disk has failed, it must be replaced. It will *not* stop flowing after the overpressure condition is relieved. These are sometimes used to protect a relief valve from corrosive or otherwise compromising process fluids, in addition to providing full flow relief in a large overpressure event (e.g., failure of a high-pressure hydrogen stream into a

	cooling water exchanger). See below under types of devices.
Set pressure	Set pressure, in psig or barg, is the inlet pressure at which the pressure relief valve is adjusted to open under service conditions. In a safety or safety relief valve in gas, vapor, or steam service, the set pressure is the inlet pressure at which the valve pops under service conditions. In a relief or safety relief valve in liquid service, the set pressure is the inlet pressure at which the valve starts to discharge under service conditions.
Superimposed back pressure	Superimposed back pressure is static pressure existing at the outlet of a pressure relief device at the time the device is required to operate. It is the result of pressure in the discharge system from other sources. This type of back pressure may be constant or variable; it may govern whether a conventional or balanced-type pressure relief valve should be used in specific applications.
Vapor depressing (or depressuring) system	A vapor depressing (or depressuring) system is a protective arrangement of valves and piping intended to provide rapid reduction of pressure in equipment by release of vapors. Actuation of the system may be automatic or manual. These are often found in hydrocrackers and some hydrotreaters where the hydrogen must be rapidly eliminated to control a runaway temperature.
Vent stack	A vent stack is the elevated vertical termination of a disposal system which discharges vapors into the atmosphere without combustion or conversion of the relieved fluid. Following a multiple fatality incident in the 2000s, this type of stack is largely being eliminated.

Types of Pressure Relief Valves

The following describes the types of relief valves commonly used in industry. These have been approved according to the ASME VIII "Boiler and Pressure Vessel" Code.

Conventional Safety Relief Valves

In a conventional safety relief valve, the inlet pressure to the valve is directly opposed by a spring closing the valve. The back pressure on the outlet of the valve changes the inlet pressure at which the valve will open. A diagram of a conventional relief valve is shown below as Fig. 1.

Balanced Safety Relief Valves

Balanced safety valves are those in which the back pressure has very little or no influence on the set pressure. The most widely used means of balancing a safety relief valve is through the use of a bellows. In the balanced bellows valve, the effective area of the bellows is the same as the nozzle seat area. Back pressure is prevented from acting on the top side of the disk. Thus the valve opens at the same inlet pressure, even though the back pressure may vary. A diagram of a balanced safety relief valve is shown as Fig. 2.

Pilot-Operated Safety Relief Valves

A pilot-operated safety relief valve is a device consisting of two principal parts: a main valve and a pilot valve. Inlet pressure is directed to the top of the main valve piston with more area exposed to pressure on the top of the piston than on the bottom. Pressure, not a spring, holds the main valve closed. At the set pressure, the pilot opens, reducing the pressure on top of the piston, allowing the main valve to go fully open.

Resilient-Seated Safety Relief Valves

When metal-to-metal seated conventional or bellows-type safety relief valves are used where the operating pressure is close to the set pressure, some leakage can be expected through the seats of the valve (refer to API Standard 527, "Commercial Seat Tightness of Safety Relief Valves with Metal-to-Metal Seats").

Resilient-seated safety relief valves, with either an O-ring seat seal or a plastic seat, such as Teflon, provide seat tightness. Limitations of temperature and chemical compatibility of the resilient material must be considered when using these valves. They often do not reseat after a relief event. They also do not work well in high-pressure differential applications.

Rupture Disk (RD, PSE)

A rupture disk consists of a thin metal diaphragm held between flanges. The disk is designed to rupture and relieve pressure within tolerances established by the ASME Code.

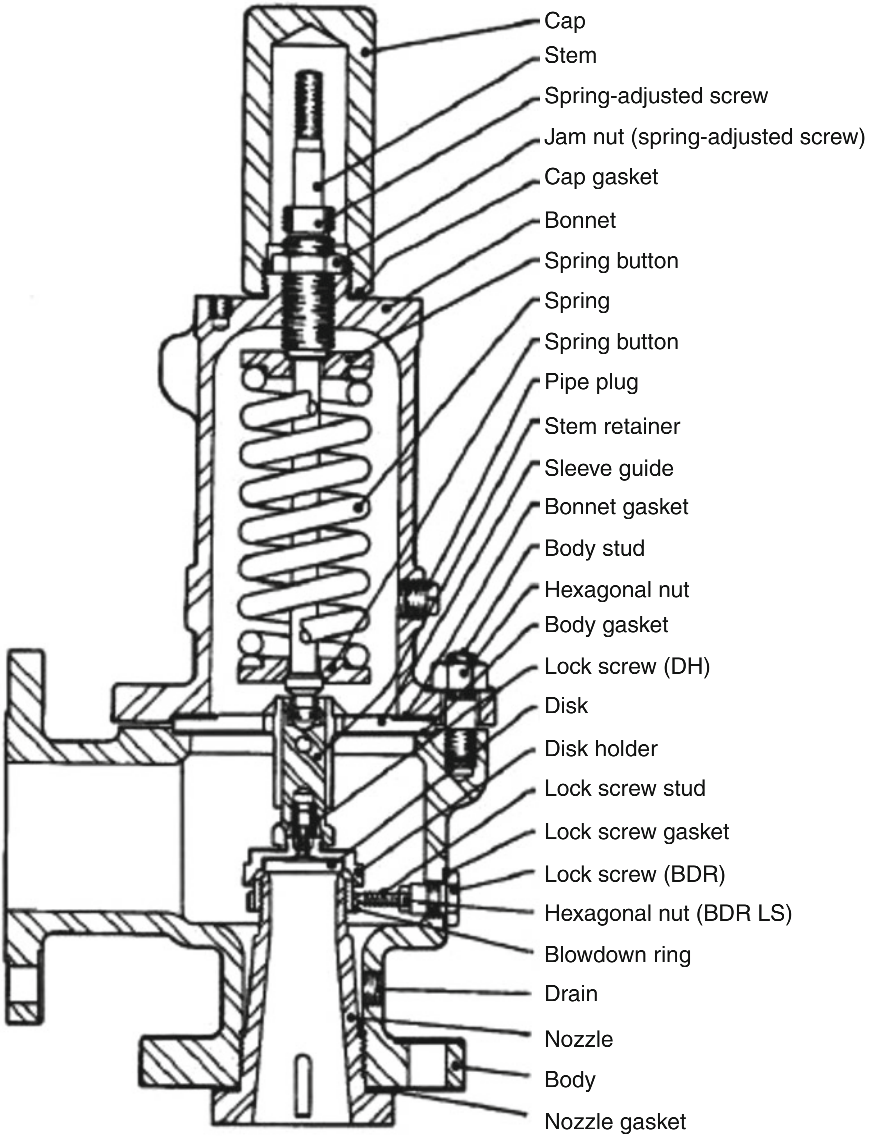


Fig. 1 A diagram of a conventional safety relief valve

Relief Capacity

The maximum amount of material to be released during the largest single risk emergency determines the size of the safety relief valves in any given system. Any calculation to determine valve sizing must therefore be preceded by a calculation or some determination of the maximum amount. Among the most common sizing

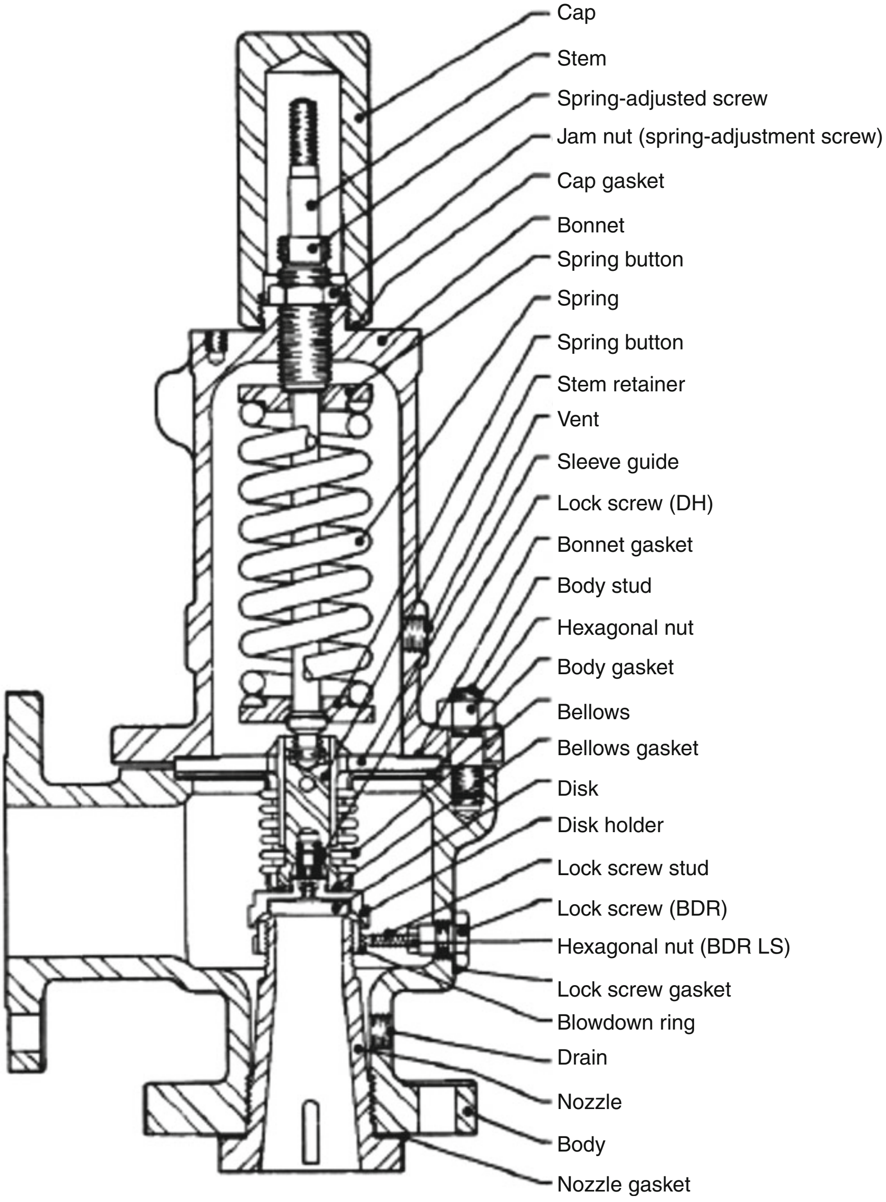


Fig. 2 A diagram of a balanced safety relief valve

criteria are the event of fire and its effect on the contents of exposed vessels. There are also other criteria which can determine maximum release that are attributable to operational failure or one of the other scenarios listed in section "Determination of Relief Cases."

Capacity Due to Fire

The exact method of making this calculation must be established from the appropriate codes which apply, API RP-520, Part I, API Standard 2510, and NFPA No. 58, or local codes which may apply. Each of the listed codes or standards approaches the problem in a slightly different manner.

Liquid systems – Many of the systems that are encountered will contain liquids or liquids in equilibrium with vapor. Fire relief capacity in this situation is calculated on the basis of heat energy from the fire translated in terms of vapor generated in the boiling liquid.

API RP-520, Part I, applies to refineries and process plants. It expresses requirements in terms of heat input:

$$Q = 21,000FA^{0.82} \tag{1}$$

where:

Q = Btu/h heat input.
A = area in sq ft of wetted surface of the vessel up to 25 f. above grade.
Wetted surface is calculated at the maximum fill level. Grade is the ground level under the vessel.
F = fireproof factor due to insulation becoming 1.0 for a bare vessel (see Fig. 3).

The amount of vapor generated with this is then calculated from the latent heat of the material at the relieving pressure of the valve by the following equation. For fire relief only this may be calculated at 120 % of maximum allowable working pressure. All other conditions must be calculated at 110 % of maximum allowable working pressure; thus,

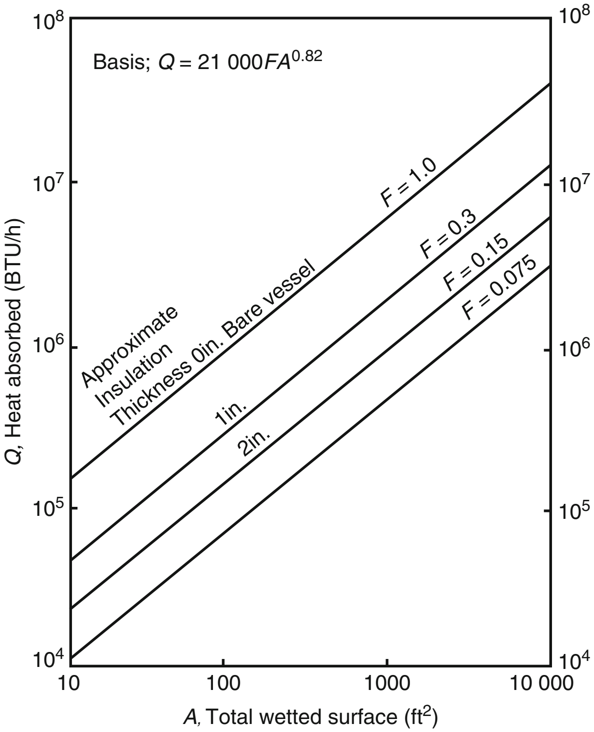
$$Q/H_t = W \tag{2}$$

where:

Q = Btu/h heat input to the vessel.
H_t = Btu/lb latent heat of the material being relieved.
W = lb/h of vapor to be relieved by the relief valve.

The latent heat of pure and some mixed paraffin hydrocarbon materials may be estimated using the data given in API RP-520. A more accurate latent heat evaluation for mixed hydrocarbons will be found by utilizing vapor-liquid equilibrium K data and making a flash calculation. Mixed hydrocarbons will fractionate, beginning with the lowest temperature boiling mixture and progress to the highest temperature mixture; therefore, consideration must be given to the condition which will cause the largest vapor generation requirements from the heat input of a fire.

Fig. 3 Insulation factors for fire relief loads



Latent heat will approach a minimum value near critical conditions; however, the effect does not go to zero. An arbitrary minimum value that may be used is 50 Btu/lb.

Other Capacity Scenarios

Section "Determination of Relief Cases" listed a few of the other scenarios that must be considered when sizing relief valves and systems. The other capacity scenarios, briefly, are the following:

- Blocked discharge
- Electrical power failure (partial and total)
- Coolant/cooling water failure
- Reflux failure (towers)
- Other failures in the process

Considerable effort may be required to define the other capacity scenarios. It is common that the capacity required for one of these scenarios greatly exceeds the fire relief case and will set the relief valve capacity requirement.

Overall Relief and Recovery System Loads

All the various vents and relief valves are tied into the relief and recovery system, usually connected to the flare. It is often necessary to perform a flare system or relief study to determine the superimposed back pressure on the relief devices before the final sizing can be completed. For this study, the entire flare or relief system must be hydraulically modeled with the various scenarios for relief load each calculated.

The modeling must be done carefully because the pressure drops are very low and small changes in the pressure drop can have significant implications on sizes and design flows. You may find that the back pressure in some scenarios exceeds the allowable working pressure for a vessel or tower – meaning it could not relieve under that scenario. If it does not need to relieve anyway, then there is little consequence (unless you consider double jeopardy). If the device would need to relieve, then alternatives and other controls need to be considered to reduce back pressure/backflows to an acceptable level.

Having a flare system model is a good practice and is very helpful in understanding options in plant emergency scenarios.

Relief Valve Load Specification

It is normal practice for the relief valve load calculations and bases to be summarized on a “relief valve load calculation data sheet.” There is normally one sheet for each relief valve service. The sheet typically includes source (e.g., vessel) data, process data, each relieving condition (including quantity, relieving fluid properties, phases, required valve area), sketches, and other data required for the valve.

The load calculation sheet, with the supporting calculations, satisfies one of the PSM compliance requirements.

Sizing of Required Orifice Areas

The safety relief valve manufacturers have standard orifice designations for area and the valve body sizes which contain these orifices (API Standard 526, “Flanged Steel Safety Relief Valves for Use in Petroleum Refineries”). The standard orifices available, by letter designation and area, are in Table 1.

Sizing for Gas or Vapor Relief and Sonic or Critical Flow

Safety relief valves in gas or vapor service may be sized by use of one of these equations:

$$A = \frac{W\sqrt{T}\sqrt{Z}}{CKP_{\mathrm{i}}K_{\mathrm{b}}\sqrt{M}} \tag{3}$$

$$A = \frac{V\sqrt{T}\sqrt{M}\sqrt{Z}}{6.32\,CKP_{\mathrm{i}}K_{\mathrm{b}}} \tag{4}$$

Table 1 Standard relief valve orifice sizes

D orifice	0.110 in.^{2}
E orifice	0.196 in.^{2}
F orifice	0.307 in.^{2}
G orifice	0.503 in.^{2}
H orifice	0.785 in.^{2}
J orifice	1.287 in.^{2}
K orifice	1.838 in.^{2}
L orifice	2.853 in.^{2}
M orifice	3.60 in.^{2}
N orifice	4.34 in.^{2}
P orifice	6.38 in.^{2}
Q orifice	11.05 in.^{2}
R orifice	16.0 in.^{2}
T orifice	26.0 in.^{2}

Note: However, many small safety relief valves are manufactured with orifice areas smaller than “D,” and many pilot-operated types contain orifice areas larger than “T”

$$A = \frac{V\sqrt{T}\sqrt{G}\sqrt{Z}}{1.175\,CKP_iK_b} \tag{5}$$

where:

W= flow through valve, lb/hr.

V= flow through valve, scfm.

C= coefficient determined by the ratio of the specific heats of the gas or vapor at standard conditions.

K = coefficient of discharge, obtainable from the valve manufacturer (usually 0.6–0.7).

A = effective discharge area of the valve, inch^2.

P_i = upstream pressure, psia. This is set pressure plus overpressure plus the atmospheric pressure.

K_b= capacity correction factor due to back pressure. This can be obtained from Fig. 4 for conventional valves or pilot-operated valves and from Fig. 5 for balanced bellows valves.

M = molecular weight of gas or vapor.

T= absolute temperature of the inlet vapor in °R (°F +460).

Z= compressibility factor for the deviation of the actual gas from a perfect gas.

G= specific gravity of gas referred to air, 1.00 at 60 °F and 14.7 psia.

Sizing for Liquid Relief

Conventional and balanced bellows safety relief valves in liquid service may be sized by use of the following equation. Pilot-operated relief valves should be used

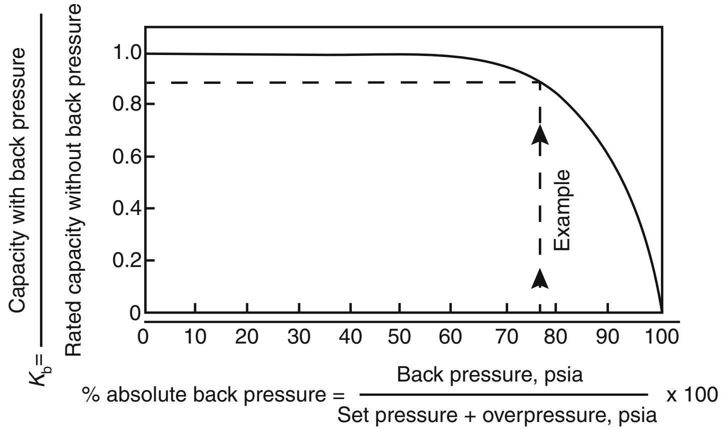


Fig. 4 Back pressure sizing factor K_b for conventional valves

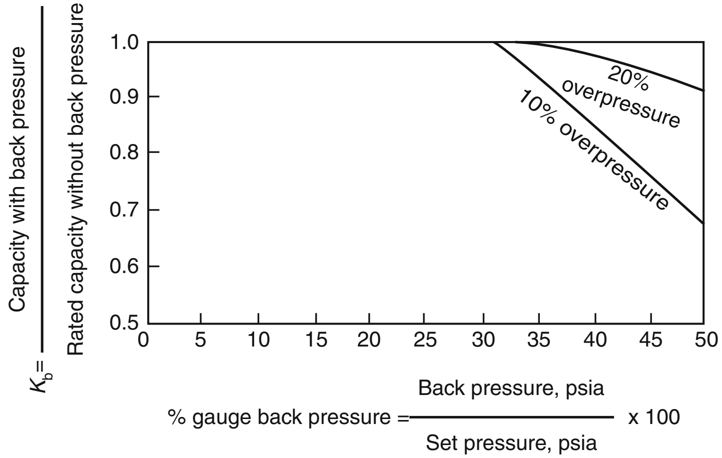


Fig. 5 Back pressure sizing factor K_b for balanced valves

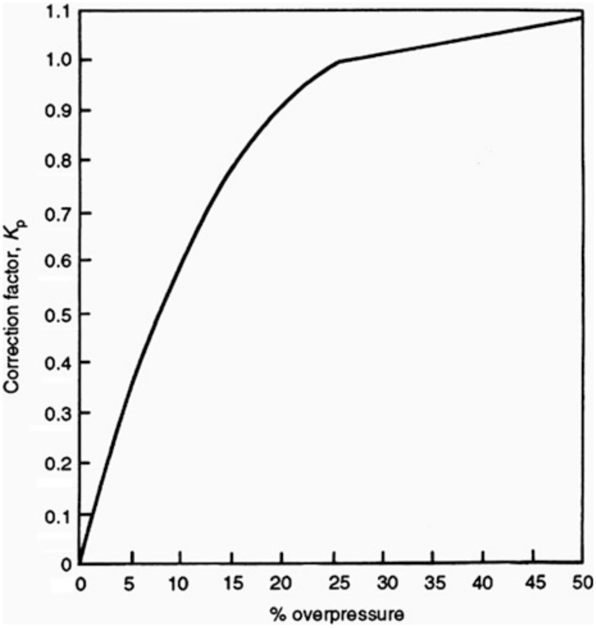
in liquid service only after determining from the manufacturer that they are suitable for the service:

$$A = \frac{\text{gpm}\sqrt{G}}{38K\left(K_p K_w K_v\right)\left(1.25P - P_b\right)^{1/2}} \tag{6}$$

Note: A coefficient of discharge of 0.62 is normally used for K.
where:

gpm = flow rate at the selected percentage of overpressure, in US gals.
A = effective discharge area, inch^2.

Fig. 6 Capacity correction factor due to overpressure K_p



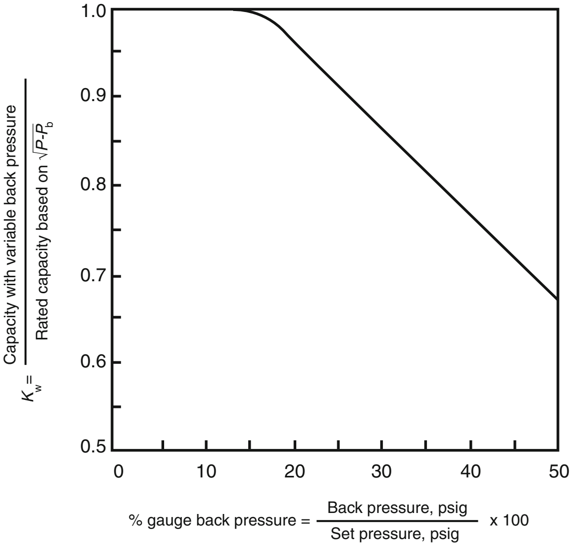


Fig. 7 Capacity correction factor K_w

K_p = capacity correction factor due to overpressure, for 25 % overpressure.

K_p = 1.00. The factor for other percentages of overpressure can be obtained from Fig. 6.

K_w = capacity correction factor due to back pressure and is required only when balanced bellows valves are used. K_w can be obtained from Fig. 7.

K_v = capacity correction factor due to viscosity. For most applications, viscosity may not be significant, in which case $K_v = 1.00$. When viscous liquid is being relieved, see method of determining K_v as described below.
P = set pressure at which relief valve is to begin opening, psig.
P_b = back pressure, psig.
G = specific gravity of the liquid at flowing temperature referred to water, 1.00 at 70 °F.

When a relief valve is sized for viscous liquid service, it is suggested that it be sized first as for nonviscous-type application in order to obtain a preliminary required discharge area, A. From manufacturers' standard orifice sizes, the next larger orifice size should be used in determining the Reynolds number, R, from either of these relationships:

$$R = \frac{\text{gpm}\,(2,800G)}{\mu\sqrt{A}} \tag{7}$$

$$R = \frac{12,700\,\text{gpm}}{U\sqrt{A}} \tag{8}$$

where:

gpm = flow rate at the flowing temperature, in US gpm.
G = specific gravity of the liquid at the flowing temperature referred to water, 1.00 at 70 °F.
μ = absolute viscosity at the flowing temperature, in centipoise.
A = effective discharge area, in sq in. (from manufacturers' standard orifice areas).
U = viscosity at the flowing temperature, in Saybolt universal seconds.

After the value of R is determined, the factor K_v is obtained from Fig. 8. Factor K_v is applied to correct the "preliminary required discharge area." If the corrected area exceeds the "chosen standard orifice area," the above calculations should be repeated using the next larger standard orifice size.

Sizing for Mixed-Phase Relief

When a safety relief valve must relieve both liquid and gas or vapor, it may be sized by the following steps:

(a) Determine the volume of gas or vapor and the volume of liquid that must be relieved.
(b) Calculate the orifice area required to relieve the gas or vapor as previously outlined.
(c) Calculate the orifice area required to relieve the liquid as previously outlined.
(d) The total required orifice area is the sum of the areas calculated for liquid and vapor.

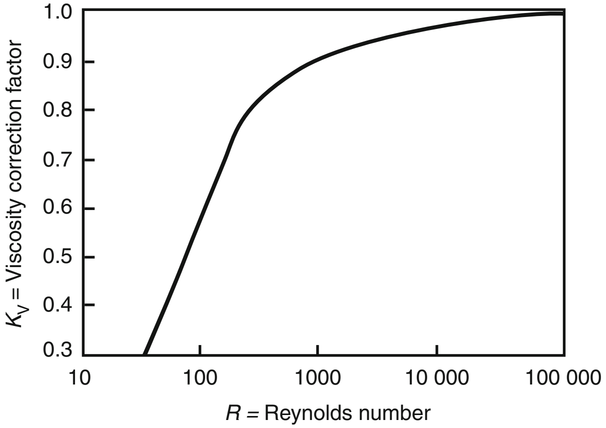


Fig. 8 Capacity correction factor due to viscosity K_v

Sizing for Flashing Liquids

The conventional method is to determine the percent flashing from a Mollier diagram or from the enthalpy values. Then consider the liquid portion and vapor portion separately as in mixed-phase flow. A method to calculate the percent flashing is shown in the following equation:

$$\% \text{ Flash} = \frac{h_f(1) - h_f(2)}{h_{fg}(2)} \times 100 \tag{9}$$

where:

$h_f(1)$ = enthalpy in Btu/lb of saturated liquid at upstream temperature.
$h_r(2)$ = enthalpy in Btu/lb of saturated liquid at downstream pressure.
$h_{fg}(2)$ = enthalpy of evaporation in Btu/lb at downstream pressure.

Sizing for Gas or Vapor on Low-Pressure Subsonic Flow

When the set pressure of a safety relief valve is very low, such as near atmospheric pressure, the K_b values obtainable from Fig. 5 are not accurate. Safety relief valve orifice areas for this low-pressure range may be calculated:

$$A = \frac{Q_v \sqrt{GT}}{863KF\sqrt{(P_1 - P_2)P_2}} \tag{10}$$

where:

A = effective discharge area of the valve, inch^2.
Q_v = flow through valve, scfm.

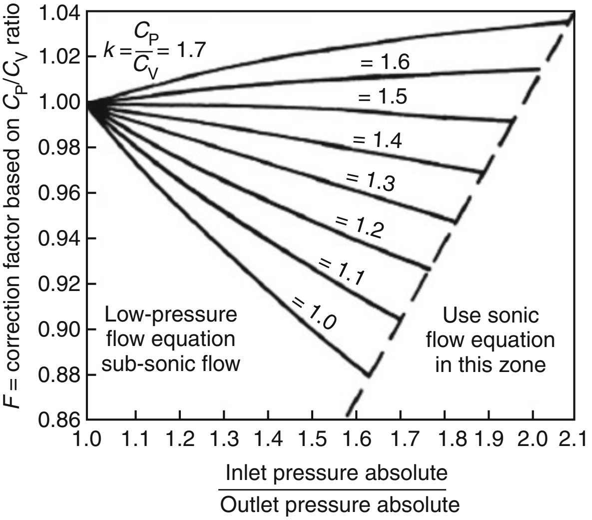


Fig. 9 Flow correction factor "F" based on specific heats

G = specific gravity of gas referred to air, 1.00 at 60 °F and 14.7 psia.
T = absolute temperature of the inlet vapor, °R = °F +460.
K = coefficient of discharge, available from the valve manufacturer.
F = correction faction based on the ratio of specific heats. This can be obtained from Fig. 9.
P_1 = upstream pressure in psia = set pressure plus overpressure plus atmospheric pressure.
P_2 = downstream pressure at the valve outlet in psia.

An example calculation covering the sizing of a relief valve is given in Appendix of this chapter.

Temperature Safety

Most petroleum processes involve elevated temperatures. These are normally well controlled, but there are safety risks posed by temperature. Of course, high temperatures always present physical hazards from simple heat that can cause burns. Many processes operate at temperatures which, if someone were exposed to them, would immediately cause severe burns. We will take the hazards of burns from operating conditions and fluids as a given.

Our focus here will be on two cases in which temperature can lead essentially to overpressuring equipment with a resulting loss of containment:

- Thermal relief
- Reaction runaway

Thermal Relief

When a hydrocarbon or another fluid is trapped in a fixed equipment volume, usually between block valves in a pipeline, and that fluid is heated, the pressure within the trapped fluid increases as the fluid expands. At the same time, the piping also expands with temperature, but not necessarily at the same rate as the fluid. For fluids like LPGs, the expansion of the fluid can be substantial and can include vaporization.

If the fluid expands more than the space in which it is contained, the pressure can exceed the yield strength of the equipment and the equipment will rupture. This releases the fluid to the atmosphere – an uncontrolled release.

For equipment, this situation is addressed as the fire load when sizing the relief valve load. For a blocked-in pipeline, the heat source can be the sun, heat tracing, or nearby hot process equipment; but the case can be much worse if the heat source is a pool fire or other nearby fires. Piping has also ruptured due to hydrogen evolution from corrosion in the blocked-in line. Release of additional combustible materials from pipe rupture can just make a fire worse.

To avoid rupturing a long, blocked-in pipeline, it is customary to provide thermal relief valves (TRVs). These are also called thermal safety valves (TSVs). They are normally small, conventional relief valves. They may be vented to grade or, in many cases, they can be designed to jump around one of the block valves at either end of the line to contain the fluids (these have to be managed when isolating equipment). In many facilities, there are more of these TSVs in the plant, especially in off-site areas, than there are any other relief valve services.

The set points for the TSVs are normally much higher than the operating pressures of the lines they protect. They are set at the maximum pressure allowed in the pipe (considering temperature).

There are two primary codes and standards applicable to this situation:

- API Recommended Practice 521, section 3.14
- ASME B31.3, paragraph 301.2.2

Some practical exceptions are usually made if the contained fluid is not a dangerous liquid (loosely defined):

- Short lines generally do not require TSVs.
- Small-diameter pipes do not require TSVs.
- Pipes that are blocked in with a contained hot fluid will subsequently cool.

To determine the need for thermal relief in a line, the following analysis applies:

- Calculate the net volume of liquid expansion beyond the pipe volume using the equation:

$$\Delta V = (V_t - V_{t0}) - \Delta V_p - \Delta V_{Pr} \tag{12}$$

Table 2 Some typical coefficients of cubic expansion for liquids(Brahmbhatt 1984)

Liquid	Range, °C	a, 10^{-3}	b, 10^{-6}	c, 10^{-8}
Benzene	11–81	1.17626	1.27755	0.80646
Toluene	0–100	1.028	1.779	0
Methanol	−38– + 70	1.18557	1.56493	0.91113
Ethyl acetate	–36– + 72	1.2585	2.95688	0.14922
Sulfuric acid	0–60	0.5758	−0.864	0
n-Pentane	−190– + 30	1.50697	3.435	0.975

Coefficients for tr =0 °C

Example for benzene: $V_t = V_{tr}\left(1 + 1.17626 \times 10^{-3}\,t + 1.27755 \times 10^{-6}\,t^2 + 0.80646 \times 10^{-8} t^3\right)$

where:

V_t = volume of liquid at the final temperature.

V_{t0} = volume of fluid at the initial temperature.

ΔV_p = pipe volume expansion due to temperature.

ΔV_{Pr} = increase in pipe volume from increasing pressure.

- Now we use the cubic form of the equation to determine the volumetric expansion of the fluid:

$$V_t = V_{tr}\left(1 + at + bt^2 + ct^3\right) \tag{13}$$

where:

V_{tr} = base volume at a reference temperature.

a, b, c = cubic volumetric expansion coefficients (see Table 2 examples).

The easiest way to do this is to calculate the relative fluid volume at the initial temperature and the relative volume at the final temperature. The change in volume is the ratio of final to initial relative volumes times the total initial volume.

- The pipe expansion is given by

$$\Delta V_p = \pi/4\left[(D + CD)^2(L + CL) - D^2L\right] \tag{14}$$

where:

D = pipe ID in feet (initial condition).

C = linear coefficient of expansion at final temperature (Table 3).

L = total pipe length including all fittings in feet (initial condition).

- We will assume that the ΔV_{Pr} is negligible. This is a relatively safe assumption.
- To determine the relief need, compare the change in volume of the liquid to the change in volume of the pipe, both due to thermal expansion. If the liquid volume change exceeds the pipe volume change, it is normally advisable to include a TSV.

The most common TSVs are ¾ × 1 in. with a special 0.06 square inch orifice. This size of TSV can be used for most fluids up to total piping lengths of

Table 3 Typical linear coefficients of thermal expansion for metals

Temp, °F	Carbon steel, × 10^{-6}	18-8 stainless, × 10^{-6}	25 Cr-20 Ni, × 10^{-6}	Wrought iron, × 10^{-6}
50	−0.14	−0.21	−0.16	−0.16
70	0	0	0	0
100	0.23	0.34	0.28	0.26
125	0.42	0.62	0.51	0.48
200	0.99	1.46	1.21	1.14
250	1.40	2.03	1.70	1.60
300	1.82	2.61	2.18	2.06
400	2.70	3.80	3.20	3.01
500	3.62	5.01	4.24	3.99
700	5.67	7.50	6.44	6.06
900	7.81	10.12	8.78	8.26

Example: Carbon steel at 100 °F is expanded by a factor of 0.23×10^{-6} compared to carbon steel at 70 °F – i.e., 100 f. of carbon steel at 70 °F will be $100 \times 1.00000023 = 100.000023$ f. long at 100 °F

10,000 f. of 4 in. piping. For longer pipes, larger pipes, and fluids with large expansion coefficients (like liquefied gases), the appropriate TSV size would have to be determined using the fluid properties and the heat input rate. The TSV is set at the design pressure of the pipe.

A couple of final thoughts on TSVs:

- It is easy to forget about the TSVs on piping and equipment, especially in remote areas. The TSVs need to be tracked and routinely serviced just like any other relief valves in order to serve their purpose when needed.
- TSV discharges need to be monitored to ensure there is no leakage. If a TSV discharges to the atmosphere, monitoring is easy. If a TSV jumps around a block valve, monitoring is harder.
- When isolating a line, do not forget to include to isolate the TSV if it jumps around a block valve.
- Provide root valves and bleeders for TSVs to enable servicing them online, like any other relief valve.

Managing Runaway Reactions

Many processes in petroleum refining are exothermic, that is, they evolve heat. Combustion is an obvious example; but here we are talking about processes like:

- Hydroprocessing (e.g. hydrocracking, hydrotreating, isomerization)
- Acid/base reactions – e.g., amine absorption
- Methanation
- Alkylation unit acid runaway

The processes depend on various mechanisms to control the heat of reaction:

- Hydrocrackers, hydrotreaters, and isomerization units depend on the continuous flow of oil and hydrogen through the reactors along with injected cold quench gas to move the heat away.
- Polymerization reactors may depend on coolant-jacketed or exchanger-style reactors or may have large recycle cooling streams with quenches.
- Amine absorption and other acid/base reactions depend on dilution of the heat in a flowing mass or a circulating cooling system.
- Methanators depend on flow and short residence times to carry heat away.
- An alkylation unit depends on maintaining proper chemistry to avoid acid runaway conditions.

Failures of the control mechanisms can lead to very high temperatures in the units. Hydrocrackers, for example, can exceed 1,900 °F in a runaway and those temperatures can be reached in only a few minutes or seconds.

Loss of containment can result when the reaction temperature exceeds the allowable metal temperature with the equipment still at pressure (i.e., you exceed the ultimate yield stress of the material under the process condition).

Industry, including process licensors, has developed specific methods to manage the affected processes in runaway temperature conditions. We will briefly discuss some of the techniques that work. Working with your process licensor can help add more information on runaway control methods.

Hydroprocessing Units

If temperatures in a hydroprocessing unit exceed about 850 °F (~454 °C), the unit can enter a hydrocracking runaway condition in which catalytic and thermal cracking will drive temperatures up rapidly. Once started, the reaction is self-sustaining. A hydrocracking catalyst does *not* have to be present for this to occur.

The reactor seldom fails in a runaway because the metal mass slows its heat up. The normal failure point is at the reactor outlet line or the first effluent exchanger. Fatalities have resulted from these failures.

Control of a true hydrocracking runaway requires immediate and aggressive depressuring of the unit to the flare. The depressuring point is usually the cold high-pressure separator; although if there is an amine absorber, depressuring may be downstream of it. Depressuring rate would typically be somewhere between 100 and 300 psi/min to start (this decays as pressure drops). The unit should be at flare pressure within about 15 min. It should not be repressured until cooled, possibly using nitrogen gas. Licensors have specific guidelines for these procedures and the required equipment.

Not all units can get into a runaway, so analysis is needed to determine the requirements. Some specific scenarios to consider when determining the needs for a depressuring system are the following:

- Does the unit have a hydrocracking catalyst?
- Does the unit operate near 850 °F at any point in its run?

- If flow stops (either treat or recycle gas or a single quench flow), will the bed get too hot?
- Can a sudden change in feedstock (like a lot more cracked feed) drive temperatures quickly to runaway conditions?

The depressuring system is normally manually activated for hydrotreaters. It may be automatically activated under defined conditions for hydrocrackers, with manual activation also available.

For units where runaway is only a remote possibility, the unit should still be capable of depressuring in a reasonable amount of time in case of a fire or other release scenarios. This is part of the API Recommended Practices.

Temperature coverage can be a challenge in these units. You only know temperatures at a few points in a reactor and, possibly, on the reactor shell. Maldistribution (from, e.g., internal damage, previous runaway, or bad catalyst loading) can result in undetected hot spots. If a hot spot happens to be near a reactor wall, you can miss it completely. Careful consideration of the numbers and placement of temperature measuring points is required, both in the reactors and on the reactor shells. Licensors have guidelines for temperature monitoring locations, and many companies have their own, more complete guidelines or requirements.

If an automatic depressuring system is prescribed, it normally will be a safety integrity, integrated, or instrumented system (SIS), with appropriate security, redundancy, maintenance, and testing requirements.

Polymerization Reactions

Polymerization reactions in petroleum processing can be highly exothermic. Loss of temperature control in these processes can occur if the coolant is lost – such as loss of boiler feed water in an exchanger-style reactor.

Control approaches may include:

- Stopping feed for continuous processes.
- Ensuring relief capacity is adequate for generated gases and polymer.
- Alternate coolant sources or types.
- In some reactions, an inhibitor injection may be used to kill the reaction.
- For some batch polymerizations, the reactor contents may be dumped to a special relief system designed to contain and manage the reacting mass with a separate flare.

Acid/Base Reactions

For many acid/base reactions, temperature is controlled by a large circulating stream or a large base volume of cool material, with injection of acid or base into the much larger mass. If temperatures get too high, they can be controlled just by stopping feed of one or more of the reactants.

An interesting case is presented in amine and other absorbers that depend on an acid/base reaction. The reaction generates a significant amount of heat.

The heat is moderated by using a much larger circulating mass of the absorbent solution. This acts as a flywheel to control temperature. If the solution rate gets too low, the temperatures in the absorber can rise to the point where the solution actually begins regenerating in the absorber tower. This results in a phenomenon where the absorber accumulates hot liquid in the trays and periodically blows the hot liquid overhead. The process repeats on some frequency. The remedy is increasing the absorbent rate to ensure the rich solution loading is at the correct level. This is not normally a safety problem, but it can become one if not controlled.

Methanation

Methanation is a highly exothermic reaction that is part of older hydrogen plants and other units where carbon oxides in hydrogen may poison a process. A methanator can get into a runaway condition if the upstream carbon oxide removal process fails or the incoming CO and CO_2 exceed the tolerable levels (usually only a few %). These reactors generally have good thermocouple coverage. Because they are in a vapor phase, maldistribution is normally not a problem.

The reactors have normally relatively thinner walls than hydroprocessing units, so they can heat up extremely quickly. Fast action is needed to avoid loss of containment.

If a runaway condition is detected in a methanator by any high reactor or outlet temperature, the reactor is automatically shut down by a feed block valve and the incoming gas is sent to flare until the problem is resolved. The auto-shutdown system will generally be an SIS-type design with appropriate security, redundancy, maintenance, and testing requirements. There are provisions for manually activating the shutdown also.

Alkylation Unit Acid Runaway

An acid runaway in an alkylation unit can result when the acid strength drops too low. The more dilute acid promotes rapid, exothermic polymerization of olefins over the reaction of an olefin and isobutane as desired. The polymers tend to dissolve in the acid, further diluting it and pushing more polymerization.

From a simple standpoint, an acid runaway is controlled by stopping the olefinic feed, but leaving the paraffinic feed in. Fresh acid is brought in to restore the acid strength.

Vendors have recommended approaches in much more detail for managing acid runaway.

Oxygen-Deficient Environments

The following discussion is presented for information only. Governmental regulations, company/contractor procedures, and legal considerations control all aspects of dealing with oxygen-deficient environments at a given facility.

Hazards and Potential Exposures

Many materials handled in petroleum processing facilities are hazardous, and some are immediately dangerous to life or health (IDLH). Examples of IDLH materials include some of the more obvious compounds, like H_2S and HF acid. These types of materials have well-known hazards and defined approaches to dealing with them.

Other potential IDLH exposures are not so obvious, like nitrogen or CO_2 atmospheres. In these cases, one of the highest risks is oxygen deficiency. According to the US Chemical Safety Board, nitrogen asphyxiation resulted in 80 deaths between 1992 and 2002. Lack of oxygen in your lungs can quickly lead to death, unless you can get to oxygen quickly. A person will lose consciousness after only one or two breaths of nitrogen. There is no warning.

Even low oxygen levels can be an issue. Below 16 % of O_2, the brain makes you breathe faster and deeper, which can make the situation worse. This can affect someone simply walking near where a large nitrogen vent is located. Exposure to 4–6 % of O_2 for about 40 s will result in coma. A person must get oxygen within minutes to survive. There is still residual risk of cardiac arrest.

Carbon dioxide has the added hazard of being toxic in concentrations above about 3 % and fatal on short exposures (5 min) over 9 %.

So, where could these types of atmospheres be found in a refinery? Some of the possible exposure routes include:

- Nitrogen:
  - Loading and unloading of pyrophoric or self-heating catalysts (both inside a reactor and outside during handling).
  - Vessels or containers kept under inert gas blanket or purge to prevent air intrusion.
  - Gas-blanketed tanks or drums.
  - Air-freeing procedures for equipment prior to start-up.
  - Gas-freeing procedures for equipment during shutdown.
  - Equipment protected from oxygen contact to avoid polythionic acid stress corrosion cracking or other materials damage mechanisms caused by air exposure.
  - Backup instrument air systems.
  - Bad breathing air (incorrectly mixed or using nitrogen bottle instead of air).
  - Leakage of nitrogen from an inerted pipe or system into a system that is not supposed to be inert through leaks or improper blinding or valve lineup. An example would be nitrogen accumulation in a firebox from a leaking furnace tube that is being held under nitrogen.
  - Blinding or blanking piping and equipment under nitrogen purge.
  - Some welding procedures.
- Carbon dioxide:
  - Gas-freeing tanks or other equipment for start-up or maintenance
  - Blinding or blanking piping and equipment under carbon dioxide blanket

  - Hydrogen plant CO_2 product lines
  - Flue gases and ducting
  - Sewer boxes and manholes
  - Some welding procedures

Since these gases are colorless, there is little warning they may be present. Carbon dioxide at least has some warning once encountered – it has a bad taste in your mouth, even at low concentrations.

Managing Oxygen-Deficient Environments

The remarks in this section are meant to indicate only some of the types of practices that have been employed to manage oxygen-deficient environments and prevent worker exposure to IDLH conditions. The comments are not all-inclusive. Each facility should establish its own requirements. Most companies and contractors already have their own programs and requirements for use and control of these types of situations.

Some of the good practices for managing oxygen-deficient environments (focusing mostly on nitrogen) include:

- Implementation of a warning system and exclusion zones around any area where inert is being used for purging or inerting.
  - Persons within the “hot zone” closest to the vent location must usually be in fresh air equipment.
  - Signs are posted indicating nitrogen or CO_2 in use and potential for inadequate oxygen environment.
  - The area is usually taped or barricaded for a defined distance around the vent point.
- Testing before entry is permitted into equipment, followed by continuous monitoring of confined or enclosed space atmosphere during entry:
  - Testing would include oxygen, toxics, and combustibles/% LEL.
- Special procedures are used for inert vessel or reactor entry when work must be performed within an inert atmosphere:
  - Normally, an effort is made to avoid inert entry, but it is sometimes used – such as in pyrophoric catalyst dumping or for metallurgy protection.
  - Procedures usually include much more detailed testing, permitting, and equipment requirements and require higher approval levels than a normal entry.
  - Fresh air equipment with backup and emergency egress air supplies would be used.
  - Often the workers use hard helmets with supplied air that they cannot remove themselves while in a reactor or IDLH environment.
  - Entry is normally done by contract personnel who do this type of work on a regular basis.

  - Monitoring of the vapor space is continuous during entry – normally for oxygen (which you want near zero in this case), H_2S, LEL, CO, and temperature. Entry is immediately terminated if any of the parameters goes out of the allowable range.
- For equipment that is supposed to be full of air (not inerted), fresh air ventilation is normally maintained before and during any entry or other work.
- Adequate ventilation is required anywhere inert gas may accumulate. For instance, if a plant uses vaporized nitrogen to back up the instrument air system, the nitrogen should not be allowed in any operator shelter or control room without ventilation. It is actually probably better to avoid this situation by addressing instrument air reliability rather than use nitrogen.
- Ensure you have a rescue system and plan for a "man down" in an inert environment. Unfortunately, a large number of the fatalities resulting from oxygen-deficient environments are would-be rescuers that enter without the proper air supply.
- If fresh breathing air is being used:
  - Test the breathing air (even if it is "certified" breathing air) to ensure it has sufficient oxygen. Some breathing air is made by blending vaporized liquid nitrogen and oxygen. Sometimes, this ends up being 100 % nitrogen instead due to a control problem. Often every air bottle is tested for oxygen.
  - Alternately, some companies insist on the breathing air in the bottles being compressed atmospheric air – no blending. In this case, the air intake location is carefully reviewed to ensure the incoming air is not contaminated.
  - Air connections should not be capable of being connected to nitrogen or CO_2 supplies. The standard connectors for the gases are different. Sometimes, there is "creativity" in making connections, however.
  - Ensure breathing air supply is uninterruptable with backup supply and egress bottles.
- Everyone who may be potentially exposed to an oxygen-deficient atmosphere, both employee and contractors, should be trained in the hazards, procedures, and equipment used at the specific facility.

People work safely around, and sometimes in, inert and oxygen-deficient environments every day. Understanding the hazards and using good management practices can prevent harm to people who must deal with this type of IDLH environment.

Confined Space Entry

The following discussion is presented for information only. Governmental regulations, company/contractor procedures, and legal considerations control all aspects of confined space entry at a given facility.

Hazards of Confined Space Entry

We have talked a little about confined space entry in discussing oxygen-deficient environments above. Here we will review some of the other hazards when someone enters an enclosed or confined space to work.

From the US Occupational Safety and Health Administration (OSHA) definition of a confined space [1910.146(b)]:

"Confined space" means a space that:

1. Is large enough and so configured that an employee can bodily enter and perform assigned work
2. Has limited or restricted means for entry or exit (e.g., tanks, vessels, silos, storage bins, hoppers, vaults, and pits are spaces that may have limited means of entry)
3. Is not designed for continuous employee occupancy

Examples of confined spaces in a petroleum processing facility would normally include:

- Reactors and absorbers/adsorbers
- Vessels
- Tanks
- Sewer boxes
- Heat exchanger shells
- Fireboxes
- Convection section ducting
- Very large piping

Some facilities may include equipment such as cooling tower cells and other relatively open structures in their definition of confined space because of specific hazards.

Confined spaces are of concern to us because they may present hazards from:

- A hazardous atmosphere:
  - Flammable (e.g., hydrocarbon vapors evolved from sludge)
  - Dusty (e.g., catalyst handling)
  - Oxygen deficient (e.g., inert reactor entry)
  - Toxic or hazardous gas (e.g., H_2S or NH_3)
  - Any other IDLH condition
- Possible engulfment risk from materials (e.g., catalyst falling in on a worker)
- Possible risk of being trapped or asphyxiated by configuration (e.g., inward sloping walls like an FCC cyclone)
- Other recognized, serious hazards

For confined spaces which do, or could, present one or more of these hazards, a permit is usually required to enter the space. In the OSHA definitions, these would be "permit-required confined spaces (permit spaces)."

There are other types of confined spaces for which some facilities may not require a permit. Many facilities just default to defining essentially all confined spaces as "permit spaces," with only some permit conditions differing.

Managing Confined Spaces

Facilities generally have a specific safety program to deal with confined spaces. There are legal/regulatory requirements for these programs. In general, programs governing confined spaces will have provisions that include:

- Identification of any opening into a confined space (e.g., signs and/or tape over all possible entry routes into the confined space).
- If the confined space is inert or may present some other atmospheric hazard, warning signs indicate the hazards. There may also be barriers or exclusion areas around any opening.
- A permit is required for anyone entering the confined space to work. The permit conditions will usually address things such as:
  - Allowable activities within the space for the specific permit.
  - Verification of complete isolation (blinds and blanks) of the confined space from other systems or potential energy sources.
  - Testing of the atmosphere inside the space to verify it meets the required conditions –usually flammability (LEL), oxygen (inert or air), CO, H_2S, and temperature.
  - Requirements for continuous monitoring of the space during entry.
  - Requirements for appropriate PPE.
  - Requirements for a "hole-watch" and/or standby personnel, including what equipment they must have available.
  - Verification of training of the entrant, hole-watch, and other personnel involved.
  - Conditions which would terminate or cancel the permit.
  - A time limit on the permit validity. Usually permits have to be renewed periodically, like each shift or each day. And entry must start within a specific time frame or the permit is canceled.
  - Requirement for continuous presence of someone at the entry point until entry is complete. This ensures the space is never left unattended, even over lunches or breaks.
  - Requirement to sign in and sign out of the space, with entry and exit through the same "hole." This is to ensure everyone is accounted for.
  - A rescue plan if needed. The hole-watch may be required to have a radio or another emergency signal device available.

- Additional permits and plans may also be required, for example:
  - Hot work permit for welding work inside equipment
  - Inert entry permit for catalyst or other work requiring exclusion of air during entry

Entry into confined spaces and work within the spaces are safely performed on a routine basis. The risks, hazards, requirements, and contingencies have to be thoroughly considered to protect the entrants from harm.

Facility Siting Hazards and Considerations

On 23 March 2005, an explosion occurred at BP's refinery in Texas City, Texas, in the USA that resulted in 15 fatalities and over 170 injuries. One of the refinery units was starting up after turnaround when a problem caused the release of hydrocarbon to an unfired vent stack. The hydrocarbon vapors found an ignition source and exploded. There is a great deal more detail in the BP and U.S. Chemical Safety Board (CSB) reports on the incident, but of interest to us here is a statement from the BP Executive Summary report:

> "The severity of the incident was increased by the presence of many people congregated in and around temporary trailers which were inappropriately sited too close to the source of relief."

Consideration of facility siting has always been an element of process safety management, but this incident elevated the importance of considering where facilities, both permanent and temporary, are located relative to process equipment. It prompted reevaluation and actions on the part of many facilities which could have similar risks.

Hazards relevant to facility siting can include injuries to workers in occupied structures from blast, fire, and release of toxic materials. In some cases, there may be off-site consequences.

Operator shelters are generally located close to the units they operate. These structures are often occupied. Consideration of their locations is appropriate relative to the different hazards presented by the units. The response time required to reach the unit when necessary is normally balanced against the hazards and risks. Some facilities "harden" the operator shelters to resist blasts and provide the capability for positive pressurization and sheltering in place to protect workers in the event of a toxic release. Alarm systems are provided in most plants to notify workers of releases or other problems and initiate egress in emergencies. Self-contained breathing apparatuses (SCBAs) are usually located throughout a unit and at operator shelters. The shelters usually have minimal windows, to prevent flying glass in the event of an incident.

Control rooms, increasingly, are centralized and located away from the process units. These "central control rooms" are often blast resistant, pressurized, and capable of isolating themselves for sheltering in place.

Administration, maintenance, firehouses, and other buildings are usually located far enough away from the process units and hazards that they are not a major risk. However, the locations of these buildings relative to the possible pressure waves or releases of toxics have been considered by some refiners. In some cases, some of these building are not in good locations. Some have been replaced with buildings further from the potential hazards.

The considerations for siting of structures have grown, with the BP incident, to also include temporary facilities. It used to be common to locate project trailers, turnaround trailers, lunch tents, and other temporary facilities close to where the work was to be done. This can expose workers to risks similar to the operator shelters, but these facilities are not designed for blast or atmospheric hazards.

Today, the temporary facility locations are considered much more carefully. Some rental companies have developed hardened, blast-resistant temporary “buildings” (really converted shipping containers), for use in process facilities when the office has to be near the work. When the office does not have to be in the plant, temporary trailers, lunch tents, and other facilities are being located away from the units in a safe distance.

As an additional protective measure, many facilities have a policy of evacuating all unnecessary personnel from any unit that is in start-up or shutdown. While this slows work, it minimizes the potential exposure of workers to a problem.

Practices and options for both permanent and temporary facility siting continue to develop and improve.

Material Failures and Prevention Programs

Process safety management regulations require a facility to maintain mechanical integrity (MI) of the equipment. Facilities should have a well-documented inspection and repair program to ensure the equipment and piping are well maintained to prevent losses of containment and process safety incidents. A primary MI concern is materials damage and prevention. The MI program is usually based on the risks and corrosion rates of the various process services and materials used (e.g., risk-based inspection).

API 510 (Pressure Vessel Inspection Code: In-Service Inspection, Rating, Repair, and Alteration) defines the US refining industry requirements for mechanical integrity. API 579 (Fitness for Service) provides methods and requirements for evaluation of equipment to continue operating in a facility. Refer to these publications in creating or evaluating your own mechanical integrity programs.

API Recommended Practice 571 (RP-571) provides a detailed discussion of the materials damage mechanisms and methods of control for each major type of process unit in a refinery. Many of these can be extrapolated to other types of petrochemical facilities. We will not propose to repeat the information in RP-571. Table 4 provides a summary of the materials damage mechanisms discussed in RP-571 for reference. Please refer to that publication for details.

Table 4 Refinery materials damage mechanisms (Reference: API Recommended Practice RP-571)

Affected Unit	**Crude/Vacuum**	**Delayed Coker**	**Fluid Catalytic Cracking**	**FCC Light Ends Recovery**	**Continuous Catalytic Reforming (CCR)**	**Catalytic Reforming (Cyclic, Semi-regen)**	**Hydroprocessing (Treating, Cracking)**	**Alkylation, Sulfuric Acid**	**Alkylation, HF**	**Amine Treating**	**Sulfur Recovery**	**Sour Water Stripper**	**Isomerization**	**Hydrogen Plant**
Damage Mechanisms														
Mechanical & Metallurgical Failure														
Graphitization			■											
Softening (Spheroidization)														
Temper Embrittlement			■		■		■							■
Strain Aging														
885°F Embrittlement	■	■	■				■							■
Sigma Phase / Chi Embrittlement			■				■							
Brittle Fracture							■							
Creep / Stress Rupture	■	■	■		■	■	■							■
Thermal Fatigue		■	■			■								■
Short-term Overheating - Stress Rupture	■	■	■		■		■							■
Steam Blanketing			■								■			■
Dissimilar Metal Weld (DMW) Cracking	■								■					■
Thermal Shock		■												■
Erosion / Erosion-Corrosion	■	■	■	■	■		■		■	■		■		
Cavitation														
Mechanical Fatigue					■	■								■
Vibration-Induced Fatigue														
Refractory Degradation			■			■					■			■
Reheat Cracking			■		■									■
Uniform or Localized Loss of Thickness														
Galvanic Corrosion									■					
Atmospheric Corrosion														
Corrosion Under Insulation (CUI)		■						■					■	
Cooling Water Corrosion					■									
Boiler Water / Condensate Corrosion			■								■			■
CO2 Corrosion	■													■
Flue Gas Dew Point Corrosion											■			
Microbiologically Induced Corrosion (MIC)		■												
Soil Corrosion														
Caustic Corrosion	■							■					■	
Dealloying		■												
Graphitic Corrosion														
Amine Corrosion							■			■				■
Ammonium Bisulfide Corrosion (Alkaline Sour Water)		■		■			■			■		■		
Ammonium Chloride Corrosion	■	■	■	■	■	■	■							
Hydrochloric Acid (HCl) Corrosion	■				■	■	■						■	
High Temperature H2/H2S Corrosion						■	■							
Hydrofluoric Acid (HF) Corrosion									■					
Naphthenic Acid Corrosion (NAC)	■	■					■							
Phenol (Carbolic Acid) Corrosion														
Phosphoric Acid Corrosion														
Sour Water Corrosion (Acidic)														
Sulfuric Acid Corrosion								■			■			
High Temperature Corrosion [400°F, 204°C]														
Oxidation	■	■	■		■	■					■			■
Sulfidation	■	■	■				■				■			
Carburization		■	■		■	■								
Metal Dusting					■	■								■
Fuel Ash Corrosion	■													
Nitriding														
Decarburization			■											
Environment-Assisted Cracking														
Chloride Stress Corrosion Cracking (Cl^-SCC)	■		■				■					■		■
Corrosion Fatigue														
Caustic Stress Corrosion Cracking (Caustic Embrittlement)	■							■	■				■	
Ammonia Stress Corrosion Cracking	■	■			■									
Liquid Metal Embrittlement (LME)	■													■
Hydrogen Embrittlement (HE)					■		■							
Polythionic Acid Stress Corrosion Cracking (PASCC)	■		■				■							■
Amine Stress Corrosion Cracking							■			■				■
Wet H2S Damage (Blistering, HIC, SOHIC, SCC)	■	■	■	■			■			■	■	■		
Hydrogen Stress Cracking - HF									■					
Carbonate Stress Corrosion Cracking			■	■										
Other Mechanisms														
High Temperature Hydrogen Attack (HTHA)					■	■	■							■
Titanium Hydriding										■		■	■	

Appendix: Example Calculation for Sizing a Relief Valve

Problem

A vessel containing naphtha C_5–C_8 range is uninsulated and is not fireproofed. The vessel is vertical and has a skirt 15′ in length. Dimensions of the vessel are I/D 6′0″, T-T 20′0″, and liquid height to HLL 16′0″. Calculate the valve size for fire condition relief. Set pressure is 120 psig.

Solution

Latent heat of naphtha at 200 °F is 136 Btu/lb=H_L

$Q = 21{,}000\ \mathrm{FA}^{0.82}$

A = Wetted area and is calculated as follows:

$$\begin{aligned}\text{Liquid height above grade} &= 15 + 16\ \text{ft}\\ &= 31\ \text{ft}\end{aligned}$$

Therefore wetted surface of vessel need only be taken to 25 f. above grade which is 25–15 = 10 f. of vessel height:

$$\begin{aligned}\text{Wetted surface} &= \pi D \times 10\,\text{ft for walls}\\ &= 188.5\,\text{sq ft}\\ &\quad\ \text{plus}\,28.3\ \text{sq ft for bottom}\\ &= 216.8\,\text{sq ft}\\ Q &= 21{,}000 \times 1.0 \times (216.8)^{0.82}\\ &\ \ 1.729 \times 10^6\ \text{Btu/h}\\ Q/H_\text{L} &= \frac{1.729 \times 10^6}{136} = 12{,}713\ \ \text{lbs/h} = W\\ A &= \frac{W\sqrt{T}\sqrt{Z}}{CKP_1K_\text{b}\sqrt{M}}\end{aligned}$$

where:

A = effective discharge area in sq in.

W = flow through valve in lbs/h, 12,713.

T = absolute temp of inlet vapor, 460 + 200 = 660 R (Bubble point of C_5-C_8 at, say, 10 psig).

Z = 0.98 (nC_5).

C = 356.06 (based on $C_A/C_V = 1.4$).

K = 0.65 (typical coefficient of discharge).

$K_b = 0.9$
$M = 100$ (use C_7).
$P_1 =$ set pressure of valve, 134.7 psia.

$$A = \frac{12,713 \times 25.7 \times 0.99}{356 \times 0.65 \times 134.7 \times 0.9 \times 1} = 1.153 \text{ in.}^2$$
$$\text{nearest orifice size } = \text{'}J\text{' at } 1.287 \text{ in.}^2$$

References

PSM and Related Programs

American Petroleum Institute, Management of Process Hazards, *API Recommended Practice 750* (1990, Since Withdrawn)

J. Atherton, F. Gil, (AIChE CCPS, 2008), *Incidents that Define Process Safety* (American Institute of Chemical Engineers, Center for Chemical Process Safety/Wiley, New York/Hoboken,, 2008)

Center for Chemical Process Safety (CCPS), American Institute of Chemical Engineers, New York, several references

J. B. Christian, (Osram Sylvania Inc., 1997), Combine fault and event trees for safety analysis, Chem. Eng. Progress. 72–75 (1997)

M.M.R. Eastman, J.R. Sawers (Knowledge Technologies, 1998), Learning to document management of change. Chem. Process. 15–22 (1998)

K.A. Ford, A.E. Summers, (Triconex, 1998), Are your instrumented safety systems up to standard? Chem. Eng. Progress 55–58 (1998)

R.W. Garland (Eastman Chem. Co., 2012), An engineer's guide to management of change. Chem. Eng. Progress 49–53 (2012)

L. Goodman (Fluor Daniel, 1996), Speed your hazard analysis with the focused what if? Chem. Eng. Progress 75–79 (1996)

W.K. Goddard (Solutia Inc., 2007), Article: Use LOPA to determine protective system requirements, Chem. Eng. Progress, Feb, pp. 47–51 (2007)

R.K. Goyal, (BAPCO, 1993), FMEA, the alternative process hazard method. Hydrocarb. Process. 95–99 (1993)

R.K. Goyal (BAPCO, 1994 and 1995), Understand quantitative risk assessment. Hydrocarb. Process. 105–108 (Dec 1994), 95–99 (Jan 1995)

ISA, *Standard: Application of Safety Instrumented Systems for the Process Industries*, ANSI/ISA-SP 84.01-1996 (ISA, Research Triangle Park, 1996)

R.E. Knowlton, (Chemetrics, 1987), *An Introduction to Hazard and Operability Studies: The Guide Word Approach.* (Chemetrics Int'l, Vancouver, 1987)

H. Ozog, H.R. Forgione, (ioMosaic Corp., 2012), OSHA's new chemical NEP: how to make the grade and earn extra credit, Chem. Eng. Progress 27–34 (2012)

K.E. Smith, D.K. Whittle (EQE Int'l, Inc., 2001), Six steps to effectively update and revalidate PHAs. Chem. Eng. Progress 70–77 (2001)

R.P. Stickles, G.A. Melhem, (Arthur D. Little, Inc., 1998), How much safety is enough?, Hydrocarb.. Process. 50–54 (1998)

Wikipedia, several articles on www.wikipedia.org. Accessed Feb 2014

Oxygen Deficient Environments

J. Cable, NIOSH report details dangers of carbon dioxide in confined spaces. Occup. Hazards. (30 Dec 2004)

National Institute for Occupational Safety and Health (NIOSH), *Guidance Document: Criteria for a Recommended standard, Occupational Exposure to Carbon Dioxide* (National Institute for Occupational Safety and Health, Menlo Park, 1976)

U.S. Bureau of Land Management, Health risk evaluation for carbon dioxide (CO_2). (2005)

U.S. Chemical Safety and Hazard Investigation Board, Bulletin: Hazards of nitrogen asphyxiation, Safety Bulletin No. 2003-10-B, June 2003 (2003)

Confined Space Entry

U.S. Occupational Safety and Health Administration, *Standard: Permit-Required Confined Spaces*, Standard No. 1910.146. www.osha.gov

Facility Siting Hazards and Consideration

BP USA, *Public report: Fatal Accident Investigation Report, Isomerization Unit Explosion*, Final Report, Texas City. (BP, Texas, 2005)

S.R. Brahmbhatt, (MG Ind., 1984), Are liquid thermal relief valves needed? Chem. Eng. 70 (1984)

Hazardous Materials in Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_21

Abstract

Although the fire hazard is always a primary concern in the refining of petroleum, there are other hazards present that need to be addressed. Among these are the handling of some of the chemicals that are used or generated in the refining processes. This chapter provides general information on the hazards and handling of several chemicals. The information is not intended to substitute for regulatory, local, or company standards or medical expertise. Included here, are discussions of: amines, ammonia, benzene, carbon monoxide, catalysts and sorbents, caustic soda, furfural, hydrofluoric acid, hydrogen, hydrogen sulfide, methyl ethyl ketone, nickel carbonyl, nitrogen, sulfiding chemicals, and sulfuric acid.

Keywords

Refinery • Hazardous materials • Materials handling • Safety • Toxicity • Exposure limits

Introduction to Handling Hazardous Materials

Disclaimer: Please note that the discussions presented in this chapter are for informational purposes only. They are not meant to be specifications and are not all-encompassing. We defer to industrial hygiene, medical, and other experts and to your company to evaluate and determine the appropriate, current methods for handling these hazardous materials and for emergency responses and procedures relevant to each chemical. Many resources (e.g., MSDSs, chemical suppliers, licensors) are available to assist in these efforts.

From the very nature of crude oil, its refining and processing can create potentially hazardous situations. The most commonly recognized hazard we expect is, of course, the danger of fire. Considerable effort is made to prevent fires and, if a fire does occur, to combat and restrain it in the most effective manner. Fire prevention and firefighting are discussed in detail in the chapter "▶ Fire Prevention and Firefighting in Petroleum Processing" of this handbook.

Although the fire hazard is always a primary concern in the refining of petroleum, there are other hazards that are present and always need to be addressed. Among these are the handling of toxic and dangerous chemicals that are used in the refining processes. For many of the chemicals used in refining, there is also a danger to life or health from exposure to toxic materials that are produced in some of the refining processes. Perhaps the most notable is hydrogen sulfide, which is common to all modern refineries.

This chapter deals with the nature and handling of some of the common hazardous materials used or produced in refining. The specific materials addressed are:

- Amines
- Ammonia
- Benzene
- Carbon monoxide
- Catalysts and sorbents
- Caustic soda (AKA sodium hydroxide, NaOH)
- Furfural
- Hydrofluoric acid (HF, AHF)
- Hydrogen
- Hydrogen sulfide
- Methyl ethyl ketone
- Nickel carbonyl
- Nitrogen
- Sulfiding chemicals
- Sulfuric acid (H_2SO_4)

Some of these materials are discussed in other chapters, but we have tried to pull the relevant materials all together here.

In all cases, it is strongly recommended that you consult the material safety data sheet (MSDS) for each material for the most up-to-date information about its hazards and handling.

Amines for Gas Treating

Discussion and Hazards of Amines

Amine solvents are used in petroleum and natural gas refining to remove hydrogen sulfide and carbon dioxide from the various streams. In petroleum refining, the monoethanolamine (MEA) compound of the homologue used to be common in the treating processes. Diethanolamine (DEA) and methyl diethanolamine (MDEA) have become much more common. Proprietary compounds of amine such as Sulfinol and ADIP follow in usage. All of these amines, however, are similar with respect to their hazards, handling, and health effects.

Table 1 Properties of amines used in petroleum refining

Type	MEA	DEA	MDEA	DGA	ADIP	Sulfinol
Mole weight	61.1	105.1	119.16	105.14	133.19	120.17
Boiling Pt °F (°C)	338.5 (170)	515.1 (268)	477 (247)	405.5 (208)	479.7 (249)	545 (285)
Boiling range 5–95 % °F (°C)	336–341 (169–172)	232–237 (111–114)	477 (247)	205–230 (96–110)	–	–
Freezing Pt °F (°C)	50.5 (10.2)	77.2 (25.1)	−9.3 (−23)	9.5 (−12.5)	107.6 (42)	81.7 (27.6)
S.G. @ 77 °F (25°C)	1.0113	1.0881	1.0418 (20 °C)	1.0572	0.99	1.256
Viscosity @ 77 °F (25 °C)	18.95 cP	351.9 cP	36.8 cSt (100 °F [38 °C])	40 cP	870 cP	12.1 cP
Viscosity @ 140 °F (60 °C)	5.03 cP	–		6.8 cP	86 cP	4.9 cP
Flash Pt °F (°C)	200 (93.3)	295 (146)	265 (129)	260 (127)	255 (124)	350 (177)
Fire Pt °F (°C)	205 (96)	330 (166)	–	285 (141)	275 (135)	380 (193)
Typical solvent concentration, wt%	15–25	25–35	50	50–70	NA	Varies

For the purpose of this work, only MEA will be considered. However, as a point of reference, Table 1 provides the physical properties of those amines used in petroleum refining (see also the chapter entitled "▶ Refinery Gas Treating Processes").

MEA is corrosive and a combustible liquid and requires special handling and personnel protection considerations.

All amines are injurious to personnel. As a guide, the effects of exposure to MEA are as follows:

- *Target organs:* Kidneys, central nervous system, and liver.
- *Potential health effects*
  - *The eyes:* MEA causes severe eye irritation and burning.
  - *The skin:* May be absorbed through the skin in harmful amounts. Causes moderate skin irritation.
  - *Ingestion:* Causes gastrointestinal tract burns.
  - *Inhalation:* Inhalation of high concentrations may cause central nervous system effects. This is characterized by headaches, dizziness, unconsciousness, and coma. Also causes respiratory tract irritation.
  - *Chronic:* May cause liver and kidney damage.

Safe Handling of Amines

MEA is transported by road or rail tanker in its concentrated form. It is transferred in the normal way to an onsite storage bullet or tank, which is blanketed by an inert gas. MEA is degraded on exposure to air. The use of this, and other ethanolamines, in the refinery processes is in a dilute form. This dilution and its onsite storage are very often in a suitably constructed pit, usually in the proximity of the user plant. In some cases, a cone roof tank may be used for onsite storage. In all cases, though, the product must be kept free from exposure to air by inert gas blanketing. The dilution of MEA for use in the refinery process is between 15 and 25 wt%. The water for this dilution is usually treated boiler feed water or condensate, which are essentially free of impurities.

Vessels and piping in the process in which the amine is used should be of a suitable grade of carbon steel. The amine process temperatures should not exceed 300 °F (149 °C) anywhere in the process.

Personnel likely to be exposed to the amine should wear protective clothing, including eye protection (goggles and/or face shield in addition to safety glasses). As in the case of handling AHF, the minimum protection for operating and maintenance personnel should be:

- Coveralls, with sleeves to the wrist
- Chemical safety goggles
- Hard hat
- Gauntlets (polyvinyl chloride)
- Standard safety footwear

In addition to the standard, protective clothing listed, certain operating and maintenance work requires the use of a respirator. Such an instance would be in the changing of the amine filter (see the chapter entitled "▶ Refinery Gas Treating Processes") cartridge. Although the filter will have been steam cleaned prior to opening the filter vessel, respiratory protection is essential until no presence of amine or H_2S is verified. The verification is established by gas testing and the special processes to determine the absence of the sulfide (lead acetate test).

In some services, such as hydrogen plants, where MEA is used, arsenic is sometimes used as a corrosion inhibitor. This can increase the hazards of the amine and the equipment during servicing. Procedures to operate and decontaminate equipment for maintenance must ensure the operators and maintenance hands do not come in contact with the arsenic compounds.

Equipment and Piping for Amines

As is the case with all alkaline substances, amines cause stress corrosion. Consequently, all vessels and piping (welds) are stress relieved. Valves and piping are normally carbon steel, as are pumps and heat exchanger tubes.

Ammonia (NH_3)

Discussion of Ammonia

In petroleum processing facilities, ammonia may be used for NOx control in combustion flue gases and for refrigeration. In some facilities it is used to control corrosion in tower overheads and to suppress catalyst activity during hydrocracker startup.

Ammonia is produced in a refinery by hydroprocessing, when nitrogen compounds are removed from petroleum products. It is a major constituent of sour water stripper gases. When economic, some facilities recover ammonia as a by-product.

Ammonia itself may be present as a colorless, pressurized liquid or a colorless gas with a characteristic, pungent smell. Under typical ambient conditions, it is a gas. It is common to handle ammonia in an anhydrous liquid form under pressure or as an aqueous solution (5–30 % ammonia, AKA aqua ammonia) at ambient conditions. A typical aqua ammonia concentration is 19 wt% (for SCR-grade ammonia). See the separate topic "▶ Utilities in Petroleum Processing" for a discussion of ammonia systems and uses in the refinery.

Properties of Ammonia

Table 2 summarizes some of the key properties of anhydrous and aqua ammonia grades.

Ammonia Hazards

Ammonia, in any form, is an irritant and corrosive to the skin, eyes, respiratory tract, and mucous membranes. It can cause severe chemical burns to eyes, lungs, and skin. Any existing skin or respiratory illnesses are aggravated by exposure to ammonia. Ammonia is not recognized as a carcinogen. Evaporating anhydrous ammonia can produce frostbite if skin contacts equipment where it is being vaporized.

When mixed with air, ammonia vapor is flammable between 15 and 28 vol%. Because the autoignition temperature is high, a fairly hot ignition source is needed to start combustion. Welding and similar activities are hot enough, so care should be taken to ensure equipment that has contained ammonia is completely clear before welding. Ensure there are no vapors in the area if welding near an ammonia storage tank or a line.

Ammonia does not normally corrode steel or iron but can react rapidly with copper, brass, zinc, and many alloys, especially those containing copper. Experience has shown that aqua ammonia will corrode carbon steel slowly, however. Only steel and ductile iron are normally used in ammonia service. For aqua ammonia, stainless steel should be used ahead of any vaporizers.

The exposure limits for ammonia (as vapor) are summarized in Table 3.

Table 2 Some key ammonia properties

Concentration	Anhydrous	29.4 wt% (26° Baumé)	19 wt% (∼20.5° Baumé) SCR grade
Specific gravity	Vapor: 0.59 (Air = 1)	0.8974 (60/60 °F, 15/15 °C)	0.9294 (60/60 °F, 15/15 °C)
	Liq: 681.9 kg/m^3 (−33.3 °C), 42.6 lb/ft^3 (−28 °F)		
Boiling point	−28.01 °F (−33.34 °C)	85 °F (29 °C)	123 °F (∼51 °C)
Freezing point	−107.9 °F (−77.7 °C)	−110 °F (−79 °C)	−30 °F (−34 °C)
Solubility in water	47 wt% @ 32 °F (0 °C)		
	31 wt% @ 77 °F (25 °C)		
	28 wt% @ 122 °F (50 °C)		
Solution pH		13.5	∼12.9
Viscosity	0.276 cP (−40 °F,−40 °C)		
Autoignition temperature	1204 °F (651 °C)		
Explosive limits	15–28 vol%		

Table 3 Ammonia exposure limits and toxicity

Agency	Limit type	ppm	mg/m^3	Basis
US OSHA	PEL	50	35	8 h TWA
US NIOSH	STEL	35	27	15 min
	REL	25	18	10 h TWA
	IDLH	300		
ACGIH	TLV	25	18	8 h TWA
	STEL	35	27	15 min

Toxicity: LD50 (Oral, Rat) =350 mg/kg

Clothing and Personal Protective Equipment for Ammonia

Proper ammonia handling PPE includes safety goggles and/or face shield, rubber gloves, in addition to the normal flame-retardant clothing, safety glasses, safety-toe shoes, and hardhat. Do not wear contact lenses when handling ammonia. It is also a good idea to wear ammonium hydroxide impervious clothing and rubber boots when loading or unloading.

Adequate ventilation should be provided in any ammonia handling area. There should be a safety shower and eyewash near any ammonia handling area.

If there is a possibility that the inhalation exposure limits may be approached, then respiratory protection approved by NIOSH/MSHA (or equivalent agencies) should be used. For escape in emergencies, approved respiratory protection that consists of a full-face mask, and canisters or SCBA are needed. Regulations 29 1910.134 and ANSI: Z88.2 apply. Only a positive-pressure SCBA should be used for entry into an ammonia-contaminated area if the atmosphere could contain over 300 vppm ammonia (IDLH).

For hazardous materials response to an ammonia spill, Level A and/or Level B gear should be used, including a positive-pressure SCBA.

Release Measures

In the event of a significant ammonia release, the following steps are recommended:

- Initiate the facility emergency response system.
- Evacuate the immediate area. This evacuation area may need to be very large if the spill is large.
- Eliminate all possible ignition sources in the area.
- Shutoff or isolate the leak, if possible. This will either stop or minimize the amount.
- Control ammonia vapors with water spray around the spill. The runoff water will be contaminated and may require treatment.
- Response personnel should have SCBAs with escape bottles. They should be in chemical-resistant suits with resistant gloves for major spills.

Storage and Handling

Anhydrous ammonia is shipped in pressurized tank trailers and tank wagons. Aqua ammonia is normally shipped in 6,700 gal (~26,000 l or ~25 MT) tank trucks (at low or ambient pressure) or in drums.

Refer to the topics entitled "▶ Utilities in Petroleum Processing" and "▶ Environmental Control and Engineering in Petroleum Processing" for discussions of the types of bulk storage facilities used for ammonia. For drum storage of aqua ammonia, the drums should be kept cool and out of the weather. The ammonia in the drums will be near its boiling point at about 85 °F (29 °C).

Sometimes anhydrous ammonia is supplied in pressurized cylinders. These should also be stored in a covered location out of the sun.

Proper PPE as discussed in section "Clothing and Personal Protective Equipment for Ammonia" should be used when handling cylinders or transferring ammonia. Gloves are especially important in handling cylinders and drums. Cylinders and drums should never be dragged.

Proper safety showers and eye washes should be available near any handling area.

Benzene

General Discussion of Benzene

Benzene is found in many processes and petroleum products within a refinery and related facilities. In some cases, the product may be benzene that is deliberately recovered. In other streams, such as gasoline or reformate, the benzene is present as part of the hydrocarbon mixture.

Some benzene finds its way into waste water effluents, where it is governed by both water and air regulations (NESHAP).

We will briefly discuss benzene in a petroleum processing setting along with handling hazards. Many of the hazards and protective measures for benzene are also applicable to other aromatics (like toluene and xylene) which are a little less hazardous but still need some of the same precautions.

Key Properties of Benzene

Benzene is the simplest aromatic compound found in petroleum. It occurs naturally but is also made in refining. Some of the key chemical and physical properties of benzene are listed in Table 4.

Hazards of Benzene

There are two primary areas where benzene presents hazards in handling:

- Health hazards
- Fire hazard

The fire hazard can be perceived from the key properties table. Benzene can cause a flash fire.

From a health standpoint, the exposure limits and toxicity of benzene are summarized in Table 5.

Table 4 Some key properties of benzene

Molecular formula	C_6H_6
Molecular weight	78.11
Appearance	Clear, colorless, stable liquid
Odor	Sweet aromatic, gasoline-like
Odor threshold	61 ppm
Specific gravity, 20/20 °C (68/68 °F)	0.8765
Boiling point	176.18 °F (80.1 °C)
Vapor pressure	99 mmHg (77 °F, 25 °C)
Freeze/melting point	41.9 °F (5.5 °C)
Solubility in water	1.79 g/l (59 °F, 15 °C)
Flash point	11.9 °F (−11.15 °C) CC
Autoignition temperature	1097 °F (591.65 °C)
Vapor density	2.7 (Air =1)
Flammable limits in air, vol%	LEL: 1.3; UEL: 7.1
Extremely flammable, especially near open flames	

Table 5 Exposure limits and toxicity of benzene

Agency	Type	Limit	Notes
ACGIH (2012)	TLV	0.5 ppm	8 h TWA
	STEL	2.5 ppm	15 min
NIOSH (2008)	REL	0.1 ppm	10 h TWA
	STEL	1 ppm	15 min
OSHA (2006)	PEL	1 ppm	8 h TWA
	STEL	5 ppm	15 min
Toxicity data			
LC50 (rate)	Inhalation	10,000 ppm	7 h
LD50 (rat)	Ingestion	930–1,800 mg/kg	

Known carcinogen (leukemia). Suspected mutagen.

Looking at the health hazards and effects from an exposure route standpoint:

- Inhalation: Irritating to mucous membranes and upper respiratory tract. May be fatal in high concentrations. Can cause central nervous system depression, headaches, dizziness, fatigue, and excitation followed by depression.
- Eyes: Irritant.
- Skin: Irritating. Harmful if absorbed through the skin. Skin inflammation characterized by itching, scaling, reddening, or blistering. Prolonged or repeated skin contact can defat the skin and lead to irritation, cracking, and/or dermatitis.
- Ingestion: Aspiration hazard. Can enter lungs and cause damage. May be fatal if swallowed. Can cause dizziness, headaches, breathing difficulties, diarrhea, vomiting, and possible pneumonia.
- Chronic effects: Following low-level exposure, adverse effect on hematological (blood-forming) system and myelodysplastic syndrome (disease that affects bone marrow and blood).
- Benzene is a known carcinogen.

Summarizing, symptoms of over-exposure to benzene include:

- Dizziness
- Excitation
- Pallor followed by flushing
- Weakness
- Headache
- Breathlessness
- Chest constriction
- Irritation of the eyes, skin, nose, and respiratory system
- Nausea
- Staggered gait
- Fatigue

Benzene is extremely reactive or incompatible with oxidizers, nitric acid, and many fluorides and perchlorates.

The HIMA (USA) rating for benzene is 2-3-0 (health-fire-reactivity). The US NFPA rating is also 2-3-0.

Personnel Protection from Benzene

The primary PPE worn by refinery personnel in the plant will provide some level of protection from limited fire hazards. It does not protect from the chemical and other hazards, however.

Additional PPE for handling high benzene content streams or for spills include:

- Respiratory protection appropriate to the exposure risk
- Impervious gloves
- Chemical splash goggles (possibly face shield)
- Full impervious suit for large quantities or concentrations
- Rubber boots
- SCBA or other positive fresh air equipment

As for most materials discussed in this chapter, an eyewash and safety shower should be immediately available near locations where high concentrations of benzene are handled.

Storage and Handling of Benzene

Benzene is not corrosive, so handling is normally in carbon steel equipment – tanks, lines, vessels, etc. Metallurgy may be determined more by the other materials mixed with the benzene.

When transferring benzene, the safety precautions required are essentially the same as those for gasoline, including grounding or bonding all equipment involved in the transfer electrically.

For releases of benzene:

- Small spills:
  - Absorb in absorbent material.
  - Put absorbent in metal container.
  - Dispose as hazardous waste.
- Large spills:
  - Flammable liquid risk.
  - Don the appropriate PPE.
  - Contain spill if possible and stop flow.
  - Evacuate area.

- Eliminate possible ignition sources from area – remember the vapors can spread through low-lying areas.
- Ventilate area.
- Absorb benzene in dry earth, clay, sand, or other noncombustible material.
- Do not allow runoff to enter drains or sewers.
- Dike area for containment.
- There will be notifications necessary.

A fire or explosion involving benzene will evolve large amounts CO and CO_2 vapors as well as being very hot. Fresh air equipment must be worn when fighting these fires. Cooling water sprays may be used for equipment containing benzene. Minimize and contain runoff which may contain benzene for subsequent processing. Do not let it enter the wastewater treatment system, drains, or sewers.

Most facilities never handle benzene as a pure substance. Because of this, the normal concerns are with flammability of the product containing the benzene. Higher concentrations of benzene would trigger more diligence toward preventing personnel exposure.

Carbon Monoxide (CO)

Discussion of CO

Large quantities of carbon monoxide are present in all combustion gases (stacks, flares, incinerators, etc.), in partial-burn FCC regenerator gases, and as a by-product of manufacturing hydrogen. It may also be created by smoldering hydrocarbon solids, like coke or coke-coated catalysts. In a plant with cryogenic separation of refinery make gases, CO may be encountered as both gas and liquid. Care is normally taken to ensure the CO is exhausted at a safe location from elevated stacks or, in the case of hydrogen plants, destroyed by further reaction or completion of combustion. Solids are normally kept wet to avoid smoldering.

It is still possible for personnel to encounter CO in a facility. Atmospheric conditions may cause stack gases to drift or settle in locations where someone may be exposed – such as a nearby tower or structure. Sampling of flue gas or hydrogen plant gases can expose someone to CO. Burner problems in furnaces can result in CO outside the firebox and stack.

Precautions and response plans need to consider the possible presence of CO. Here we will discuss the hazards and basic protection methods available.

Chemical and Physical Properties of CO

Table 6 lists the relevant key physical and chemical properties of CO. Note that CO will normally be a colorless, odorless, tasteless gas at conditions encountered in a refinery. The exception would be in cryogenic units, where it may be a liquid, and in

Table 6 Some key properties of CO gas

Molecular weight	28.01
Specific gravity	Vapor: 0.97 (Air = 1)
Boiling point	−311.8 °F (−191 °C)
Freezing point	−337 °F (−205 °C)
Solubility in water	27.6 mg/l (77 °F/25 °C)
Autoignition temperature	1121 °F (605 °C)
Explosive limits	12.5–74.2 vol%

flue gases, where it is mixed with other gases that do have a warning odor (like SO_2). We will focus here on CO as a gas, however.

Things to note in the properties of CO are that it has essentially the same molecular weight as nitrogen, so is likely to be found along with nitrogen. It also has a wide explosive limit, meaning that it will support combustion fairly readily.

Hazards of CO

CO is a flammable gas and may cause a flash fire. It may be fatal if inhaled in sufficient concentrations. See Table 7 below for exposure limits.

Specific organs at risk from CO include the blood, lungs, nervous system, heart, cardiovascular system, and central nervous system. Frostbite can also occur as a result of rapidly expanding gas or vaporizing liquid, but this is unlikely in a refinery setting.

The primary route of exposure that is most frequently encountered is inhalation. Once in the lungs, CO bonds to the hemoglobin in the blood and reduces the blood's ability to carry oxygen. This is often hard to identify because blood saturated with CO is still red, while the victim is effectively suffocating. Studies indicate that 667 ppm of CO in the atmosphere can bind 50 % of the hemoglobin in the blood. This loss of oxygen capacity may result in seizure, coma, and fatality. Half-life of CO in the blood is about 5 h, so there is a cumulative effect of exposure.

Symptoms of CO poisoning include:

- Headache
- Nausea
- Vomiting
- Dizziness
- Fatigue
- Feeling of weakness
- Confusion
- Disorientation
- Visual disturbances
- Seizures
- Cherry-red blood and appearance (not necessarily reliable)

Most victims of CO poisoning believe they have food poisoning.

Table 7 Exposure limits for CO

Agency	Limit type	ppm	mg/m^3	Basis
US OSHA	PEL (2010)	50	55	8 h TWA
US NIOSH	STEL	200	229	
	REL	35	40	10 h TWA
	IDLH	1,200		
ACGIH (USA)	TLV (2010)	25	29	8 h TWA

LC50 (Rat) by inhalation: 6,600 ppm (30 min); 3,760 ppm (1 h); 1,807 ppm (4 h)

Protective Equipment for CO

The first level of protection against CO exposure is adequate ventilation in locations where CO may accumulate or be encountered. Stack elevations are normally specified to be a minimum height above and a minimum distance from any nearby structure to ensure dissipation of stack gases. These distances are specified by each company.

The normal PPE worn by a refinery worker will not protect against CO inhalation hazards. If exposure to CO is anticipated or possible the following may be used:

- Personal CO monitor with visual, vibration, and audible alarms. In the event of an alarm, the worker should immediately evacuate the area to a safe location.
- Air-purifying respirator up to the maximum CO concentration for the specific respirator. It is advisable to consider this only for escape. These are not for an oxygen-deficient atmosphere.
- Supplied-air respirator with an escape bottle (SCBA or airline respirator) for any significant exposure risk (spills, fires, etc.).

Handling of CO Streams

The PPE measures for handling streams which may contain CO are listed above.

Aside from small amounts of calibration gases, CO is normally a product of the refining processes. There is normally no reason to receive any bulk CO in a facility. The primary handling focus is on getting rid of the CO produced.

CO in stack gases is dispersed in the atmosphere. Operation of the fired heaters, CO boilers, and other services minimize the amount of CO emitted.

CO from processes, such as hydrogen production, is either burned as fuel gas in the SMR heater or reduced to methane (methanated) in the case of a conventional hydrogen plant.

When exposure to any hazardous level of CO is possible, fresh air respirators should be worn. This would include sampling of hydrogen plant intermediate streams, for instance.

Catalysts and Sorbents

General Discussion of Catalysts and Sorbents

Petroleum processing facilities employ a wide range of catalysts and sorbents in the various units. Many of these are designated as hazardous wastes when they are spent. Others may be classified as hazardous wastes based on their characteristics. In some cases, the fresh catalyst or sorbent may present a hazard that should be recognized. Here we will focus on some of the more common materials that present hazards and the methods employed to manage the hazards:

- Fresh and spent hydroprocessing catalysts
- Fresh and spent hydrogen plant nickel catalysts
- PSA adsorbents
- Mole sieve or zeolite adsorbents

Hazardous Catalyst and Sorbent Properties

Table 8 lists some of the physical properties and hazards of concern for the materials of interest.

Many of these materials are self-heating or pyrophoric. They may combust, generating hazardous gases. Others are hazardous because they heat up on or may release adsorbed hazardous vapors when exposed to moisture, such as in the air. Methods to manage these factors are well established.

The topic titled "▶ Environmental Control and Engineering in Petroleum Processing" of this handbook discusses the management of spent catalysts and characteristic hazardous wastes in detail.

Health effects of the above materials by various exposure routes are summarized in Table 9.

Catalyst and Sorbent Handling

In addition to the normal petroleum facility safety gear (hardhat, safety glasses, flame-retardant clothing, safety boots, gloves), the following PPE are also common when handling the catalysts and sorbents:

- Handling in air:
  - Dust respirator or HEPA half-face mask is adequate normally.
  - If hazardous gases may be released, an appropriate air-purifying or supplied-air respirator may be used.
  - In the case of nickel catalysts, refer to the discussion of nickel carbonyl in this chapter.

Table 8 Some common catalyst and sorbent properties and hazards

Material	Hydroprocessing catalysts	Hydrogen plant catalysts	PSA adsorbents	Molecular sieves or zeolites
Service	Hydrotreating, hydrocracking	Reforming, methanation	Hydrogen recovery, other	Air drying. O_2 or N_2 generators
Composition				
Fresh	Oxides of Ni, Mo, and Co on alumina base: May contain silica. Sulfided forms, also	NiO and reduced nickel	Activated carbon. Mole sieves (silica)	Mole sieves, zeolite
Spent	Sulfides of the metals. Coke. FeS. Heavy metal or As accumulations. Adsorbed aromatics	NiO and reduced nickel. Adsorbed CO and other gases. Coke	Activated carbon. Mole sieves (silica). Residual adsorbed gases like CO and H_2S	Mole sieves, zeolite, contaminants picked up in service
Typical density range	25–75 lb/cft (400–1,200 kg/m^3)	~40–100 lb/cft (640–1,600 kg/m^3)	30–45 lb/cft (480–720 kg/m^3)	30–60 lb/cft (480–960 kg/m^3)
Hazardous properties				
Fresh	Metal dusts. Some may be self-heating	Ni dust	Heat of adsorption for water. Silica dust	Heat of adsorption for water. Silica dust
Spent	Self-heating. Potentially pyrophoric. Desorption of gases	Ni dust. CO. Ni $(CO)_4$. Other hazards presented by gases	Heat of adsorption for water. Release of adsorbed CO, H_2S, and other gases. Silica dust	Heat of adsorption for water. Silica and other dust (coke, metals)
Waste designation	Most are K172 (U.S. RCRA)			
Comments	Refer to the topic on "Environmental control and engineering" for discussion of hazardous waste characteristics for these materials			
	Materials may be tested and reclassified based on actual waste characteristics as defined by US EPA			

- Inert handling:
  - Positive-pressure, supplied-air respirator – the inert atmosphere overrides other risks generally.
  - Refer to the inert entry safety discussion in the separate topic "▶ Safety Systems for Petroleum Processing."
- Suspected hazardous contaminants (e.g., arsenic):
  - Wear protective clothing appropriate for the hazard.
  - Provide decontamination for persons leaving the handling area.
  - Use positive-pressure, supplied-air, full-face respirator.

Table 9 Health effects of typical catalysts and sorbents

Material	Hydroprocessing catalysts	Hydrogen plant catalysts	PSA adsorbents	Molecular sieves or zeolites
Fresh material				
Inhalation	Excessive dust. Respiratory tract irritation. Cough. Difficulty breathing	High levels of dust irritating to resp. tract. Slow to clear	Irritation of respiratory tract. Potential lung damage (e.g., silicosis)	Irritation of respiratory tract. Potential lung damage (e.g., silicosis)
Ingestion	Irritation of mouth and throat. Discomfort. Malaise, nausea, diarrhea	Low oral toxicity. Irritation of the GI tract	Burns to moist body tissue from heat of adsorption	Burns to moist body tissue from heat of adsorption
Eyes	Irritant	Dust causes irritation to eyes	Irritant. Dust heats up in contact with eyes	Irritant. Dust heats up in contact with eyes
Skin	Skin sensitizer. Irritation	Unlikely to be absorbed	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact
Chronic	Carcinogenic (Ni, Co)	Carcinogenic (Ni). Liver damage	May cause damage to lungs. May contain silica, which is a carcinogen	May cause damage to lungs. May contain silica, which is a carcinogen
Symptoms	Coughing, difficulty breathing. Delayed onset of flu-like symptoms	Allergic skin reactions. Redness, inflammation, itching, burning. Asthma	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust
Hazard ratings (H/F/R)	HMIS: 3/1/0 NFPA: 3/1/0	HMIS: 2/1/0	NFPA: 1/0/1	NFPA: 1/0/1
Spent material				
Inhalation	Respiratory tract burns. Allergic respiratory response. H_2S may be evolved	High levels of dust irritating to resp. tract. Slow to clear. Additional hazards may be present from adsorbed gas release	Irritation of respiratory tract. Potential lung damage (e.g., silicosis). Additional hazards may be present from adsorbed gas release	Irritation of respiratory tract. Potential lung damage (e.g., silicosis). Additional hazards may be present from adsorbed gas release

Ingestion	May be fatal. Burns to mucous membranes, throat, esophagus, and stomach	Low oral toxicity. Irritation of the GI tract	Burns to moist body tissue from heat of adsorption	Burns to moist body tissue from heat of adsorption
Eyes	Causes eye burns	Dust causes irritation to eyes	Irritant. Dust heats up in contact with eyes	Irritant. Dust heats up in contact with eyes
Skin	Skin burns. Allergic skin reaction. May be fatal if materials absorbed through skin	Unlikely to be absorbed	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact	Irritant. Dust heats up in contact with skin. Burns if prolonged, moist contact
Chronic	Allergic respiratory and skin reactions. As and Ni may increase cancer risk. Co and Ni are carcinogens	Carcinogenic (Ni). Liver damage	May cause damage to lungs. May contain silica, which is a carcinogen	May cause damage to lungs. May contain silica, which is a carcinogen
Symptoms	Burns to skin, eyes, and mucous membranes. Aggravates preexisting conditions. See H_2S discussion	Allergic skin reactions. Redness, inflammation, itching, burning. Asthma	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust	Irritation, burns to wet surfaces, respiratory difficulties from heavy dust
Hazard ratings (H/F/R)	HMIS: 3/1/0	Normally HMIS: 2/1/0	Normally NFPA: 1/0/1	Normally NFPA: 1/0/1
	NFPA: 3/1/0			
Environmental effects	Toxic to aquatic life. Long effect	Limited information. Product is insoluble, so limited aquatic exposure	Limited information. Products not particularly hazardous once wetted	Limited information. Products not particularly hazardous once wetted

To avoid release of hazardous gases, keep the solids dry or coated with an oil film. It is also possible to fully saturate the materials with enough water to manage the heat of adsorption, but this will generate gases that will require control. Dust management is normally the key control measure to prevent exposure or release of the materials.

If the materials are potentially self-heating, pyrophoric, or otherwise present a hazard if exposed to air, they should be handled in purged and/or sealed systems and stored in purged and sealed containers. Refer to the discussion of inert handling of solids.

Caustic Soda (Sodium Hydroxide, NaOH)

Discussion and Hazards of Caustic Soda

Caustic soda solution is used in oil refining mostly for the absorption of hydrogen sulfide or light mercaptans from light petroleum products from LPG through the kerosene cut. Very often the compound is delivered to the refinery in a strong aqueous solution to be further diluted on site to the strength required by a specific process. Sodium hydroxide in a solution is a white, odorless, nonvolatile liquid. It will not burn, but it is highly reactive. It can react violently with water and numerous commonly encountered materials, generating enough heat to ignite nearby combustible materials. Contact with many organic and inorganic chemicals may cause fire or explosion. Reaction with some metals (like aluminum and zinc) releases flammable hydrogen gas.

Sodium hydroxide is produced mainly in three forms:

- ~50 % aqueous solution (most commonly used)
- ~73 % aqueous solution
- Anhydrous sodium hydroxide in the form of solid cakes, flakes, or beads

The major impurities include sodium chloride, sodium carbonate, sodium sulfate, sodium chlorate, potassium, and heavy metals such as iron and nickel. The following discussion reviews the information relevant to solutions.

Chemical data are in Table 10.

Handling Hazards for Caustic Soda

Skin

Sodium hydroxide is extremely corrosive and is capable of causing severe burns with deep ulceration and permanent scarring. It can penetrate to deeper layers of the skin, and corrosion will continue until removed. The severity of injury depends on the concentration of the solution and the duration of exposure. Burns may not be immediately painful; onset of pain may be delayed minutes to hours. Several human

Table 10 Physical and chemical properties of caustic soda

Molecular weight	40.00
Melting point	12 °C (53.6 °F) (50 % soln.; freezing point)
	62 °C (143.6 °F) (70–73 % solution)
Boiling point	140 °C (284 °F) (50 % solution)
Specific gravity	1.53 (50 % solution)
	2.0 at 15.5 °C (70–73 % solution)
Solubility in water	Soluble in all proportions
Solubility in other liquids	Soluble in all proportions in ethanol, methanol, and glycerol
pH values	12 (0.05 % solution)
	13 (0.5 % solution)
	14 (5 % solution)

studies and case reports describe the corrosive effects of sodium hydroxide. A 4 % solution of sodium hydroxide, applied to a volunteer's arm for 15–180 min, caused damage which progressed from destruction of cells of the hard outer layer of the skin within 15 min to total destruction of all layers of the skin in 60 min. Solutions as weak as 0.12 % have damaged healthy skin within 1 h. Sodium hydroxide dissolved the hair and caused reversible baldness and scalp burns when a concentrated solution (pH 13.5) dripped onto a worker's head and treatment was delayed for several hours.

Owing to its corrosive nature, repeated or prolonged skin contact with dust and weak solutions would be expected to cause drying, cracking, and inflammation of the skin (dermatitis).

Eyes

Sodium hydroxide is extremely corrosive to the eye tissues. The severity of injury increases with the concentration of the solution, the duration of exposure, and the speed of penetration into the eye. Damage can range from severe irritation and mild scarring to blistering, disintegration, ulceration, severe scarring, and clouding. Conditions which affect vision such as glaucoma and cataracts are possible late developments. In severe cases, there is progressive ulceration and clouding of eye tissue which may lead to permanent blindness.

Inhalation

A worker, exposed for 2 h per day over 20 years to mists from boiling a solution of sodium hydroxide in two large containers in a small room with inadequate ventilation, developed severe obstructive airway disease. It was concluded that the massive and prolonged exposure induced irritation and burns to the respiratory system eventually leading to the disease. It was noted that chronic exposure had not previously been reported, probably since the strong and immediate irritation would normally deter workers from further exposure. Actual exposures to sodium hydroxide aerosols were not measured, and it could not definitely exclude late onset asthma as a cause of the man's condition.

A report of workers exposed to sodium hydroxide aerosol for at least 16 months was confounded by the presence of high concentrations of Stoddard solvent and other solvent vapors, as well as other chemicals.

There was no trend of increased mortality in relation to duration (up to 30 years) or intensity of exposure (0.5–1.5 mg/m^3) among 291 workers exposed to sodium hydroxide dust during the production of flakes or beads of concentrated sodium hydroxide from chlorine cell effluent. This study was limited by the small population size.

Ingestion

There are no reported cases of industrial workers ingesting sodium hydroxide solutions. Non-occupational ingestion has produced severe corrosive burns to the esophageal tissue, which has in some cases progressed to stricture formation. Should ingestion occur, severe pain; burning of the mouth, throat, and esophagus; vomiting; diarrhea; collapse; and possible death may result.

Long-Term Effects

Sodium hydroxide has been implicated as a cause of cancer of the esophagus in individuals who have ingested it. The cancer may develop 12–42 years after the ingestion incident. Similar cancers have been observed at the sites of severe thermal burns. These cancers may be due to tissue destruction and scar formation rather than the sodium hydroxide itself.

A case-control study reported an association between renal cancer and history of employment in the cell maintenance area of chlorine production. The major exposures in this work were presumed to be to asbestos and sodium hydroxide. An association was made between renal cancer and sodium hydroxide exposure. This study was limited by factors such as small numbers of exposed workers, multiple exposures, and reliance on work histories and is not considered sufficiently reliable.

First Aid and Personal Safety for Caustic Soda

Contact with the Skin

Avoid direct contact with this chemical. Wear chemical-resistant protective clothing, if necessary. As quickly as possible, remove contaminated clothing, shoes, and leather goods (e.g., watchbands, belts). Flush contaminated area with lukewarm, gently flowing water for at least 60 min, by the clock. DO NOT INTERRUPT FLUSHING. If necessary, keep emergency vehicle waiting. Transport victim to an emergency care facility immediately. Discard contaminated clothing, shoes, and leather goods.

Contact with the Eyes

Avoid direct contact. Wear chemical-resistant gloves, if necessary. Quickly and gently blot or brush away excess chemical. Immediately flush the contaminated eye (s) with lukewarm, gently flowing water for at least 60 min, by the clock, while holding the eyelid(s) open. Neutral saline solution may be used as soon as it is available. DO NOT INTERRUPT FLUSHING. If necessary, keep emergency vehicle waiting. Take care not to rinse contaminated water into the unaffected eye or onto the face. Quickly transport victim to an emergency care facility.

Suffering from Inhalation

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Ingestion

DO NOT INDUCE VOMITING! Give large quantities of water or milk if available. Never give anything by mouth to an unconscious person. Get medical attention immediately.

Protective Clothing for Caustic Soda

Personal Respirators (NIOSH Approved)

If the exposure limit is exceeded and engineering controls are not feasible, a half-face piece particulate respirator (NIOSH type N95 or better filters) may be worn for up to 10 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. A full-face-piece particulate respirator (NIOSH type N100 filters) may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. If oil particles (e.g., lubricants, cutting fluids, glycerin, etc.) are present, use a NIOSH type R or P filter. For emergencies or instances where the exposure levels are not known, use a full-face-piece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection

Wear impervious protective clothing, including boots, gloves, lab coat, apron, or coveralls, as appropriate, to prevent skin contact.

Eye Protection

Use chemical safety goggles and/or a full-face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

Materials of Construction for Caustic Soda

Carbon steel can be used throughout at moderate temperatures. At temperatures in excess of 350 °F (177 °C), nickel or nickel alloy is recommended. All carbon steel piping, flanges, welds, and vessel must be stress relieved. Caustic soda solution also attacks glass and dissolves it to some extent. As caustic soda is used in cleaning process plants during commissioning, sight glasses and level gauges are removed and replaced with silica glasses for this cleaning phase of the commissioning. Plastic or plastic lined-pipe can also be used for handling caustic soda at low temperatures. Consult plastic manufacturers for compatibility information.

Furfural

Discussion and Hazards of Furfural

Furfural is used in petroleum refining for the production of lube oils. It is a solvent in the extraction of undesirable compounds such as naphthenes and aromatics from lube oil stocks to improve the color of the lube oil product (see the separate topic "▶ Non-energy Refineries in Petroleum Processing"). Furfural or furfuraldehyde, C_4H_3OCHO, is a viscous, colorless liquid that has a pleasant aromatic odor, which upon exposure to air turns dark brown or black. It boils at about 160 °C (320 °F). It is commonly used as a solvent. It is soluble in ethanol and ether and somewhat soluble in water.

Furfural is the aldehyde of pyromucic acid. It has properties similar to those of benzaldehyde. A derivative of furan, it is prepared commercially by dehydration of pentose sugars obtained from cornstalks and corncobs, husks of oat and peanut, and other waste products. It is used in the manufacture of pesticides, phenolfurfural resins, and tetrahydrofuran. Tetrahydrofuran is used as a commercial solvent and is converted in starting materials for the preparation of nylon.

Chemical properties of furfural are in Table 11.

Hazards Associated with Handling Furfural

Inhalation

Causes irritation to the mucous membranes and upper respiratory tract. Symptoms may include sore throat, labored breathing, and headache. Higher concentrations act on the central nervous system and may cause lung congestion. Inhalation may be fatal.

Table 11 Physical properties of furfural

Appearance	Colorless to yellowish liquid
Odor	Almond odor
Solubility	8 g/100 g water @ 70 °F (21 °C)
Specific gravity	1.16 @ 77 °F (25 °C)
% Volatiles by volume @ 70 °F (21 °C)	100
Boiling point	324 °F (162 °C)
Melting point	−38 °F (−39 °C)
Vapor density (Air = 1)	3.3
Vapor pressure (mm Hg)	1 @ 64 ° F (18 °C)

Ingestion

Highly toxic. May cause gastrointestinal disorders. Can cause nerve depression and severe headache. May be fatal. Other effects are not well known.

Skin Contact

Irritant to skin. May cause dermatitis and possibly eczema, allergic sensitization, and photosensitization. May be absorbed through the skin with possible systemic effects.

Eye Contact

Vapors irritate the eyes, causing tearing, itching, and redness. Splashes may cause severe irritation or eye damage.

Chronic Exposure

Can cause numbness of the tongue, loss of sense of taste, and headache. Other effects are not well known.

Aggravation of Preexisting Conditions

Persons with preexisting skin disorders or eye problems or impaired liver, kidney or respiratory function may be more susceptible to the effects of the substance.

First Aid and Personal Safety with Furfural

Inhalation

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Ingestion

If swallowed, give large quantities of water to drink and get medical attention immediately. Never give anything by mouth to an unconscious person.

Skin Contact

Immediately flush skin with plenty of soap and water for at least 15 min while removing contaminated clothing and shoes. Get medical attention, immediately. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Eye Contact

Immediately flush eyes with plenty of water for at least 15 min, lifting lower and upper eyelids occasionally. Get medical attention immediately.

Protective Clothing and Equipment for Furfural Handling

Airborne Exposure Limits

The recommended airborne exposure limit is between 2 and 5 ppm.

Ventilation System

A system of local and/or general exhaust is recommended to keep employee exposures below the airborne exposure limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area. Please refer to the ACGIH document, *Industrial Ventilation, A Manual of Recommended Practices*, most recent edition, for details.

Personal Respirators (NIOSH Approved)

If the exposure limit is exceeded, a full-face-piece respirator with organic vapor cartridge may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-face-piece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection

Wear impervious protective clothing, including boots, gloves, lab coat, apron, or coveralls, as appropriate, to prevent skin contact.

Eye Protection

Use chemical safety goggles and/or a full-face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

Fire Prevention and Firefighting for Furfural

Fire

The relevant combustion properties of furfural are in Table 12.

Explosion

Above the flash point, vapor-air mixtures are explosive within flammable limits noted above. Reacts violently with oxidants. Reacts violently with strong acids and bases causing fire and explosion hazards. Sealed containers may rupture when heated. Sensitive to static discharge.

Fire Extinguishing Media

Water spray, dry chemical, alcohol foam, or carbon dioxide can be used as fire extinguishing media. Water spray may be used to keep fire-exposed containers cool.

Table 12 Furfural combustion properties

Flash point	140 °F (60 °C) Pensky-Martens
Autoignition temperature	601 °F (316 °C)
Flammable limits in air % by volume	LEL: 2.1; UEL: 19.3
Flammable liquid and vapor!	

Water may be used to flush spills away from exposures and to dilute spills to nonflammable mixtures.

Special Information

In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full-face piece operated in the pressure demand or other positive-pressure mode.

Materials of Construction and Storage for Furfural

There are no special materials of construction required for furfural. A suitable grade of carbon steel is adequate. Storage and handling of furfural must exclude air. Furfural polymerizes readily on exposure to air. In refinery practices, startup of furfural extraction plants usually requires that the equipment which handles furfural be first filled with either the lube oil feed or a suitable middle distillate to eliminate air.

Hydrofluoric Acid (HF, AHF)

Discussion and Hazards of HF

Because of anhydrous hydrofluoric acid's (AHFs) highly toxic and corrosive nature, this section highlights its characteristics and the safe handling of the acid.

Anhydrous hydrofluoric acid is a colorless, mobile liquid which boils at 67 °F (19.4 °C) at atmospheric pressure and therefore requires pressure containers. The acid is also hygroscopic; therefore, its vapor combines with the moisture of air to form "fumes." This tendency to fume provides users with a built-in detector of leaks in AHF storage and transfer equipment. On the other hand, care is needed to avoid accidental spillage of water into tanks containing AHF. Dilution is accompanied by a high release of heat. The physical properties of AHF are given in Table 13.

AHF vapor, even at very low concentrations in air, has a sharp penetrating odor that is an effective deterrent to willful overexposure by operating personnel. Both the vapor and liquid forms of AHF cause severe and painful burns on contact with the skin, eyes, or mucous membranes.

Hydrofluoric acid is very corrosive. It attacks glass, concrete, and some metals – especially cast iron and alloys which contain silica (e.g., Bessemer steels). The acid

Table 13 The physical properties of anhydrous hydrofluoric acid (AHF)

Boiling point at 1 atm, °F (°C)	66.9 (19.4)
Freezing point, °F (°C)	−117.4 (−83)
Specific gravity at 32 °F (0 °C)	1.00
Weight per gallon at 32 °F (0 °C), lb (MT/m^3)	8.35 (1.0)
Viscosity at 32 ° F (0 °C), cP	0.31

also attacks such organic materials as leather, natural rubber, and wood, but does not promote their combustion.

Although AHF is nonflammable, its corrosive action on metals, particularly in the presence of moisture, can result in hydrogen forming in containers and piping to create a fire and explosion hazard. Potential sources of ignition (sparks and flames) should be excluded from areas around equipment containing hydrofluoric acid.

Despite its corrosive nature, AHF can be handled with relative safety if the hazards are recognized and the necessary precautions taken. The next few sections describe certain procedures for the safe handling of large bulk quantities of AHF.

Safe Handling Practices for HF

The safe handling of AHF requires that well-designed equipment be properly operated and maintained by well-trained, adequately protected, responsible personnel.

Tanks and other containers of AHF should be protected from heat and the direct rays of the sun. Storage-area temperatures should preferably remain below 100 °F (38 °C). If they reach or exceed 125 °F (51.7 °C), means for cooling the containers must be applied.

Acid transfer lines between the unloading station and the storage tank should be designed to free drain toward the storage tank. Thermal relief valves should be installed in those sections of acid transfer lines where acid may be entrapped between two closed valves in the line, because expansion of the liquid might create excessive pressure and rupture the line. The relief will need to discharge toward the tank, not to atmosphere.

No open fires, open lights, or matches should be allowed in or around acid containers or lines. The possibility of acid acting on metal to produce hydrogen gas is ever present. Only non-sparking tools and spark-proof electrical equipment should be used in the AHF storage and handling areas.

Safety showers should be readily accessible at the unloading station, in the storage area, and at other locations where acid is handled. The showers should be capable of supplying volume flows of 30 GPM (114 l/min) through quick-opening valves in 2 in. (50 mm) water lines. Handles at hip level should actuate the valves which, with a 0.25 in. (6.4 mm) weep hole directly above the valve, should be positioned below the frost line and surrounded by crushed rock or gravel to provide drainage.

A water hydrant and hose should also be available in the unloading area to flush away spilled acid. Good drainage should be provided and also a supply of dry soda ash, ground limestone, or hydrated builders lime. Accidental spills of acid on walkways or equipment should be washed off immediately with large volumes of water and, if necessary, neutralized with one of the agents mentioned.

Personal Protective Equipment Requirements for HF

Personal protective equipment is not a substitute for good, safe working conditions. Its purpose is to protect the wearer in the event of an accident – major or minor. The extent of protection needed depends upon the degree of potential exposure attending the particular job at hand. Protective equipment should not be worn or carried beyond the operating area. It should be thoroughly washed with sodium bicarbonate solution immediately after each use.

The minimum protection required for operating and maintenance personnel includes the following items:

- Coveralls with sleeves to the wrists
- Face shield or chemical safety goggles
- Hard hat
- Poly(vinyl chloride) – or neoprene-dipped gauntlets
- Poly(vinyl chloride) – or neoprene-soled rubber shoes

When taking acid samples, opening equipment which may contain hydrofluoric acid, or performing similar hazardous duties, operators should wear the following:

- Poly(vinyl chloride) or neoprene overalls
- Poly(vinyl chloride) or neoprene boots
- Lightweight poly(vinyl chloride) or neoprene gloves under poly(vinyl chloride) – or neoprene-dipped gauntlets
- Poly(vinyl chloride) or neoprene jumper
- Airline hood

Air should be applied to the hood until the absence of fumes in the work area has been fully established.

Unloading and Transfer of AHF

AHF is shipped in rail tank cars having capacities ranging from approximately 5,400 to 25,000 gal ($\sim$20–94 MT) and in road tank trucks of approximately 5,250 gal ($\sim$20 MT) AHF capacity. Compressed dry gas (air, hydrocarbon, or nitrogen) is the preferred means for transferring bulk quantities of AHF, but a centrifugal, rotary, or positive-pressure pump can be used, if necessary.

The unloading of AHF tank cars or tank trucks, with transfer of the acid to plant storage, consists of five steps:

1. Spotting the tank car or tank truck at the unloading station
2. Connecting the plant compressed-gas (or vapor) and AHF-unloading lines to the proper valves on the carrier tank

3. Transferring the AHF from the carrier tank to the storage tank
4. Disconnecting the plant compressed-gas (or vapor) and AHF-unloading lines from the carrier tank valves
5. Releasing the tank car or tank truck for return to the shipper

Equipment for HF Service

Mild steel is satisfactory for storing and handling AHF at temperatures up to 150 °F (~65 °C) maximum. Type 300 stainless steels are useful up to 200 °F (~93 °C). "Monel" nickel-copper alloy and "Hastelloy" C nickel steel are suitable for higher temperatures. TEFLON TFE fluorocarbon resin is completely resistant to all concentrations of hydrofluoric acid at temperatures up to 500 °F (260 °C).

Steel should not be used for movable parts because the corrosion-product film will cause movable parts to "freeze." Cast iron, type 400 stainless steel, and hardened steels are unsatisfactory for AHF handling. Copper is velocity sensitive. Stressed Monel may stress crack if exposed to moist vapors or aerated acid containing water. Welds in Monel corrode rapidly.

The selection of construction materials used for AHF equipment depends very much on such corrosion-affecting variables as moisture, temperature, aeration, fluid velocity, and impurities. Each storage and handling situation requires separate study to evaluate these factors before selecting materials which must meet the requirements of the installation.

Additional information on metallurgy and materials for HF service can be found in API Recommended Practice 571 and is available from process licensors.

Storage Tank

The capacity of the storage system should be approximately 1.5 times the maximum quantity normally ordered to insure against running out of acid between receipts of shipments. As a rule, too large a storage system is preferable to too small a system. The additional investment required for the larger installation is not great. The larger installation permits further expansion, less precise scheduling of shipments, and larger inventories when desired.

The horizontal cylindrical storage tank should be manufactured according to the current ASME Code for Unfired Pressure Vessels or other equivalent codes which meet state or local mandatory requirements. It is further recommended that the wall thickness of the tank be at least 1/8 in. (3.2 mm) in excess of the ASME Code requirements. The tank should be double-welded, butt-joint construction, the welds to be slag-free (conforming to ASME Code, Section 8) and ground smooth inside to facilitate inspection. X-ray inspection of welds is recommended.

The storage tank should be suitably supported above ground level. Structural steel supports or concrete saddles (protected with an acid-resistant paint) are satisfactory. Secondary containment is normally required. An emergency water wall system may also be required.

Safety devices for relieving abnormal internal tank pressures should be obtained from qualified manufacturers who are familiar with AHF. The maximum working pressure of the storage system should not exceed two thirds the rated relief or bursting pressure of the safety devices. A dual relief system is recommended which has a two-way valve and rupture disks ahead of the relief valves and also a separate rupture-disk line in case of relief valve failure.

Piping

All pipe lines should be installed so that they drain toward the storage tank or toward the point of consumption. This will prevent the accumulation of acid in low points, thereby eliminating possible safety hazards when repairs are necessary. Relief valves should be installed in the various sections of the lines in case acid becomes confined between two closed valves in the line. All flanges in the lines should preferably be coated with an acid-indicating paint, such as Mobil #220-Y-7 hydrofluoric acid-detecting paint, which changes in color from orange to yellow in the presence of AHF liquid or vapor.

The line from the unloading station to the storage tank should be equipped with a gate valve so acid flow can be stopped at any time. The line should also be securely anchored to the storage tank as considerable vibration may occur, especially when unloading by means of compressed gas.

Extra heavy (Schedule 80) or, better, triple extra-heavy black seamless or welded steel pipe, which is free from non-metallic inclusions, is satisfactory.

Fittings

Larger lines (2 in. [50 mm] and larger) should preferably be welded to conform to ASME Code, Section 8. Alternatively, properly gasketed forged steel flanges can be used.

On smaller lines, extra-heavy forged steel, screw-type unions with steel-to-steel seats can be used for pipe joints. Graphite-and-oil is satisfactory as lubricant.

Gaskets

Gaskets made of TEFLON TFE fluorocarbon resin are recommended.

Valves

Jamesbury "Double-Seal" ball valves have given excellent service to AHF manufacturing operations. The valve seats are preferably of TEFLON TFE; the balls and bodies of 316 stainless steel, Durimet 20 austenitic stainless steel alloy, or equivalent. Gate valves should be of the O, S, and Y flange type, with a ring of TEFLON TFE or "Kel-F" fluorocarbon thermoplastic material on the plug seat and packing of either TEFLON TFE or Kel-F.

Globe valves can be of Monel nickel-copper alloy or have a forged steel body and trim of Monel.

Good service has been reported for Hills-McCanna diaphragm valves with body of Durimet 20 or equivalent, or Monel alloy; diaphragm of polyethylene, Kel-F, or a laminate of neoprene and TEFLON TFE; and a wheel closure.

Plug valves of Monel with a sleeve of TEFLON TFE have been found satisfactory.

Check valves should be of the forged ball and body type – made of Monel metal.

Pressure Gauges

Pressure gauges should be constructed of 316 stainless steel or Monel metal Bourdon tubes. The bottom connection of the gauge should be 1/2 inch. The case should have a "blow-out" back.

Pumps

Centrifugal, rotary, or positive-pressure types of pumps are satisfactory. The 300 series stainless steels; Durimet 20 or equivalent, Hastelloy C, Monel alloys; nickel, bronze, and acid bronze have been recommended as construction materials.

Level Gauges

AHF Manufacturers suggest the use of a magnetic-type level gauge, such as a Fischer & Porter Model 13 C 2265 W Liquid "Levelrator" with donut-type float.

An alternative means for monitoring storage-tank content is to set the tank on load cells or strain gauges.

Filters

Where the critical nature of the process has warranted, cartridge-type filters in the storage tank-to-process line have been recommended. Two such filters are normally mounted in parallel to permit replacing the cartridge in one line while diverting the acid flow through the other. Construction materials used in fabricating the filters are the same or similar to those described above for other auxiliary equipment.

Polypropylene can be used as filter material for AHF alone if the liquid temperature remains below 200 °F (93 °C).

When a fouled filter is removed for replacement, it should be promptly flushed with water, neutralized with a solution of soda ash, and rinsed before discard.

Personal Safety When Handling HF

Liquid AHF causes immediate and serious burns to any part of the body on contact.

Dilute solutions of hydrofluoric acid often do not cause an immediate burning sensation where they came in contact with skin. Several hours may pass before the solution penetrates the skin sufficiently to cause redness or a burning sensation.

Wearing clothing which may have absorbed small amounts of hydrofluoric acid (such as leather shoes or gloves) can result in painful delayed effects similar to those caused by dilute acid solutions.

Hydrofluoric acid vapor causes skin irritation and inflammation of the mucous membranes; the burns become apparent a few hours after exposure. Inhaling the vapor in high concentrations may cause lung damage (pulmonary edema).

In the United States, the American Conference of Governmental Industrial Hygienists recommends a threshold limit value of 3 parts (by volume) AHF vapor (hydrogen fluoride) per million parts air. This value refers to a time weighted concentration for a seven- or 8-h workday and 40-h work week.

The 3 vppm figure is based on both experimental and occupational evidence; however, nosebleeds and sinus troubles have reportedly occurred among metal workers exposed to even lower concentrations of a fluoride or fluorine in air. Therefore, for protection against acute irritation, 3 ppm should be considered a ceiling limit.

Anyone who knows or even suspects he has come in contact with hydrofluoric acid should immediately seek first aid.

In the event of an accident, the medical response should be called immediately; however, all plant supervisors should be aware of first aid procedures for HF burns. All affected persons should be referred to a physician even when the injury seems slight.

Hydrogen

General Discussion of Hydrogen

Hydrogen is present throughout refining and petroleum processes today. It is:

- Generated in reformers and hydrogen plants
- Recovered from fuel and refinery make gases
- Consumed in hydrotreaters, hydrocrackers, isomerization units, benzene saturators, and sulfur plants

It is critical to meeting modern product specifications.

Most hydrogen is produced within a facility and used within the facility. In some cases, hydrogen may be received in bulk from a supplier for specific purposes, such as naphtha reformer startup or calibration gases. Hydrogen may also be supplied in bulk by pipeline from an outside facility.

The primary hazards presented by hydrogen are fire and explosion. When released to the atmosphere, hydrogen quickly rises and dissipates, but local concentrations may present risks.

High velocity releases of hydrogen (as in a vent) may generate a static electrical charge that can create a spark to ignite the vent.

Physical and Chemical Properties of Hydrogen

Table 14 summarizes the key properties of hydrogen of concern here.

Hydrogen gas is extremely flammable and easily ignites, even from hot equipment. It is colorless, odorless, and tasteless.

Hydrogen has the unusual property of a reverse Joule-Thompson effect – it will heat up when it rapidly expands.

Table 14 Key properties of hydrogen gas

Molecular weight	2.02
Specific gravity	Vapor: 0.0696 (air =1)
Boiling point	−423.4 °F (−253 °C)
Freezing point	−434.5 °F (−259.15 °C)
Solubility in water	27.6 mg/l (77 °F/25 °C)
Autoignition temperature	932–1060 °F (500—571 °C)
Explosive limits	4—76 vol%

Hazards of Hydrogen

The most obvious and well-known hazard of hydrogen is its flammability. It burns with a clear flame that is hard to detect. Personnel have been known to walk into a hydrogen flame without seeing it.

The heat generated from the reverse Joule-Thompson effect of hydrogen, along with the static electricity generated in a leak, can result in fires or explosions from hydrogen leaking from pressures over about 1,000 psig (69 barg).

Sometimes hydrogen is received as compressed gas (2,000 psig [138 barg] plus). In these cases, additional hazard is presented by the high pressure.

Hydrogen will burn aggressively with any oxidizer.

Hydrogen is not particularly toxic but may cause asphyxiation in high enough concentrations, e.g., near a hydrogen vent. The rapid dissipation of vented hydrogen normally limits asphyxiation risk.

Protective Equipment for Hydrogen Handling

The common refinery PPE (hardhat, safety glasses, flame-retardant clothing, and safety shoes) provide some protection against a hydrogen flash fire. They will not provide protection from a significant fire or explosion, an oxygen deficiency, or physical hazard from high pressures involving hydrogen. Major events involving hydrogen require SCBA and flash suits. There should be an SCBA nearby when handling bulk hydrogen.

It is best to focus on preventing a hydrogen fire from affecting surrounding equipment until the hydrogen can be stopped at the source.

Ventilation of areas where hydrogen may accumulate is the best way to protect personnel.

Storage and Handling of Bulk Hydrogen

Hydrogen is normally generated and used within a facility or may be received by pipeline over the fence. As such, no more handling is involved than for the hydrocarbon streams. Precautions and PPE used for handling hydrocarbon gases are adequate for hydrogen in general.

When hydrogen is received in bulk, normally pressurized gas in tube trailers or in cylinders, the normal precautions that apply to compressed gases are adequate.

Hydrogen Sulfide (H_2S)

Discussion and Hazards of H_2S

Hydrogen sulfide in a refinery is usually formed during the desulfurizing processes used to sweeten product streams. Hydrogen sulfide (H_2S) is a colorless, extremely poisonous gas that has a very disagreeable odor, much like that of rotten eggs, in low concentrations. In high concentrations that are IDLH, it deadens the sense of smell.

It is slightly soluble in water and is soluble in carbon disulfide. Dissolved in water, it forms a very weak dibasic acid. Hydrogen sulfide is flammable, and in excess air, it burns to form sulfur dioxide and water. Where less than stoichiometric oxygen is present, it forms elemental sulfur and water.

It may be made by reacting hydrogen gas with molten sulfur or with sulfur vapors or by treating a metal sulfide (e.g., ferrous sulfide, FeS) with an acid. Hydrogen sulfide reacts with most metal ions to form sulfides; the sulfides of some metals are insoluble in water and have characteristic colors that help to identify the metal during chemical analysis.

Hydrogen sulfide also reacts directly with silver metal, forming a dull, gray-black tarnish of silver sulfide (Ag_2S). One method of detecting small concentrations of hydrogen sulfide is to expose it to a filter paper impregnated with lead acetate. The paper turns black (due to the precipitation of lead sulfide). The degree of H_2S concentration is measured by the shade of “blackness” of the lead acetate paper compared with standard colors.

The relevant properties of hydrogen sulfide are given in Table 15.

Hazards and Toxicity of Hydrogen Sulfide

Table 16 indicates the toxicity of hydrogen sulfide.

The following discussion uses the present US OSHA limits as a basis.

At 1 ppm, most people can smell the gas. A strong smell does not necessarily mean a high concentration, and a slight smell does not mean a low concentration. A person could work in a 10 ppm concentration of H_2S for 8 h. If the concentration exceeds 10 ppm for a short period of time, then the time must be reduced.

A concentration of 15 ppm can be tolerated for a period of time not exceeding 15 min. There can be no more than four exposures of 15 ppm in an 8 h shift with 1 h between exposures. If the concentration of H_2S exceeds 20 ppm, a worker must wear approved breathing apparatus. If the concentration is not known, a worker must wear breathing apparatus until the concentration is determined.

Table 15 Properties of hydrogen sulfide

Chemical formula	H_2S
Relative density	1.189 (air = 1.0)
Autoignition temperature	500 °F (260 °C)
Flammability	Very flammable
Lower explosive limit	4.3 vol% in air
Upper explosive limit	46 vol% in air
Color	Colorless, invisible
Odor	Strong rotten egg at low concentrations; cannot smell at IDLH concentrations
Vapor pressure	17.7 atm at 20 °C (68 °F)
Boiling point	−77 °F (−61 °F)
Melting point	−122 °F (−86 °F)
Reactivity	Dangerous with acids and oxidizers
Solubility	In water, hydrocarbons, alcohol

Quoted from National Safety Council Data Sheet 1-284-67

Table 16 Toxicity of hydrogen sulfide

ppm	Percent	Comments
1	0.0001	Most people can smell the gas
10	0.001	Occupational exposure limit. Maximum continuous exposure for 8 h
15	0.0015	Occupational exposure for 15 min
20	0.002	Ceiling occupational exposure limit. This level of exposure cannot be exceeded at any time without respiratory protection
100	0.01	Dulls sense of smell. Causes burning sensation in the eyes and throat
500	0.05	Attacks the respiratory center of brain; causes loss of reasoning and balance
700	0.07	Victim quickly loses consciousness; breathing will stop, and death will result if not rescued promptly
1,000	0.1	Unconscious immediately; permanent brain damage or death occurs if victim is not rescued and resuscitated immediately

If exposed to a concentration of 100 ppm (1/100 of 1 %), the sense of smell will be lost or become ineffective within 2–15 min. The H_2S might cause a burning sensation to the eyes, throat, and lungs and could cause headache or nausea.

A 200 ppm concentration will cause immediate loss of smell and a burning sensation in the eyes, throat, nose, and lungs. (The hydrogen sulfide combines with alkali in body fluids to form caustic sodium sulfide.)

At a concentration of 500 ppm, the victim will appear to be intoxicated, and will lose his sense of balance and reasoning. In this state, the victim may attempt to continue with the job he was doing when he encountered the gas. For this reason, a person *must* know the people he works with and be able to detect any unusual behavior of a coworker. Obviously, persons under the influence of alcohol, or any other mind-altering drugs, should never be allowed in an area which may contain sour gas. A victim must be watched very closely and may require resuscitation. A victim should be taken for medical attention and not allowed to return to work for at least 8 h.

At 700 ppm, the victim will be rendered unconscious very quickly and may develop seizures similar to those caused by epilepsy. Loss of bladder and bowel control can be expected. Breathing will stop, and death will result, if not rescued and resuscitated promptly. At a concentration of 1,000 ppm (1/10 of 1 %), the victim will be rendered unconscious immediately. THE VICTIM WILL NOT BEGIN BREATHING VOLUNTARILY IF BROUGHT TO FRESH AIR. ARTIFICIAL RESUSCITATION MUST BE COMMENCED WITHIN THREE MINUTES OF EXPOSURE TO THIS LEVEL OF HYDROGEN SULFIDE!

Protective Clothing and Personal Safety for H_2S

The appropriate personal protective equipment when working around gaseous H_2S, or in areas where H_2S may be present and is typically the same as the minimum required in a facility:

- Hardhat
- Flame-retardant clothing
- Safety glasses
- Safety-toe shoes

In addition, many (if not most) refiners now require workers to wear personal H_2S monitors, which provide an audible and visual alarm at a specified concentration of H_2S. These personal monitors complement area H_2S monitors in many facilities.

In areas where H_2S exposure is possible, appropriate supplied-air respirators must be readily available, if not actually worn. If exposure to H_2S is expected, such as during sampling of sour gas streams or when setting blinds on a sour line, procedures generally call for the use of fresh air equipment.

In confined areas, such as enclosed compressor or pump houses which handle sour gas or liquids, constant monitoring for H_2S concentration in the atmosphere by automatic area air analyzers with alarms is common. Failing this, a routine analysis using a lead acetate paper should be made. In addition, all such buildings should always be properly vented using an exhaust fan system.

Materials of Construction in H_2S Service

Atmospheres containing hydrogen sulfide and completely or almost free of oxygen give rise to rapid corrosion of unalloyed steel by forming a sulfide film on its surface. The corrosion rate in hydrogen/hydrogen sulfide increases as the content of hydrogen sulfide increases up to about 5 vol.%, while increases beyond that point generally only have a slight effect on the corrosion rate. Steels alloyed with chromium and aluminum have improved resistance to hydrogen sulfide, while nickel has no deleterious effect.

Moist and aqueous solutions of hydrogen sulfide cause some minor pitting in unalloyed steel, and there is a risk of stress corrosion. This pitting corrosion is about 1 mm/year. This rate can be considerably reduced to about 0.1 mm/year using an alloyed steel of 18 % chrome and 9 % nickel. Vessels and piping should all be stress relieved.

The API provides detailed guidance on materials of construction for various types of H_2S services.

Methyl Ethyl Ketone (MEK)

Discussion of MEK

Methyl ethyl ketone (MEK) is used in oil refining for the removal of wax from lube oil stock (see the separate chapter "▶ Non-energy Refineries in Petroleum Processing"). Methyl ethyl ketone is a colorless liquid with a sweet/sharp, fragrant, acetone-like odor. It is extremely flammable in both the liquid and vapor phase. The vapor is heavier than air and may spread long distances, and distant ignition and flashback are possible. MEK is highly volatile. Its basic properties are in Table 17.

Hazards Associated with MEK

Inhalation

Causes irritation to the nose and throat. Concentrations above 200 ppm may cause headache, dizziness, nausea, shortness of breath, and vomiting. Higher concentrations

Table 17 Properties of methyl ethyl ketone

Appearance	Clear, colorless, stable liquid
Purity, % minimum	99.5
Water content, % maximum	0.30
Acidity, % maximum (as acetic acid)	0.003
Color, Pt-Co maximum	10
Specific gravity, 20/20 °C (68/68 °F)	0.805–0.807
Nonvolatile matter (g/100 ml), maximum	0.002
Boiling point	176 °F (80 °C)
Vapor pressure	3 in Hg @ 68 °F (76 mmHg @ 20 °C)
Flash point	−9 °C (16 °F) CC
Autoignition temperature	404 °C (759 °F)
Flammable limits in air, vol%	LEL: 1.4; UEL: 11.4
Extremely flammable	

may cause central nervous system depression and unconsciousness. The airborne exposure limits are:

- Permissible exposure limit (PEL): 200 ppm (TWA)
- Threshold limit value (TLV): 200 ppm (TWA), 300 ppm (STEL)

Ingestion

May produce abdominal pain, nausea. Aspiration into lungs can produce severe lung damage and is a medical emergency. Other symptoms expected to parallel inhalation.

Skin Contact

Causes irritation to skin. Symptoms include redness, itching, and pain. May be absorbed through the skin with possible systemic effects.

Eye Contact

Vapors are irritating to the eyes. Splashes can produce painful irritation and eye damage.

Chronic Exposure

Prolonged skin contact may defat the skin and produce dermatitis. Chronic exposure may cause central nervous system effects.

Aggravation of Preexisting Conditions

Persons with preexisting skin disorders or eye problems or impaired respiratory function may be more susceptible to the effects of the substance.

First Aid and Personal Protection

Inhalation

Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Ingestion

Aspiration hazard. If swallowed, vomiting may occur spontaneously, but DO NOT INDUCE. If vomiting occurs, keep head below hips to prevent aspiration into lungs. Never give anything by mouth to an unconscious person. Call a physician immediately.

Skin Contact

Immediately flush skin with plenty of soap and water for at least 15 min while removing contaminated clothing and shoes. Get medical attention. Wash clothing before reuse. Thoroughly clean shoes before reuse.

Eye Contact

Immediately flush eyes with plenty of water for at least 15 min, lifting upper and lower eyelids occasionally. Get medical attention.

Clothing and Protective Equipment

Ventilation System

A system of local and/or general exhaust is recommended to keep employee exposures below the airborne exposure limits. Local exhaust ventilation is generally preferred because it can control the emissions of the contaminant at its source, preventing dispersion of it into the general work area.

Personal Respirators

If the exposure limit is exceeded and engineering controls are not feasible, a full-face-piece respirator with organic vapor cartridge may be worn up to 50 times the exposure limit or the maximum use concentration specified by the appropriate regulatory agency or respirator supplier, whichever is lowest. For emergencies or instances where the exposure levels are not known, use a full-face-piece positive-pressure, air-supplied respirator. WARNING: Air-purifying respirators do not protect workers in oxygen-deficient atmospheres.

Skin Protection

Wear impervious protective clothing, including boots, gloves, lab coat, apron, or coveralls, as appropriate, to prevent skin contact. Butyl rubber is a suitable material for personal protective equipment.

Eye Protection

Use chemical safety goggles and/or a full-face shield where splashing is possible. Maintain eye wash fountain and quick-drench facilities in work area.

Fire Prevention and Fighting

Fire

MEK is extremely flammable. Refer to Table 17 for flammability data.

Explosion

Above the flash point, vapor-air mixtures are explosive within flammable limits noted in Table 17. Vapors can flow along surfaces to distant ignition sources and flash back. Contact with strong oxidizers may cause fire. Sealed containers may rupture when heated. They are sensitive to static discharge.

Fire Extinguishing Media

Dry chemical, foam, or carbon dioxide are suitable extinguishing agents. Water spray may be used to keep fire-exposed containers cool, dilute spills to nonflammable mixtures, protect personnel attempting to stop leaks, and disperse vapors.

Special Information

In the event of a fire, wear full protective clothing and NIOSH-approved self-contained breathing apparatus with full-face piece operated in the pressure demand or other positive-pressure mode. This highly flammable liquid must be kept from sparks, open flame, hot surfaces, and all sources of heat and ignition.

Accidental Release Measures

Ventilate the area of any leak or spill. Remove all sources of ignition. Wear appropriate personal protective equipment as noted above. Isolate the hazard area. Keep unnecessary and unprotected personnel from entering. Contain and recover liquid when possible. Use non-sparking tools and equipment. Collect liquid in an appropriate container or absorb with an inert material (e.g., vermiculite, dry sand, earth) and place in a chemical waste container. Do not use combustible materials, such as sawdust. Do not flush to sewer! If a leak or spill has not ignited, use water spray to disperse the vapors, to protect personnel attempting to stop leak, and to flush spills away from exposures.

Storage and Handling

MEK is usually delivered to a refinery by road or rail truck. It may be stored in small bullets or a cone roof tank under an inert gas blanket. The materials of construction normally include appropriate grades of carbon steel.

Nickel Carbonyl ($Ni(CO)_4$)

General Discussion of Nickel Carbonyl

Nickel carbonyl is one of the most toxic substances which may be encountered in a petroleum processing facility anywhere CO is present along with nickel in a reduced state. From experience, the nickel does not need to be present as metal directly; $Ni(CO)_4$ has been detected when spent NiMo hydrotreating catalyst has been exposed to air and smoldered.

It is stable at ambient pressure below ~400 °F (~204 °C).

Nickel carbonyl is formed by the reaction of CO with nickel via the equation:

$$Ni(s) + 4CO(g) \longleftrightarrow Ni(CO)_4(g) \tag{1}$$

While most literature on $Ni(CO)_4$ discusses it as a liquid, it would be most likely encountered as a gas in the refining environment. It has been found in hydrogen plant vapors from the reforming furnace (Ni catalyst and CO present) and is likely to be present in methanator reactor effluent (also CO and Ni). As noted above, it has been detected in gases from smoldering spent NiMo hydrotreating catalysts. It can also be adsorbed on NiMo catalysts and released on exposure to air.

There should be no reason to handle nickel carbonyl in bulk. Your primary concern is the possible presence of it as a trace gas and managing it as a hazardous material within the process equipment, especially during maintenance activities.

Chemical and Physical Properties of Nickel Carbonyl

Some of the key chemical and physical properties of nickel carbonyl are listed in Table 18.

Note that it is a heavy vapor that may accumulate in low elevations.

The formation of stable nickel carbonyl depends strongly on the partial pressure of CO, assuming nickel is present. The equilibrium equation is:

$$P_{\mathrm{Ni(CO)_4}} = [P_{\mathrm{CO}}]^4 \times 10^{[8546/T - 21.64]} \tag{2}$$

where:

$P_{\mathrm{Ni(CO)_4}}$ = partial pressure of nickel carbonyl, atmospheres
P_{CO} = partial pressure of CO, atmospheres
T = absolute temperature, °K

Once formed, the dissociation back to nickel and CO is not instantaneous but may require several minutes. The formation of $Ni(CO)_4$ is hindered by the oxide

Table 18 Some key properties of nickel carbonyl

Chemical formula	$Ni(CO)_4$
Molecular weight	170.73
Relative density	5.9 (air = 1.0)
Autoignition temperature	140 °F (60 °C)
Flammability	Very flammable
Explosive limits	2–34 vol% in air
Color	Colorless, invisible
Odor	Musty, like brick dust (don’t try to find out, however) (threshold = 1–3 ppm)
Boiling point	109 °F (43 °C)
Melting point	1.0 °F (−17.2 °C)
Reactivity	Dangerous with oxidizers and bases
Solubility in water	0.018 g/100 ml (50 °F, 10 °C)
Solubility in organics	Soluble

coating of Ni catalyst and oxygen. Formation of $Ni(CO)_4$ is accelerated by ammonia and H_2S.

Hazards of Nickel Carbonyl

This is one of the most toxic materials encountered in refining (or any industry for that matter). Table 19 lists the applicable exposure limits.

Via the various exposure routes, the toxic effects are:

- Inhalation:
  - Short-term: Cough, fever, nausea, vomiting, diarrhea, chest pain, difficulty breathing, irregular heartbeat, headache, dizziness, disorientation, bluish skin color, blood disorders, liver enlargement, convulsions, and death
  - Long term: Reproductive effects and cancer
- Skin contact:
  - Short-term: Irritation, allergic reactions, rash, itching. It may be absorbed through the skin and produce effects similar to inhalation.
  - Long term: Irritation and allergic reactions. May experience reactions similar to inhalation.
- Eye contact:
  - Short-term: irritation.
  - Long term: No information available.
- Ingestion:
  - Short-term: Cough, fever, nausea, vomiting, diarrhea, chest pain, difficulty breathing, irregular heartbeat, headache, dizziness, disorientation, and bluish skin color
  - Long term: No information available

In addition to the health impacts, nickel carbonyl in sufficient quantities is highly flammable and can be detonated by shock, friction, or moderate heating. You should not normally encounter it in any concentration that would cause these hazards, however.

NFPA rating for nickel carbonyl is 4 (health) – 3 (flammability) – 3 (reactivity).

Table 19 Exposure limits and toxicity of nickel carbonyl

Agency	Limit type	pp***b***	mg/m^3	Basis
US OSHA	PEL	1	0.007	8 h TWA
US NIOSH	REL	1	0.007	10 h TWA
	IDLH	(~3 ppm)		
ACGIH (USA)	TLV	1	0.007	10 h TWA

LC50 (Rat) by inhalation: 35 ppm (30 min)
Known human carcinogen

Protective Equipment for Nickel Carbonyl

If exposure to significant amounts of nickel carbonyl may be possible, the normal precautions (in addition to the normal hardhat, safety glasses, flame-retardant clothing, and safety shoes) are:

- Provision of adequate ventilation, which may include explosion-resistant fans.
- Eye protection: splash-resistant chemical goggles with face shield. Emergency eyewash in immediate area.
- Clothing: chemical-resistant clothing if liquid may be present.
- Gloves: chemical-resistant gloves if liquid may be present.
- Respirator: Full-face, self-contained, or supplied-air respirator operating on pressure demand (or other positive-pressure mode) with an escape bottle. A full-face, air-purifying respirator with a suitable canister is only usable for emergency escape.

If there is any possibility of IDLH atmosphere with nickel carbonyl, a supplied-air breathing apparatus is required. Do not take any chances.

Note that these precautions apply for personnel at catalyst dump points (such as at the top of flow bins) as well as those working in enclosed spaces with catalysts.

Management of Nickel Carbonyl Hazards

The primary focus of nickel carbonyl management in a refinery is prevention of its formation.

In hydroprocessing units, where nickel catalysts and deposits are common, it is normal practice to cool reactors to about 450–500 °F (232–260 °C) and then test the circulating gases for CO. Different companies and units use different limits, but the CO in the gas must normally be less than 10–100 ppm before cooling further. This ensures the nickel carbonyl content will not exceed 1 ppb as the catalyst is cooled. Purging with nitrogen further reduces the risk of formation. You have to be careful to avoid introducing any more CO after the test through the hydrogen or nitrogen used. After testing, it is normally best to avoid bringing in anything except vaporized, cryogenic nitrogen.

If the CO test shows a CO level above the allowable, the reactor should be held at temperature (or re-heated above 450 °F). The system should be purged and any possible CO (or oxygen or CO_2) sources eliminated until the CO level drops to the allowable range. Once a CO source is stopped in a circulating system with hydrogen, the remaining CO will be methanated and disappear from the system.

In hydrogen production, CO and reduced nickel catalysts are part of the process. To eliminate the possibility of nickel carbonyl formation in hydrogen plants on shutdown, the feedstock should be pulled at high temperature. No oxygen, CO_2, or other possible CO formation sources should be permitted to reenter the system during cooling. The system should be thoroughly purged with nitrogen (CO-free) before cooling below 400 °F (204 °C).

Precautions during catalyst handling include:

- Continuous monitoring of the inert atmosphere for CO and oxygen. Stop and purge if these are detected above allowable limits.
- Use fresh air equipment at the dump point where catalyst smoldering may occur.
- Keep catalyst spills wet to prevent smoldering.
- Dump potentially self-heating catalysts into inert-purge containers or flood and dump wet.

CO testing by detection tubes is normally employed to verify no CO is present. Follow the detector tube manufacturer's instructions. For Dräger tubes:

- Hydrogen gas atmosphere: use tube 8/a for CO with solid sodium hydroxide and carbon pre-tubes.
- Nitrogen or natural gas atmosphere: use tube 5/c for CO with the NaOH and carbon pre-tubes.
- Olefins present in the gas will interfere with the analysis.

While detector tubes are available for nickel carbonyl, the detector range is 0.1 ppm (100 ppb), which is too high to help in this case.

Nickel carbonyl itself can be analyzed using wet chemical or adsorption/desorption methods. US NIOSH has procedures available. This tests are too slow for most practical monitoring, however.

Nitrogen (N_2, LN_2)

General Discussion of Nitrogen

The uses and hazards of nitrogen are addressed somewhat under the topics "▶ Utilities in Petroleum Processing" and "▶ Safety Systems for Petroleum Processing" of this handbook. We will explore the hazards of handling these materials a little more quantitatively here.

As background and refresher, nitrogen is used extensively in most refineries today. Some of the common uses are:

- Purging of equipment and piping to eliminate air or hydrocarbons/hydrogen
- Purging of compressor seals
- Storage tank or vessel blanketing to prevent air contact
- As emergency backup pneumatic gas
- Chilling of some analytical instruments

In normal practice, the nitrogen is received as a refrigerated liquid. The liquid is stored in a double-walled, insulted cryogenic storage tank and is vaporized as needed to supply facility needs. For large, intermittent uses, nitrogen trailers and fired vaporizers are used. Some facilities generate their own nitrogen cryogenically or, more commonly, using a PSA or membrane system. This is discussed in more detail in the chapter on "▶ Utilities in Petroleum Processing."

Chemical and Physical Properties of Nitrogen

Table 20 lists the key properties of nitrogen relevant to the current discussion.

Nitrogen may be found in a refinery as a refrigerated liquid or as a vapor. The most common exposure risk is from inhalation of excessive nitrogen vapors.

Note that the cryogenic liquid that is normally handled in bulk is extremely cold.

Nitrogen will not support combustion at any condition normally encountered in a refinery.

Hazards of Nitrogen

Nitrogen, as used in a petroleum processing facility, presents the following hazards:

- Oxygen depletion in the atmosphere
- Risk of burns or frostbite from cryogenic liquid contact
- Physical injury from high pressure gas

The most important of these hazards is normally asphyxiation from an oxygen-deficient atmosphere. Since nitrogen is colorless and odorless, it provides no warning of oxygen deficiency.

Otherwise, nitrogen is not toxic and causes no other issues. These hazards are discussed more fully in the handbook topic "▶ Safety Systems for Petroleum Processing."

Symptoms of oxygen deficiency from a nitrogen atmosphere would include:

- Headache
- Dizziness

Table 20 Some key properties of nitrogen

Molecular weight	28.02
Specific gravity	Vapor: 0.967 (air = 1)
	Liquid: 50.46 lb/ft^3 (808.3 kg/m^3)
Boiling point	−320 °F (−196 °C)
Freezing point	−346 °F (−210 °C)
Autoignition temperature	Will not support combustion
Explosive limits	Not applicable

- Fatigue
- Nausea
- Euphoria
- Or simply unconsciousness without warning (within seconds at low oxygen levels)

Most often, unconsciousness is so rapid there is no time for other symptoms to manifest.

In working with the cryogenic liquid, any exposure of personnel to the liquid (as in skin) will result in immediate/instantaneous, severe burns.

Protective Equipment for Nitrogen Handling

The best protection against nitrogen creating an oxygen deficiency is adequate ventilation and exclusion of all personnel from areas near inerted equipment. Anyone that must approach inerted equipment must wear fresh air breathing apparatus (SCBA or supplied air).

In addition to the normal refinery PPE, areas where there may be a nitrogen deficiency are normally monitored by fixed or personal monitors for oxygen with audible, vibration, and visual alarms. Any alarm would require immediate evacuation.

Refer to the topic "▶ Safety Systems for Petroleum Processing" for additional discussion.

When handling cryogenic liquid nitrogen, chemical-resistant, insulated gloves, and face shield should be worn.

Large spills of liquid will require fresh air breathing apparatus.

Storage and Handling of Nitrogen

Refer to "▶ Utilities in Petroleum Processing" for a detailed discussion of nitrogen handling systems and to "▶ Safety Systems for Petroleum Processing" for a discussion of managing potentially oxygen-deficient atmospheres.

Fresh air equipment (e.g., SCBAs) should be immediately available where liquid nitrogen is handled and in areas where oxygen deficiency may occur.

Sulfiding Chemicals

General Discussion of Sulfiding Chemicals

Most hydroprocessing catalysts are not very active as received. The most active forms of these materials are the sulfides or the catalytic metals. To create the active forms, the catalysts are activated or "sulfided" using H_2S or one of several other sulfiding agents in a circulating hydrogen stream. Today, H_2S is not commonly used.

At one time carbon disulfide (CS_2) would have been included here; but it is rarely used today because of the extreme fire hazard it represents.

In another application, sulfiding chemicals are used to temporarily suppress cracking activity in naphtha reformers during startup.

Aside from H_2S, the most common sulfiding agents include:

- Dimethyl sulfide (DMS)
- Dimethyl disulfide (DMDS)
- Di-tertiary butyl polysulfide (TBPS)
- Di-tertiary nonyl polysulfide (TNPS)

There are proprietary versions of some of these chemicals, such as Sulfrzol® 54, but the hazards are similar.

These chemicals present a range of hazards from relatively low hazard to suspected carcinogens. We will explore the hazards and their management here.

Chemical and Physical Properties of Sulfiding Agents

Table 21 provides some of the key, relevant properties for various sulfiding agents.

Most of these chemicals have an unpleasant smell. Often the smell is associated with residual traces of the mercaptans left over from manufacturing.

Note that the polysulfides decompose on heating before they boil. The decomposition products include mercaptans and H_2S. Under some conditions, the polysulfides may form solid deposits and plug lines, especially if boiled at high temperatures without the presence of other liquid hydrocarbons.

Some of these compounds are excellent solvents for many common materials, especially shoes.

Hazards of Sulfiding Agents

The odors of these materials provide an early warning of potential exposure. Spills of the heavier liquids, however, just look like water.

Note that some people react much more strongly to even the slightest odor of some of these compounds. Reactions may include nausea and vomiting.

All the compounds present a fire hazard, in addition to health hazards. DMS is especially volatile and tends to load up the treat gas circulation with methane. It is not used much anymore. DMDS, TBPS, and TNPS (or their branded counterparts) are most common.

Table 22 summarizes the key hazards and exposure limits for these materials.

All of these materials are flammable. They are all toxic to fish and long lasting in an aquatic environment, so they should not be allowed into storm drains or effluents without treatment.

The products of combustion will include CO, SO_2, and H_2S if the materials burn.

Table 21 Some key properties of sulfiding agents

Chemical	Dimethyl sulfide (DMS)	Dimethyl disulfide (DMDS)	Di-*t*-butyl polysulfide (TBPS)	Di-*t*-nonyl polysulfide (TNPS)
Formula	$(CH_3)_2S$	$(CH_3)_2S_2$	$C_8H_{18}S_x$ (x = avg ∼2.8)	$C_{18}H_{38}S_x$ (x = avg 5.0)
Molecular weight	62.13	94.2	∼204 avg	414 avg
Color (liq)	Clear	Pale yellow	Yellow	Yellow to yellow-orange
Odor	Stench	Strong garlic-like odor	Slightly acrid	Mildly unpleasant
Odor threshold	<1 ppm	∼8–10 ppb		
Sulfur, wt%	51.5	67.9	∼44 avg	35–39
Specific gravity	Gas: 2.1 (air=1)	Gas: 3.25 (air=1)	Liq: 1.07 (68 °F, 20 °C)	Liq: 1.05 (68 °F, 20 °C)
	Liq: 0.85 (68 °F, 20 °C)	Liq: 1.06 (39 °F, 4 °C)		
Boiling point	99 °F (38 °C)	228 °F (109 °C)	342–356 °F (172–180 °C) (decomposes)	407–507 °F (208–264 °C) (decomposes)
Freezing point	−145 °F (−98.3 °C)	−121 °F (−85 °C)	37 °F (3 °C)	<−4 °F (<−20 °C)
Flash point	−54 °F (−48 °C)	59 °F (15 °C)	217 °F (103 °C) CC	277–291 °F (136–144 °C) PMCC
Solubility in water	2.0 wt% (68 °F/20 °C)	∼0.25 wt% (68 °F/20 °C)	Insoluble	Insoluble
Autoignition temperature	403 °F (206 °C)	Not available	437 °F (225 °C)	464 °F (240 °C)
Explosive limits	2.2–19.7 vol%	1.1–16 vol%	Not available	Not available
Viscosity (liq)	0.29 cP (68 °F, 20 °C)	0.62 cP (68 °F, 20 °C)	10 cP (68 °F, 20 °C)	24–34 cP (122 °F, 50 °C)

Protective Equipment for Sulfiding Chemicals Handling

In addition to the normal petroleum processing facility PPE (hardhat, flame-retardant clothing, safety glasses, safety shoes), the recommended personal protective equipment when handling these materials includes:

- Eye/face protection: Goggles, face shield. Eye wash station should be available nearby.

Table 22 Hazards and exposure limits of common sulfiding agents

Chemical	Dimethyl sulfide (DMS)	Dimethyl disulfide (DMDS)	Di-*t*-butyl polysulfide (TBPS)	Di-*t*-nonyl polysulfide (TNPS)
Exposure effects				
Inhalation	Headache, memory loss, confusion, convulsions, unconsciousness; ACGIH TLV = 10 ppm (8 h)	Nausea, headache, or dizziness, drowsiness, unconsciousness; ACGIH limit 0.5 ppm TWA	Unlikely route of exposure	Unlikely route of exposure
Eyes	Irritation, inflammation	Irritation, may be irreversible	Almost no irritation	Slight irritation
Skin	Stinging, reddening, removal of skin oils	Irritation, redness, rash, removal of oils, may also see central nervous system effects like inhalation	Allergic reaction, redness, rash	Slight irritation
Ingestion	Irritation of the mouth, throat, stomach; nausea, vomiting	Irritation of the mouth, throat, stomach; nausea, vomiting	Aspiration hazard to lungs, increased breathing and heart rate, coughing, respiratory distress	Slightly toxic
Chronic	None identified	Sensitizer	Sensitizer	No effects expected
Preexisting conditions	Aggravates respiratory diseases	No information	No information	No information
Carcinogenic	Not listed	Suspected	No information	No information
Toxicity				
Inhalation	LD50 = 40,250 ppm (102 mg/l, rat)	Slightly toxic, LC50 805 ppm (rat, 4 h)	Not available	LC50 >50 mg/l (4 h, rat)
Ingestion	LD50 = 3,700 mg/kg (mouse)	Moderately toxic, LD50 = 290–500 mg/kg (rats)	Slightly toxic, LD50 >2,000 mg/kg (rat)	Slightly toxic, LD50 = 19,550 mg/kg (rat)

Dermal	LD50 = 10,200 mg/kg (rat)	Slightly toxic, LD50 >2,000 mg/kg	Slightly toxic, LD50 >2,000 mg/kg (rat)	Slightly toxic, LD50 >2,000 mg/kg (rabbit)
Skin irritation	Mild (rabbit), LD50 >5 g/kg	Slight (rabbit)	Slight (rabbit)	Slight
Eye irritation	Severe (rabbit)	May cause irreversible eye damage	Slight (rabbit)	Slight
Fire				
Flammability	High, vapors may ignite from remote sources, possible explosion	High, vapors may ignite from remote sources, possible explosion	Moderate	Moderate
Hazardous combustion products	Sulfur dioxide, H_2S, CO	Sulfur dioxide, H_2S, CO	Sulfur dioxide, H_2S, CO	Sulfur dioxide, H_2S, CO
Hazard ratings (health/flammability/reactivity)				
HMIS	2/4/0	3/3/1	1/2/0	Not available
NFPA	1/4/0	2/4/0	2/1/0	0/1/0

References: Various MSDSs and product data sheets from manufacturers and distributors. These are the best data available, but there are conflicts among some of the data sources on effects, exposures, and ratings

- Respiration: if strong vapor or mist present, use appropriate organic vapor cartridge respirator, SCBA, or supplied-air breathing apparatus. For vessel entry or high levels of potential exposure, use SCBA or supplied air only.
- Skin/clothing: Butyl or nitrile rubber gloves (not leather). In some cases, aprons, rubber boots, or a rubber suit may be needed. A safety shower should be available in the immediate area.
- Other: Do not smoke in areas where these chemicals may be present. Wash hands and other potentially exposed areas of skin thoroughly with soap and water before eating, smoking, or using toilet facilities.

In the event of a fire involving the chemicals, wear SCBA, protective clothing (which may include a rubber suit), and gloves.

Have bleach (2–5 %) or LAB solution available in a sprayer to manage odors from small spills. See below.

Storage and Handling of Sulfiding Chemicals

These chemicals can be handled like other hydrocarbons of similar vapor pressure. They are stable under normal conditions, but the vapors can ignite readily.

Carbon and stainless steels are suitable for vessels and piping. When making up threaded piping, normal pipe compound is not suitable. Makeup temporary threaded piping with Teflon® (Rect-R-Seal™ or equal). Pressure test all temporary piping before allowing any sulfiding chemical into the lines. It is a big, stinky mess if the lines leak once they contain the sulfiding chemicals.

The sulfiding chemicals are normally brought into a facility by truck or iso-container. Some may also be handled in barrels or tote-bins, depending on the quantity required. Small quantities may be kept onsite for activities like naphtha reformer startup, but large quantities are seldom stored onsite. They are normally used directly from the tank truck or iso-container.

The trucks are staffed by experienced and trained personnel (supplied by the chemical vendor or trucking company) around the clock until the sulfiding activity is completed. Sulfiding chemicals are normally pressured out of the trucks or iso-containers by nitrogen through metering and an injection pump into the process.

In the event of small spills, spray the chemical with a *dilute* solution (~2–5 %) of bleach to neutralize odors. This converts the chemicals to dimethyl sulfoxide, which may be treated in a wastewater treatment plant. "Liquid Alive Bacteria (LAB)" solution is also effective when used in accordance with the manufacturer's instructions. Concentrated bleach or solid bleach should *not* be used as it may react violently or cause a fire.

Absorb small spills in a sorbent. Collect the sorbent in a metal container and dispose of as a hazardous waste.

In the event of a large spill or fire:

- Get people out of the area.
- Contain the spill if possible. Avoid disposal or runoff. Runoff will be an ecological problem. Get your environmental department involved.

- Eliminate all ignition sources – remember the vapors of these chemicals are heavy and can follow low spots or sleeperways for a long distance to an ignition source.
- Wear impervious gloves, skin protection (including a rubber suit).
- If the material ignites or explodes:
  - Combustion and thermal decomposition products will be toxic (CO, SO_2, H_2S), so full-face, positive-pressure fresh air equipment is required.
  - Extinguishing media: dry chemicals, CO_2, alcohol-resistant foam, and other foams. Water spray may be used also to cool and protect equipment, but contain runoff. High volume water jets are *not* suitable.
  - Keep surrounding equipment cool with water spray.

These materials are routinely handled in petroleum facilities without incident. Their odor reminds people to use care in handling them.

Sulfuric Acid (H_2SO_4)

General Discussion of Sulfuric Acid

Sulfuric acid is found in several locations in refineries or other processing facilities. It is used for pH control in cooling towers and other services. It is the primary catalyst in some alkylation processes. Some refineries even have sulfuric acid plants associated with them to dispose of sulfur removed by other processes.

Sulfuric acid is safely handled in bulk regularly in facilities, but it can be very hazardous if not handled properly. The most common form of H_2SO_4 is concentrated acid. Dilute acid is corrosive to steel, whereas concentrated acid is not very corrosive to steel at most ambient conditions. Hence, we like to handle the acid as a concentrate.

Properties of Concentrated Sulfuric Acid

Table 23 presents the relevant properties of concentrated acid, the most common used in refining. More dilute grades may be encountered.

Hazards of Sulfuric Acid

Sulfuric acid presents a number of hazards. Table 24 summarizes the exposure limits and toxicity data.

Health effects described by exposure route include:

- Inhalation: May cause severe irritation of respiratory tract with sore throat, coughing, shortness of breath, and delayed lung edema. Causes chemical burns to respiratory tract. May cause inflammation. Destructive to mucous membranes. May cause headache, vomiting, nausea, pulmonary edema. Corrosive and toxic. May be fatal.
- Eyes: Severe eye burns. May be irreversible.

Table 23 Some key properties of concentrated sulfuric acid

Chemical formula	H_2SO_4
Molecular weight	98.079
Appearance	Clear, colorless, odorless liquid
Purity, %	98
pH, 1N solution	0.3
Specific gravity	1.841 (~1.84 kg/l)
Boiling point	554 °F (290 °C)
Vapor pressure	<0.00005 in Hg @ 68 °F (<0.0012 mmHg @ 20 °C)
Freezing point	50.6 °F (10.3 °C)
Vapor density	1.2 kg/m^3
Decomposition temperature	644 °F (340 °C)
Viscosity	26.7 cP (68 °F, 20 °C)

Table 24 Exposure and toxic effects of concentrated sulfuric acid

Agency	Limit type	mg/m^3	Basis
US OSHA	Limit	1	8 h TWA
US NIOSH	REL	1	10 h TWA
ACGIH (USA)	TLV	1	10 h TWA
	STEL	3	
Toxicity			
Inhalation	LC50 (rat)	51 mg/m^3	2 h
Oral	LD50 (rat)	2140 mg/kg	
Ecology	Harmful to aquatic life in very low concentrations		
Workers exposed to sulfuric acid mist showed increase in laryngeal, nasal, sinus, and lung cancer			

- Skin: Skin burns. Defatting dermatitis with prolonged exposure. May be fatal.
- Ingestion: May cause severe and permanent damage to digestive tract, burns in mouth, pharynx, and gastrointestinal tract. May cause nausea, vomiting, and abdominal pain. Corrosive and toxic. May be fatal.
- Chronic exposure: Nosebleeds, nasal congestion, erosion of teeth, perforation of nasal septum, chest pain, and bronchitis. Eye exposure may cause conjunctivitis. May cause death. Corrosive to body tissues.

PPE for Handling Sulfuric Acid

The following minimum PPE are recommended beyond the typical refinery worker's PPE when handling sulfuric acid:

- Eye protection: Splash-proof chemical safety goggles and face shield.
- Skin protection: Neoprene or polyethylene gloves.
- Clothing: Apron or other impervious clothing (e.g., rain coat), rubber boots, other clothing to prevent skin contact.

- Respiratory protection: Use a US NIOSH-approved (or equal) respirator when necessary.
- Ventilation: Use only with adequate ventilation. In a lab, hand the acid in a fume hood.
- Other: Eye wash and safety shower should be immediately available in any area where sulfuric acid is handled.

Storage and Handling of Sulfuric Acid

For concentrated sulfuric acid, carbon steel tanks and piping are normally adequate. Temperature must be kept low in carbon steel to prevent corrosion. If higher temperatures or dilute acid are handled, higher alloys are required. Consult with a metallurgist on the proper alloys for your application.

The acid is normally stored in atmospheric vessel vented through a desiccant cartridge to prevent moisture from the air entering the tank. Sulfuric acid is a desiccant in its own right, so avoiding any moisture is critical. The storage tanks are typically within chemical containment dikes (epoxy-coated concrete). The dike drain is managed closed to ensure any leaks are not sent to the sewer uncontrolled.

There should always be an eyewash and safety shower immediately adjacent to the acid storage area.

Acid is generally unloaded and moved by nitrogen or air pressure among users. The final users will generally use pumps for controlled injection.

Sulfuric acid will not burn but can decompose to yield poisonous sulfur oxide vapors if the storage area becomes involved in a fire. Positive-pressure, supplied-air respiratory equipment is required is fighting a fire near an acid storage tank. Use water spray on the outside of the tank to keep it cool.

Do not allow water to be pumped into an acid storage tank. The heat of solution will cause foaming and possible tank failure.

Safe handling of concentrated sulfuric acid is common in a refinery, in spite of the hazards. The key points to remember are:

- Keep the acid contained and cool.
- Do not allow any personnel contact with the acid.
- Keep water away from the concentrated acid until you are ready for use, then add acid into a large excess of water.

Hazardous Materials Handling Summary

Table 25 pulls together some of the most important information from the foregoing sections of this chapter for convenience. For more details, consult the individual sections and the MSDS sheets from your supplier or company for the specific materials of interest.

Table 25 Summary of key hazardous materials handling information

a

Category	Amines for gas treating						Ammonia		
Material	Monoethanolamine	Diethanolamine	Methyldiethanolamine	Diglycolamine	Diisopropanolamine	Sulfinol	Anhydrous	26 1Bé	20.5 Bé
Abbreviation/alias	MEA	DEA	MDEA	DGA	DIPA	–	–	Aqua ammonia	Aqua ammonia
Chemical formula	$HOC_2H_4NH_2$	$(HOC_2H_4)_2NH$	$(HOC_2H_4)_2NCH_3$	$H(0C_2H_4)_2NH_2$	$(HOC_3H_6)_2NH$	Mixture	NH_3	NH_3	NH_3
Molecular weight	61.1	105.1	119.16	105.14	133.19	120.17	17.0305	–	–
Physical states	Pure liquid, as received	Pure liquid, as received	Pure liquid, as received	Pure liquid, as received	Pure liquid, as received	Aq. solution	Liq, vap	Aq. liq, vap	Aq. liq, vap
Color	Colorless	Colorless to yellow	Colorless to Lt. yellow	Colorless	Colorless	Colorless	Colorless	Colorless	Colorless
Odor	Ammoniacal	Ammoniacal	Amine-like	Mild amine	Ammonia-like	Fishy hydrocarbon	Strong acrid	Strong acrid	Strong acrid
Vapor Sp. Gr. (air = 1)	2.1	3.6	4.1	3.6	4.6	4.6	0.59	0.59	0.59
Liquid Sp. Gr. (nominal)	1.01	1.09	1.04	1.06	0.99	1.26	0.68	0.90	0.93
Boiling point, °F/°C	338.5/170	515.1/268	477/247	405.5/208	479.7/249	545/285	−28/−33	85/29	123/51
Freeze point, °F/°C	50.5/10.2	77.2/25.1	−9/−23	9.5/−12.5	107.6/42	81.7/27.6	−108/−78	−110/−79	−30/−34
Flash point, °F/°C	200/93.3	295/146	265/129	260/127	255/124	350/177	Not available	Not available	Not available
Autoignition, °F/°C	Not available	Not available	509/265	698/370	545/285	Not Available	1,204/651	See anhydrous	See anhydrous
Decomposition, °F/°C	Not available	Not available	Not available	Not available	Not available	Not available	Not available	Not available	Not available

Flammability limits (air)	Not available	Not available	0.9–8.4	2.6–11.7	1.1–8.5	Not available	15–28 %	See anhydrous	See anhydrous
Exposure limits (always verify current values)	TLV=3 ppm STEL=6 ppm	TLV=2 mg/m^3	Not available	Not available	US PEL=5 ppm, UK STEL=15 ppm	Not available	TLV= 25 ppm STEL= 35 ppm IDLH = 300 ppm	See anhydrous	See anhydrous
Primary hazard routes	Skin, inhalation	Skin, inhalation	Skin, inhalation	Skin, inhalation	Skin, inhalation	Skin, inhalation	Inhalation, skin, eyes	Inhalation, skin, eyes	Inhalation, skin, eyes
Exposure type									
Fire/explosion	Remote	Remote	Remote	Remote	Remote	Remote	X	Unlikely	Unlikely
Toxicity	X	X	X	X	X	X	X	X	X
Ecological impacts									
Aqueous env.	Toxic	Medium toxic	Slightly toxic	Slightly toxic	Not Available	Not Available	Highly toxic	Moderately toxic	Moderately toxic
Biodegradable	Yes	Yes	Yes	Yes	Not available	Not available	Yes	Yes	Yes
Firefighting media	Water spray/fog, foam, dry chemical, CO_2	Water spray/fog, foam, dry chemical, CO_2	Water spray/fog, foam, dry chemical, CO_2	Water spray/fog, foam, dry chemical, CO_2	Water spray/fog, foam, dry chemical, CO_2	Water spray/fog, alc. foam, dry chemical, CO_2	Water spray/fog, dry chemical, CO_2	Water spray/fog, dry chemical, CO_2	Water spray/fog, dry chemical, CO_2
Possible added PPE[1]									
Handling area (normal)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air
Fire or large spill (additional)	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes	SCBA or =, eye protection, protective clothes

(*continued*)

Table 25 (continued)

a

Category	Amines for gas treating						Ammonia		
Material	Monoethanolamine	Diethanolamine	Methyldiethanolamine	Diglycolamine	Diisopropanolamine	Sulfinol	Anhydrous	26 1Bé	20.5 Bé
Abbreviation/alias	MEA	DEA	MDEA	DGA	DIPA	–	–	Aqua ammonia	Aqua ammonia
Hazard ratings (health – flammability – reactivity)	NFPA 3-1-0	NFPA 2-1-0	HIMS 1-1-0	HIMS 3-1-0	NFPA 2-1-0	NFPA expect 2-10 based on ingredients	NFPA 3-1-0	NFPA 3-1-0	NFPA 3-1-0
References									
MSDS SOURCES	Dow	Dow	Acros Organics, Dow, Huntsman	Huntsman, Univar	BASF, Hazel Mercantile	Burlington Resources, Shell	Tanner Industries, Air Products	Tanner Industries, Air Products	Tanner Industries, Air Products
ARTICLES; BULLETINS; OTHER				Huntsman			Tanner Industries, Wikipedia	Tanner Industries, Wikipedia	Tanner Industries, Wikipedia

b

Category			Catalysts and sorbents						
Material	Benzene	Carbon monoxide	Hydro processing	Hydrogen plant	PSA adsorbents	Mole sieves, zeolites	Caustic soda (50%)	Furfural	Hydrofluoric acid
Abbreviation/alias	Bz	–	K172	–	–	–	–	–	AHF, HF
Chemical formula	C_6H_6	CO	Co, Ni, Mo, sulfides and oxides; alumina; silicates; coke; with contam	Ni and NiO on ceramic support	Molecular sieves, activated carbon, activated alumina	Molecular sieves, zeolites	NaOH	C_4H_3OCHO	HF
Molecular weight	78.11	28.01	N/A	N/A	N/A	N/A	40.00	96	20.01

Physical states	Liq, vap	Vap	Solid to oily solid	Solid	Solid	Solid	Aq. liq, solid	Liq, vap	Liq, Vap
Color	Colorless	Colorless	Varies	Gray	White to black depends on product	White to tan	Colorless to white	Lt. yellow to brown	Colorless
Odor	Sweet aromatic	Odorless	Hydrocarbon	None	None	None	None	Almond	
Vapor Sp. Gr. (air =1)	2.7	0.97	N/A	N/A	N/A	N/A	N/A	3.3	0.69
Liquid Sp. Gr. (nominal)	0.88	–	N/A	N/A	N/A	N/A	1.53	1.16	1.00
Boiling point, °F/°C	176/80	−312/−191	N/A	N/A	N/A	N/A	284–140	324/162	67/19
Freeze point, °F/°C	42/6	−337/−205	N/A	N/A	N/A	N/A	54/12	−38/−39	−117/−83
Flash point, °F/°C	12/–11	Not available	Varies	N/A	N/A	N/A	N/A	140/60	N/A
Autoignition, °F/°C	1097/592	1121/605	Not available	N/A	N/A	N/A	N/A	601/316	N/A
Decomposition, °F/°C	Not available	N/A	Not available (may liberate CO, H_2S, other gases)	Not available (may liberate CO, $Ni(CO)_4$, other gases)	Not available (may liberate CO or other gases if wet)	Not available (may liberate CO, H_2S, or other gases if wet)	N/A	Not available – unstable in light and air	Not available – decomposition products include halogens
Flammability limits (air)	1.3–7.1	12.5–74.2	N/A	N/A	N/A	N/A	N/A	2.1–19.3	N/A
Exposure limits (always verify current values)	TLV=0.5–1 ppm STEL=2.5–5 ppm	TLV=25 ppm STEL=200 ppm	N/A	Refer to nickel hazards	Refer to silica hazards	Refer to silica hazards	2 mg/m^3 mist or dust	TLV=2 ppm STEL=5 ppm	TLV=0.5 ppm skin, STEL=6 ppm
Primary hazard routes	Inhalation, skin	Inhalation	Inhalation (dust, vapors), skin	Inhalation (dust, vapors)	Inhalation (dust, vapors)	Inhalation (dust, vapors)	Skin, eyes, inhaled mist or dust	Inhalation, skin	Inhalation, skin
Exposure type									
Fire/explosion	X	X	Smoldering	N/A	X (act. carbon)	N/A	N/A	X	N/A

(*continued*)

Table 25 (continued)

b									
Category			Catalysts and sorbents						
Material	Benzene	Carbon monoxide	Hydro processing	Hydrogen plant	PSA adsorbents	Mole sieves, zeolites	Caustic soda (50%)	Furfural	Hydrofluoric acid
Abbreviation/ alias	Bz	–	K172	–	–	–	–	–	AHF, HF
Toxicity	X	X	X	Ni dust, carcinogen	Low	Low	X	X	High
Ecological impacts									
Aqueous env.	Not major	N/A	Slightly toxic, potential groundwater contamination	Possible hazard	Not available	Not available	Toxic, avoid contamination of effluent	Toxic	Not available
Biodegradable	Yes	N/A	No	No	Not available	Not available	No	Yes	No
Firefighting media	Water spray/fog, alc. foam, dry chemical, CO_2, Halon	Water spray/ fog, foam, dry chemical	Water spray/fog, foam, dry chemical, CO_2	N/A	Water	N/A	N/A	Water spray/fog, foam, dry chemical, CO_2	N/A
Possible added PPE[1]									
Handling area (normal)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	SCBA or =, personal CO monitor	Dust respirator, goggles, face shield, gloves, chemical-resistant clothing	Dust respirator, goggles, gloves	Dust respirator, goggles, gloves	Dust respirator, goggles, gloves	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots), vapor respirator or supplied air	Goggles, face shield, impervious acid suit, boots and gloves, SCBA
Fire or large spill (additional)	SCBA or =, eye protection, protective clothes	SCBA or =	SCBA or =	N/A	SCBA or =	N/A	N/A	SCBA or =, eye protection, protective clothes	SCBA
Hazard ratings (health – flammability – reactivity)	HIMS 2-3-0, NFPA 2-3-0	HIMS 2-4-0, NFPA 3-4-0	Varies	HIMS 2-1-0, NFPA 2-1-0	Not Available	NFPA 1-0-1	NFPA 3-0-1	NFPA 3-2-0	NFPA 4-0-1 (acid)

References									
MSDS SOURCES	Total	Airgas	CRI/Criterion, Haldor Topsoe, Porocel, Valero	Johnson Matthey		Delta Adsorbents	Orica Chemicals	Int'l Furan Chemicals	Airgas
ARTICLES; BULLETINS; OTHER	Wikipedia	Wikipedia							Wikipedia

c

Category						Sulfiding chemicals				
Material	Hydrogen	Hydrogen sulfide	Methyl ethyl ketone	Nickel carbonyl	Nitrogen	Dimethyl sulfide	Dimethyl disulfide	Di-t-butyl polysulfide	Di-t-nonyl polysulfide	Sulfuric acid (Conc.)
Abbreviation/ alias	–	**H2S**	MEK	–	**N_2, LN_2**	DMS	DMDS	TBPS	TNPS	SA
Chemical formula	H_2	H_2S	$CH_3C(O)CH_2CH_3$	$Ni(CO)_4$	N_2	H_3CSCH_3	H_3CSSCH_3	$C_8H_{18}S_x$	$C_{18}H_{38}S_x$	H_2SO_4
Molecular weight	2.02	34.08	72	170.73	28.02	62.13	94.2	~204	~414	98.08
Physical states	Vap	Vap	Lig, Vap	Vap (Liq unlikely)	Cryogenic Liq, Vap	Liq, Vap	Liq, Vap	Liq	Liq	Liq
Color	Colorless	Colorless	Colorless	Colorless	Colorless	Clear	Pale Yellow	Yellow	Yellow	Colorless
Odor	Odorless	Rotten eggs	Sweet alcohol	Musty/wet brick	Odorless	Stench	Strong garlic	Slightly acrid	Mildly unpleasant	Odorless to slight sulfur odor
Vapor Sp. Gr. (air = 1)	0.0696	1.19	2.4	5.9	0.97.	2.1	3.25	–	–	(1.2 kg/m^3)
Liquid Sp. Gr. (nominal)	–	–	0.81	–	0.81	0.85	1.06	1.07	1.05	1.84
Boiling point, °F/°C	−423/ −253	−77/−61	176/80	109/43	−320/−196	99/38	228/109	342–356/ 172–180	407–507/ 208–264	554/290
Freeze point, °F/ °C	−435/ −259	−122/−86	−123/−87	1/−17	−346/−210	−145/−98	−121/−85	37/3	≤4/≤20	50.6/10.3
Flash point, °F/° C	–	–	16/−9	4/20	N/A	−54/−48	59/15	217/103	277–291/ 136−144	N/A
Autoignition, °F/°C	932–1,000/ 500–571	500/260	759/404	140/60	N/A	403/206	Not available	437/225	464/240	N/A
Decomposition, °F/°C	N/A	N/A	Not available	~300/~149	N/A	Yes (H_2S, mercaptans)	Yes (H_2S, mercaptans)	Yes (H_2S, mercaptans,	Yes (H_2S, mercaptans,	644/340 (SOx)

(*continued*)

Table 25 (continued)

c										
Category						Sulfiding chemicals				
Material	Hydrogen	Hydrogen sulfide	Methyl ethyl ketone	Nickel carbonyl	Nitrogen	Dimethyl sulfide	Dimethyl disulfide	Di-t-butyl polysulfide	Di-t-nonyl polysulfide	Sulfuric acid (Conc.)
Abbreviation/ alias	–	H2S	MEK	–	N_2, LN_2	DMS	DMDS	TBPS	TNPS	SA
								elemental sulfur)	elemental sulfur)	
Flammability limits (air)	4–76	4.3–45.5	1.4–11.4	2–34	N/A	2.2–19.7	1.1–16	Not available	Not available	N/A
Exposure limits (always verify current values)	N/A	TLV=1 ppm STEL=5 ppm IDLH =100 ppm	TLV=200 ppm STEL=300 ppm	TLV=1 **ppb_** IDLH=3 ppm carcinogen	O_2 depletion hazard	TLV=10 ppm	TLV=0.5 ppm	Not available	Not available	TLV=1 mg/m^3 STEL=3 mg/m^3
Primary hazard routes	Inhalation	Inhalation	Inhalation, skin	Inhalation, skin (absorption)	Inhalation, skin (cryogenic liquid)	Inhalation, skin (absorption)	Inhalation, skin (absorption)	Skin	Skin	Skin, eyes, inhalation
Exposure type										
Fire/explosion	High	X	X (CO evolved)	Unlikely	N/A	X (CO, SO_2, H_2S)	X (CO, SO_2, H_2S)	X (CO, SO_2, H_2S)	X (CO, SO_2, H_2S)	N/A
Toxicity	N/A	High	Moderate	Extreme (CO, Ni)	O_2 depletion hazard	High	Moderate	Slight	Slight	High, tissue damage
Ecological impacts										
Aqueous env.	N/A	Toxic	Moderate to low toxicity	Toxic, but short lived	N/A	Moderate (evaporates so short-lived effect)	Toxic, long lived	Very toxic	Insufficient data	Harmful
Biodegradable	N/A	Yes	Not available	Not available	N/A	Evaporates	No	Not available	Insufficient data	No, but reacts
Firefighting media	Water, steam	Water spray/ fog, foam, dry chemical	Water spray/ fog, alcohol-resistant foam, dry chemical, CO_2	Water spray/ fog, alcohol-resistant foam, dry chemical, CO_2	N/A	Alcohol foam, foam, dry chemical, CO_2	Water spray/ fog, alcohol-resistant foam, dry chemical, CO_2	Water spray/ fog, foam, dry chemical, CO_2	Water spray/ fog, foam, dry chemical, CO_2	N/A

Possible added PPE[1]										
Handling area (normal)	Not normally required	Personal monitor for H_2S	Organic respirator, goggles, face shield, gloves, chemical-resistant clothing	SCBA or equal, goggles, face shield, gloves, chemical-resistant clothing	SCBA or equal, personal O_2 monitor, cryogenic gloves when handling liquid	Organic respirator, goggles, face shield, gloves, chemical-resistant clothing (including boots)	Organic respirator, goggles, face shield, gloves, chemical-resistant clothing (including boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impermeable clothing (gloves, coveralls, boots)	Goggles, face shield, impervious clothes and gloves, SCBA or respirator may be needed
Fire or large spill (additional)	SCBA or =, do not enter leak area	SCBA or =, do not enter leak area	SCBA or =	SCBA or =	N/A	SCBA or =	SCBA or =	SCBA or =	SCBA or =	SCBA or =, acid suit
Hazard ratings (health – flammability – reactivity)	HIMS 0-4-0, NFPA 0-4-0	HIMS 4-4-0, NFPA 4-4-0	NFPA 1-3-0	NFPA 4-3-3	HIMS 0-0-0, NFPA 0-0-0 (simple asphyxiant)	NFPA 4-3-0	HIMS 1-0-0, NFPA 1-0-0	NFPA 2-1-0	HIMS 1-1-0, NFPA 1-1-0	NFPA 3-0-2 (no water)
References										
MSDS SOURCES	Airgas	Airgas	Fisher Scientific	Matheson TriGas	Air Products, Airgas	Gaylord Chemical	Airgas, Arkema, Chevron Phillips	Arkema, Benntag, Chevron Phillips	Arkema, Chevron Phillips	Seastar
ARTICLES; BULLETINS; OTHER	Wikipedia			NJ Dept. of H&SS, Wikipedia, ChevronTexaco	Wikipedia					Wikipedia

Fire Prevention and Firefighting in Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_22

Abstract

Because refineries handle large quantities of highly combustible materials, fire and explosion are constant risks that must be managed. Refineries are designed to minimize the risks through proper specifications and fire prevention measures by design. Should a fire occur, however, a facility has extensive firefighting capabilities, including fixed and portable firefighting equipment, extinguishers, and an Incident Command System (ICS). These systems help in response to other incidents, such as releases and medical emergencies as well. This chapter addresses these issues, from design through operations.

Keywords

Refinery • Firefighting • Fire • Fireproofing • Extinguisher • Fire foam • Incident Command System • ICS • Prevention

Introduction

Fire prevention and protection are of paramount importance in the operation of any hydrocarbon facility. These are more important, perhaps, in oil refining than any other related facility because of the relative size of most refineries compared with petrochemical or chemical facilities. Refineries process and store huge quantities of combustible materials.

Refinery fire prevention and protection begin at the early stages of the refinery design and engineering. This chapter begins with the petroleum processing company's development of the design and engineering specifications. These instruct the design, equipment, and construction contractors in the details of the standards that are to be implemented in the building of the facility. These specifications are critical in ensuring the facility is well constructed in the first place, to minimize the risks of release, accompanied by fire or explosion.

The discussion begins with a list of the types of items usually contained in the design specifications and continues with more details of those items to illustrate how they pertain to fire prevention and firefighting. We will then discuss additional considerations in facility equipment, layout, operation, and management of the firefighting systems.

Refer also to the chapters on "▶ Safety Systems for Petroleum Processing" and "▶ Utilities in Petroleum Processing" for additional discussion of fire protection systems and emergency response.

Design Specifications

Companies each have their own flavor of design specifications in terms of format and details for the various types of equipment. Each company has preferences about how they want things done. The design specifications define all these items for the contractors.

Most design specifications will contain the following subject as a minimum.

Duty Specifications and Design Premises

These are of interest to the design process and mechanical engineers. These specifications state exactly what facilities are to be built and the duty of each item in terms of throughput and in some cases composition of the various streams. They will also give specific details of the local meteorological data and the parameters to be considered in economic decisions.

The duty specifications will include the products required and the composition of the products. They will also give full details of utilities required or available for the process. In cases of "grassroots" facilities, the duty specification will cover off-sites such as tankage, blending, loading, unloading facilities, etc.

Mechanical Specifications

These specifications define with the requirements and standards (including the codes to be used) the client wants for the equipment that will be installed. The resulting narrative specifications that the mechanical engineer will produce based on this will form part of the package to be used for procuring these items of equipment.

Included in the equipment defined by the mechanical specifications are:

- Pumps
- Compressors and turbines
- Heat exchangers (including air coolers, double pipe, etc.)
- Fired heaters
- Other miscellaneous equipment such as ejectors, blenders, and the like

Electrical and Instrument Specifications

These documents set the standards to be used for all electrical equipment and the bulk materials associated with the equipment. They will deal with the "Area Classification Codes." These set the parameters for equipment in terms of fire proofing (e.g., whether the item is to be spark proof) that will be located in the various areas of the refinery.

For instrumentation they specify the types of instruments to be used and the basic control and measuring systems to be used. The depth of the instrument standards and the resulting specifications can be extensive.

Piping and Layout Specifications

These are usually the largest section of the design specifications. They will detail the piping codes to be used and the material break points. They will proceed to establish the criteria for equipment and tankage layout, including:

- Maintenance access
- Fire prevention (e.g., distance of fired heaters from other equipment, fire mains, hydrant locations, monitor locations, etc.)
- Tank area layout and size of tank bunds
- Extent of fire protection piping for plant units and tank farm
- Underground piping corrosion protection

Other Design Specifications

These include detailed requirements for vessels, civil, and structural equipment and associated materials. They also include requirements for equipment spacing, especially as it relates to fires.

Fire Prevention Through Equipment Design and Operation

Fired Heaters

Design of fired heaters must incorporate snuffing steam facilities for the fire box for most styles of heater. Exceptions would normally be made for down-fired heaters.

With respect to the maintenance and operation of the heaters, the following points should be included in the operating procedures:

- Implementation of a formal, regularly scheduled preventive maintenance program for burners and the cleanup of any refractory debris to prevent flame impingement.

- Introduction of a mechanism to monitor and record, more accurately and thoroughly, tube skin temperature to prevent hot spots.
- Implementation of a thorough and complete procedure to deal with hot spots once detected and reported. This includes the recording of descriptions and locations of any suspected hot spot detected in a visual inspection.
- Introduction of an accurate method to determine the impact on tube life once a hot spot is detected.
- Training of the refinery personnel to recognize and respond to the changes in metallurgical properties and characteristics demonstrated by a different material in the furnaces that are subjected to high temperature and pressure, with documentation updated to reflect this information.

Pressure Vessels

These include towers, horizontal and vertical process vessels, reactors, etc. All of these must be protected properly with pressure-relieving devices (see the chapters/topics in this Handbook entitled "▶ Off-Site Facilities for Petroleum Processing" and "▶ Safety Systems for Petroleum Processing" for discussion of pressure relief facilities).

In the design of vessels, the correct wall thickness is based on the API and ASME codes, covering the design temperatures and pressures. Fireproofing of vertical vessel skirts and horizontal vessel supports must be specified. In the operation and maintenance of pressure vessels, the following items must be included as standard procedures:

- Vessel alarms must be recognized and acted upon.
- Action must be taken immediately when excessively high temperatures and/or high or low liquid levels are observed.
- In the case of a fire in the unit or an adjacent unit, the towers should be shut down according to the plant's emergency procedures.
- In the event of an emergency shutdown, a vessel may need to be purged free of hydrocarbons either by steam or inert gas. Be careful to avoid creating another problem during this procedure.
- No entry or work must be done on a vessel before it is certified as "gas free" and isolated.
- All vessels must be inspected before recommissioning after a shutdown. The inspection must ensure that all flanges are secure and the correct gaskets have been properly installed. Ensure all the internals are in place and correctly installed.
- Instruments and relief systems on the vessels must be checked and recalibrated as necessary on every scheduled or unscheduled shutdown of the plant. Safety instrumented or integrity systems (SISs) should be thoroughly tested and serviced to maintain their critical functions.
- Relief devices are usually serviced, tested, and reset during each turnaround.

- Vessels must be pressure tested before commissioning and after any work has been completed on them which could affect the vessel pressure containment (e.g., welding on the wall).
- All drains and vents on a vessel must be checked during scheduled plant turnaround or unscheduled shutdown before recommissioning the vessel to ensure they are open. And, they must all be blinded or plugged after the equipment is closed back up and placed in operation.

Heat Exchangers and Coolers

Shell and tube heat exchangers are designed and fabricated to ASME and TEMA codes. Their shell design follows closely to that of vessels with respect to design temperatures and pressures. The thickness of tubes and tube sheets are also calculated using the ASME code. In the case of air coolers, the tube sheets and tubes are also calculated to ASME codes as are the inlet and outlet manifolds. Air cooler tubes are usually finned to enhance the heat exchanger properties of the units.

The operation and maintenance of shell and tube exchangers parallel those conditions stated for vessels with respect to fire (or explosion) prevention. In the case of air coolers, however, some different rules and procedures apply. For example, most air coolers in a refinery are installed above an elevated pipe rack. The pipe rack often runs through the center of a process unit, which means there will be equipment on both sides of the rack. It is common for the pipe rack structure to be encased in a fireproof concrete (i.e., fireproofed) to prevent collapse of the rack in a pool fire. This fireproofing should extend upwards to cover the air cooler structures as well, since the fans will pull a flame up into themselves during a fire. Firewater and/or foam sprays should be considered above the tube bundles to snuff out any outbreak of tube leaks and subsequent fires.

Rotating Equipment

This group of equipment includes all pumps and compressors.

Near fired heaters, the compressor units, which may include gas-driven turbine or turbo expanders, are the items most vulnerable to fire hazards. The reason in this case is the high pressures of the gas they handle. This is more so in those units handling hydrogen (e.g., hydrotreaters, hydrocrackers, isomerization units, reformers, etc.).

All reciprocating compressors must have pressure relief facilities on the compressor discharge. Most also have an emergency shutdown system in the case of high discharge pressure, among other conditions.

Centrifugal compressors, and their drivers, require more sophisticated emergency shutdown procedures, however. Here, critical conditions can arise due to poor suction conditions, as well as high-pressure discharge. All centrifugal compressors therefore require protection against “surge” (or “pumping”) conditions.

As an example, this condition can occur when the compressor suction pressure is so low that the compressor cannot pull any of the feed gas into its impellers. Severe vibration of the unit follows. In extreme cases, the vibration can cause considerable structural damage to the compressor and even loss of containment resulting in an explosion and fire. Most modern centrifugal compressors have anti-surge systems, which, if properly maintained, will shut the compressor down long before any severe damage. These systems may be SISs.

Pumps, even those handling high-pressure liquefied petroleum gases, are a little less hazardous than compressors, but seal leaks remain a concern. Overheating due to defective seals or packing is the more common hazard that can cause a fire around a pump. Pump cavitation due to NPSH problems presents a second hazard that can cause a loss of containment.

In most present-day refineries, rotary equipment is installed in the open or in an area which has only a roof as a cover. This helps a great deal to fight any rotary equipment fire. Usually the area containing rotary equipment will have both firewater and foam facilities installed. Close monitoring of the rotary equipment during operation and regular maintenance of the items are essential for the prevention of fires from these sources.

Tanks and the Tank Farm

Tank fires are probably some of the worst types of fires in a refinery. This is because tanks hold a high inventory of hydrocarbons. The one thing that lowers the degree of hazard in the tank farm is that there is usually no direct source of ignition. There are no fired heaters or large compressors present in tank farms as a rule. Fires can occur, however, from accidents remote from the area such as a fire on a jetty or a ship nearby. There was a tank farm fire in New York during February 2003 that was caused by an explosion aboard a barge unloading gasoline at a nearby jetty. Large fuel oil tanks on shore were set ablaze by hot debris from the explosion. An explosion and fire in a process unit could have a similar impact if debris landed in the tank farm.

Another source of fire is an explosion in a product loading station while loading a light product such as gasoline. These explosions are usually caused by static electricity. Most petroleum companies have strict procedures in place to prevent such occurrences, but accidents do happen from time to time. Constant attention to their prevention is warranted.

Middle distillates and fuel oil tanks present the most difficult fires to fight and extinguish. The large inventory of these tanks and their low volatility, but high heating value, can present problems. It may take a long time to extinguish a fire in these services, even using the most up-to-date foam extinguishing techniques, once the fire has really established itself. In a large fire, the major effort is often directed at keeping adjacent tanks cool using an extensive water spray.

Fires on tanks storing lighter liquid products are a little easier to combat. Foam can be used to smother the oil inventory in these tanks. As these light products are stored in floating-roof tanks, it provides the means to build a depth of foam on the roof itself or directly on the surface of the liquid if the roof has been damaged by an earlier explosion.

Firewater sprays are installed on LPG spheres and bullets. In almost every case, the initial fire in LPG tankage causes an explosion. The material remaining can be snuffed out by foam. Again, the main focus of the firefighting effort is to activate firewater sprays on adjacent tanks to keep them cool.

Refineries today have firewater and foam spray rings on storage tanks (see the topic "▶ Off-Site Facilities for Petroleum Processing"). Water on its own should only be used to keep the tank cool from adjacent fire sources. The danger of using water alone to extinguish a fire is that it may cause the fire to spread by the hydrocarbon continuing to burn on the surface of the water stream flowing from the tank area.

In a fire, as noted above, it may be safest to let the fire burn itself out, with cooling of the nearby tanks to keep the fire from getting larger. In these cases, and if it can be done safely, as much of the contents of the burning tank(s) may be transferred to other tanks to minimize the amount burned. This is not always feasible.

The design of storage tanks and their installation must comply with the local fire regulations. In general, crude oil and petroleum products with a flash point of <130 °F (54 °C) may be stored in floating-roof tanks or, in the case of LPG, in pressurized bullets or spheres. Middle distillates and heavier are usually stored in cone roof tanks. Storage tanks, both floating roof and cone roof, are normally installed on sand or concrete pads (which will be piled if required). The space between tanks should not be less than 10 ft. (or according to local regulations). The tank area should be diked to hold at least 110 % of the largest single tank inventory. This diked or bunded area should contain adequate drainage leading to the API separator or holding pond, with the capability to block in the drain if necessary. LPG storage generally does not require a diked area; but both bullets and spheres should be installed with proper fireproofed support structures.

Jetty and Onshore Loading Stations

One of the biggest fire hazards in loading rail cars and ships is fire by spark caused by static electricity. The proper grounding, bonding, or earthing of the equipment being loaded is essential in preventing this fire hazard. There is also usually a specified wait time before the grounding connections are removed to allow static charges to dissipate.

These concerns apply to the unloading of hydrocarbons, such as crude oil feed or intermediate product streams transferred from other facilities or depots. In small refinery installations, the jetty facilities and the onshore loading islands are protected by an extension of the fire main and foam systems. In larger refineries, the jetty may have its own fire main using seawater as the main firewater medium.

Fire Main and Installed Firefighting Equipment

Fire Main Description and Control

Fire mains are usually designed as a pressurized circulating water system with an atmospheric break tank. A schematic sketch of such a system is given in Fig. 1. There may be more than one independent main in a given facility. The fire main is maintained at a pressure of around 100–150 psig (~7–10 barg) by a circulating pump or a smaller, parallel jockey pump. The pump is automatically switched on or off to maintain the fire main line pressure. When monitors, hydrants, and any other large firewater users need to deliver water to fire sources, to foam systems, or for any other application, the pressurizing pump will stay on and additional pumps normally automatically start to deliver the required firewater flow. The pumps are usually electric motor driven, with one or more spares that are usually driven by a diesel motor or a steam turbine. The spare pump(s) are automatically activated on electrical failure and the inability of the normal fire circulating pump to maintain line pressure.

The main and the main pumps are sized based on the area and types of facilities to be covered. Some companies size the pumps assuming "X" monitors and "Y" fire hoses are in use simultaneously. It is not unusual to be capable of supplying 8–15,000 gpm (1,800–3,400 MT/h) from the system.

Once a firewater pump is autostarted, it should remain running until it is intentionally shut down by the operators or firefighting crew when it is no longer needed. This means that main firewater pumps do not ever have shutdowns for high temperature bearings or low lube oil pressure. They are designed to run to destruction, if necessary. This is critical in an emergency. You do not want to ever lose firewater when you are in the middle of a fire, especially if you are on the hose!

Makeup water to the break tank is maintained under break tank level control from the refinery's fresh (or salt water) main or from an outside utility supply. Some plants have large quantities of firewater stored in basins, but the same guidelines apply. Once high firewater use begins, a large capacity makeup water supply will be needed.

The break tank is often really a very large storage tank, representing the available water supply if no makeup can be brought in. It is common to design the break tank to hold 6–8 h of firewater at full pump rates. This is especially important at remote locations, where additional water supply is limited.

In smaller refinery facilities and smaller systems, such as a jetty fire main, the system may be "dead ended." That is, the firewater pump would be used only to

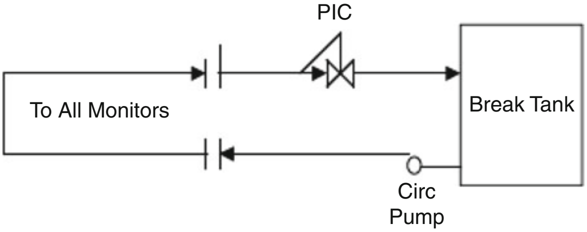


Fig. 1 Schematic fire main system

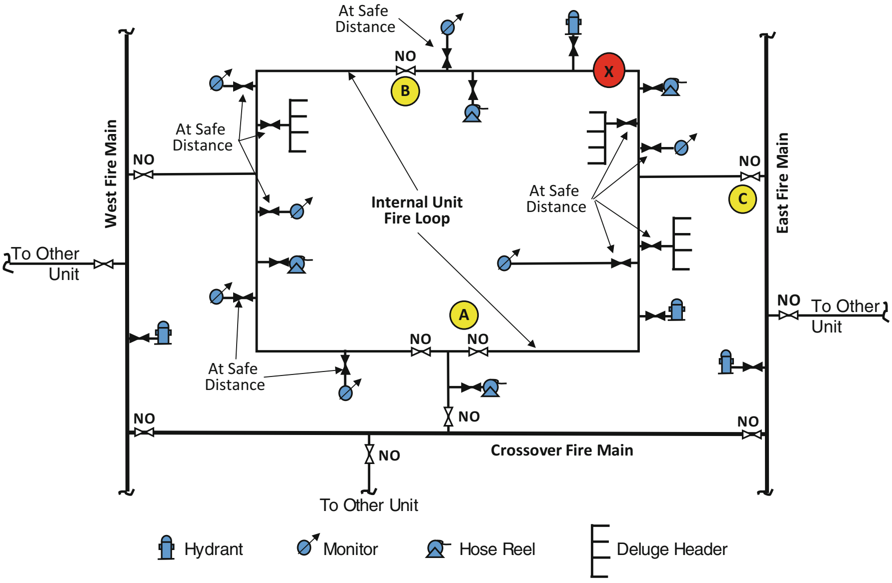


Fig. 2 Example fire loop arrangement

maintain the fire main pressure. The water would not be circulated to a break tank. A water source tank or basin would be used as the firewater source reservoir. In the case of the jetty fire main, usually seawater is used and this would be delivered from a suitable seabed pit by a vertical pump. Again an electric motor driver would be used for the normal pump with usually a steam turbine driver for the spare pump.

Firewater piping is frequently underground for freeze protection and to prevent blast or fire damage. Many of the system valves are also located underground and designed to automatically drain.

Firefighting Equipment and Layout

Generally, a firewater system is designed in loops with isolation valves for parts of the loop. The intent is to avoid any situation where damage to one part of the loop takes down the whole supply. The concept is illustrated in Fig. 2. As illustrated, the unit can pull firewater from either the east or west main or the crossover main. Within the unit, the supply lines go to different parts of a single loop. There are block valves that split the internal loop. These are normally left open. If the east internal loop is damaged at the point indicated by the X in the red circle, for instance, Blocks A, B, and C can be closed to isolate the damaged line and still get water from the west part of the internal loop. A great deal of thought must go into how the mains and submains are connected and routed to ensure water supply when needed.

Aside from the mains and supply loops, there are several types of firefighting equipment normally connected to the firewater system. The most common devices are as follows:

- *Hydrants* provide locations to connect hoses for direct use on a fire or for pumper truck suction. They are usually located at defined intervals along the mains and in the loops. Some hydrants can deliver over 1,500 gpm (~5,700 l/min). Normal capacities are 500–1,000 gpm (1,800–3,800 l/min), however.
- *Monitors* are used to provide continuous water streams on equipment. There are both permanent and portable types of monitors. They can be used directly on the fire or can be used to cool neighboring equipment and prevent a larger problem. They can be set and then left to do their job, thereby reducing exposure of personnel to the fire. A monitor can be selected to deliver a stream, cone, or fog on the fire – many can perform multiple functions. They can also be setup to be activated and controlled remotely and can be elevated on poles to better reach equipment. The block valves for monitors are normally underground to prevent blast and freeze damage. A monitor can typically deliver about 350 gpm (1,300 l/min). Their reach is usually limited to about 150 f. (~50 m) and as high as the system pressure allows. The locations of monitors need to consider the equipment to be protected as well as all the interferences around that equipment. Monitor block valves are normally located a safe distance, like 50–100 f. (~15–30 m.), from the equipment the monitor protects.
- *Hose reels and hose stations* normally have about 50–100 f. (~18–36 m) of hose with a variable nozzle on the end. The hose (AKA booster hose), normally about 1–1½ in. (2.5–4 cm) diameter, is spooled on a hose reel. The capacity of these hoses is limited to what one person can manage – usually less than 100 gpm (~380 l/min). These hoses are sometimes also used for area washdown; hence, they have to be within the ability of one person to handle. They are useful primarily just for small fires.
- *Deluge systems* may be positioned around specific equipment to provide fire or other protection in an emergency. You may find them around hot pump seal areas or around large air coolers containing hydrogen or around HF acid handling facilities as water curtains to control an acid release. These systems vary in size considerably. Many are automatically activated in an emergency. Like monitors, the block valves for deluge systems are located a safe distance from the equipment being protected.
- *Foam generators* are devices that aspirate foam chemicals at a rate of 3–6 % into a flowing water stream along with air to create a foam. Often these are permanently installed on foam lines from the fire mains. They may or may not have a foam chemical supply connected to them permanently. Often the foam is brought in for use when needed because it has a limited shelf life. Installed

foam generators are often found in the tankage or offsite area. Capacity and number of foam generators are a function of the size of equipment being protected. Hand foam generators can deliver 60–120 gpm (~220–440 l/min, on a hose reel) and monitors can push 600–2,000 gpm (~2,200–7,600 l/min) of water. The water is mixed in the nozzle with chemical to make 3 % or 6 % foam. The actual foam volume is much higher (50:1 to 200:1 expansion).

The locations of the fixed fire equipment and the portable equipment, like exchangers, are coordinated to provide the best possible coverage for a facility. The layout and protection systems are normally worked out with a fire protection engineer.

Inspection and Maintenance Program

Firewater systems require routine inspection and maintenance. Aside from inspection for corrosion, the systems are normally tested on a regular interval for operation (about quarterly). The hydrants are opened and flushed. Hose is unspooled, inspected, flushed, and respooled. Monitors may be activated and the nozzles exercised. Any problems that are noted are repaired.

Foam generators are usually just inspected and may be cleaned. You don't usually generate foam with them on any routine basis.

The deluge and water curtain systems may be part of the safety instrumented systems (SISs) and so may be included in a required testing program. Activation of the systems for functional testing may be carried out on some defined schedule when it won't hurt the operation. Repairs are made as indicated by the tests. Hot pump deluges are usually only tested when the pump is cold to avoid creating a problem from thermal stresses.

With the other activities, the firewater pumps will be cycled on and off. Firewater standby pumps are normally run at least monthly for a few hours. The pressure switches that control the autostart sequences are checked in the process.

These types of inspection and maintenance activities in the firewater systems are critical to ensure the systems are available and will perform their functions when needed.

Fire Foam and Foam Systems

Introduction

Firefighting foam is simply a stable mass of small, air-filled bubbles with a lower density than oil, gasoline, or water. The foam is made up of three ingredients:

- Water
- Foam concentrate
- Air

The water is mixed with the concentrate (proportioned) to form a foam solution. This solution is then mixed with air (aspirated) to produce the foam which is very fluid and flows readily over liquid surfaces.

Balanced pressure proportioning is the most common method used for foam system applications. The foam concentrate pressure is balanced with the water pressure at the proportioner inlets allowing the proper amount of foam concentrate to be metered into the water stream. With an aspirating discharge device, foam solution passes through an orifice, past air inlets, and into an expansion area to produce an expanded foam. With non-aspirating devices, foam solution passes through the orifice and discharge outlet where it mixes with air en route to the fire.

Potential Firefighting Foam Applications

Firefighting foam is used in a variety of applications to (1) extinguish flammable and combustible liquid fires, (2) control the release of flammable vapors, and (3) cool fuels and sources of ignition. Typical foam applications include:

- Loading racks
- Refineries
- Pumping stations
- Power plants
- Airports
- Heliports
- Marine applications
- Manufacturing plants
- Storage tanks
- Chemical plants
- Flammable liquid storage
- Offshore platforms
- Aircraft hangars
- Crash rescue vehicles
- Mining facilities
- Warehouses
- Hazardous material spill control.

Firefighting foam agents suppress fire by separating the fuel from the air (oxygen). Depending upon the type of foam agent, this is done in several ways:

- Foam blankets the fuel surface, smothering the fire and separating the flames from the fuel surface.
- The fuel is cooled by the water content of the foam.
- The foam blanket suppresses the release of flammable vapors that can mix with air.

Types of Firefighting Foam

A film-forming foam (AFFF) agent forms an aqueous film on the surface of a hydrocarbon fuel. An alcohol-resistant concentrate (ARC) will form a polymeric membrane on a polar solvent fuel. Essentially there are six general types of foam agents in two classes:

Class B fire foams

Film-forming foams

Film-forming foams (AFFF) are based on combinations of fluorochemical surfactants, hydrocarbon surfactants, and solvents. These agents require a very low energy input to produce a high-quality foam. Consequently, they can be applied through a wide variety of foam delivery systems. This versatility makes AFFF an obvious choice for airports, refineries, manufacturing plants, municipal fire departments, and any other operation involving the transportation, processing, or handling of flammable liquids. These foam-forming agents are used as 1 % and 3 % freeze-protected concentrates.

Alcohol-resistant concentrates

Alcohol-resistant concentrates are based on AFFF chemistry to which a polymer has been added. ARCs are the most versatile of the foam agents in that they are effective on fires involving polar solvents like methanol as well as hydrocarbon fuels like gasoline. When used on a polar solvent-type fuel, the ARC concentrate forms a polymeric membrane which prevents destruction of the foam blanket. When used on hydrocarbon fuels, the ARC produces the same rugged aqueous film as a standard AFFF agent. ARCs provide fast flame knockdown and good burn back resistance when used on both types of fuels.

Protein foam concentrates

Protein foam concentrates are recommended for the extinguishment of fires involving hydrocarbons. They are based on hydrolyzed protein, stabilizers, and preservatives. Protein foams produce a stable mechanical foam with good expansion properties and excellent burn back resistance characteristics. Protein foam concentrates are used in 3 % and 6 % concentrations.

Fluoroprotein foam concentrates

Fluoroprotein foam concentrates are based on hydrolyzed protein, stabilizers, preservatives, and synthetic fluorocarbon surfactants. When compared to protein foams, fluoroproteins provide better control and extinguishment, greater fluidity, and superior resistance to fuel contamination. Fluoroprotein foams are useful for hydrocarbon vapor suppression and have been recognized as very effective fire-suppressing agents for subsurface injection into hydrocarbon fuel storage tanks. Fluoroprotein foam is used as in a 3 % solution.

High-expansion foam concentrates

High-expansion foam concentrates are based on combination of hydrocarbon surfactants and solvents. They are used with foam generators for applying foam to large areas in total flooding and three-dimensional applications such as warehouses, ship cargo holds, and mine shafts. They are especially useful on fuels such as liquefied natural gas (cryogenic fuels) for vapor dispersion and control. In certain concentrations, high-expansion foams are effective on hydrocarbon spill fires of most types and in confined areas.

Class A fire foams

Class A foams are typically formulated from a combination of specialty hydrocarbon surfactants, stabilizers, inhibitors, and solvents. They reduce the surface tension of water for improved wetting and penetrating characteristics and create a clinging foam blanket that suppresses combustible vapors while cooling the fuel. Class A foams can be applied using a variety of proportioning/discharge devices and have proven to be highly effective for use in structural and forest firefighting, coal mines, tire, and rubber manufacturing, lumber mills, coal bunkers, paper warehouses, and other hazards involving ordinary combustible materials. Please note that Class B foams are acceptable for use on Class A fires; however, they are not designed for use on Class A fires as such. The foam concentrate percentage refers to the amount of concentrate that is proportioned or premixed with water to give the resulting foam solutions.

Environmental Impact and Toxicity

Most foam concentrates are formulated to maximize performance and minimize environmental impact and human exposure hazards. All concentrates are readily biodegradable – both in the natural environment and in sewage treatment facilities. However, all foam agents should be metered into the facility to prevent overloading the plant due to foam formation. They are not considered skin irritants; however, prolonged contact may cause some dryness of the skin. For this reason, it is normally recommended that areas of the skin which have come in contact with the foam concentrate be flushed with fresh water.

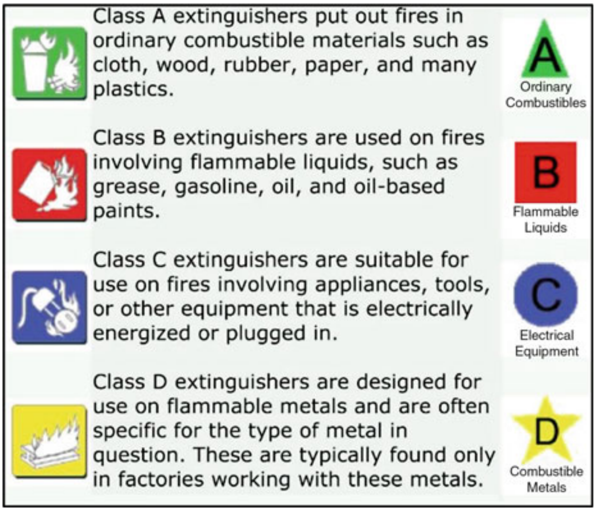
Shelf Lives of Foam Concentrates

"Shelf life" is the length of time over which foam concentrates remain stable without significant changes in performance characteristics. Many AFFF, high-expansion and Class A foam concentrates – if stored in accordance with recommended guidelines – have a normal shelf life of 20–25 years. Other foam agents – those which are not totally synthetic – have a normal shelf life of 7–10 years.

Fire Extinguishers

While the larger fires make use of the firewater system and related equipment, smaller fires are often kept from becoming larger fires through prompt action using fire extinguishers. A fire extinguisher can make short work of many seal, trash, and other relatively small fires to prevent a larger problem.

Table 1 Classes of fire extinguishers (source: Farm Bureau Insurance Company of Michigan)



Class A extinguishers put out fires in ordinary combustible materials such as cloth, wood, rubber, paper, and many plastics.	A Ordinary Combustibles
Class B extinguishers are used on fires involving flammable liquids, such as grease, gasoline, oil, and oil-based paints.	B Flammable Liquids
Class C extinguishers are suitable for use on fires involving appliances, tools, or other equipment that is electrically energized or plugged in.	C Electrical Equipment
Class D extinguishers are designed for use on flammable metals and are often specific for the type of metal in question. These are typically found only in factories working with these metals.	D Combustible Metals

Types and Applications of Fire Extinguishers

Table 1 lists the primary classes of fire extinguishers that are recognized.

The types of fire extinguishing agents for the different types of fires are listed in Table 2.

If you correlate the charts together, in general:

- Water and water-based agents are Class A.
- Class B would include foam, dry powder, and CO_2.
- Class C would include dry powder and CO_2.
- Class D agents are usually solids, like sand.

Within a refinery or petroleum processing facility, you will normally only find Classes ABC, BC, or C extinguishers. Class D is rare. You may see Class A extinguishers inside buildings. You will see Class C inside electrical switchgear buildings.

In special cases, you will also find fire suppression agents like Halon (or one of the newer substitutes) inside buildings. Halon is essentially an ABC agent and acts by eliminating air from an enclosed space – which means no personnel can be in the enclosed space when a Halon system is activated. It is not poisonous but is designed to create an oxygen-deficient atmosphere. There is normally a time delay with visual and audible warnings between the system being triggered and actuation of the Halon to give personnel time to evacuate. While Halon is a severe ozone-depleting gas, it does not damage electronics or electrical equipment. Substitutes have been developed that are less damaging to ozone and still effective. Halon also is available in a handheld extinguisher rather than a room system.

Table 2 Types of fire extinguishing agents (Texas A&M University (2012))

Extinguisher type	Type of fire Solids (wood, paper, cloth, etc.)	Flammable liquids	Flammable gases	Electrical equipment	Cooking oils and fats
Water	Yes	No	No	No	No
Foam	Yes	Yes	No	No	Yes
Dry powder	Yes	Yes	Yes	Yes	No
Carbon dioxide (CO_2)	No	Yes	No	Yes	Yes

The extinguisher size required for a particular type of hazard is specified in the United States by the National Fire Protection Association (NFPA, 2002) based on the type of hazard and distance of the exchanger from the fire.

Locations of Fire Extinguishers

Fire extinguishers are normally distributed throughout a petroleum processing facility to allow fast attack on small fires. The extinguishers are located about 50–75 ft. (15–25 m) apart, normally on pipe rack columns. They are also often located near places where they may be used, such as near hot pumps, but still far enough away to enable access in an emergency.

Extinguishers must be easy to remove from whatever bracket they are attached to – usually just a hook. The extinguisher locations should be clearly marked, usually in red. The extinguisher types within an area are appropriate to the fire risks in that area, with the normal types of extinguishers being BC and ABC dry chemicals.

Inside a control room or operator shelter, there will normally be dry chemical extinguishers and CO_2. In some cases Halon may be provided.

In power distribution centers, you do not find powder chemical agent, but may find CO_2 and Halon (or equivalent) systems or extinguishers.

Fire extinguishers in the field are exposed to the elements and may deteriorate. Extinguishers in the field should be covered for protection. The covers must be easy to remove when needed and should be replaced when they deteriorate.

Some facilities have large, cart-mounted extinguishers. These should be easy to move and should not be blocked by other materials, debris, or trash.

Fire Extinguisher Inspection and Testing Program

The availability of fire extinguishers brings with it the need to make sure the extinguishers will work when required. From the US NFPA standards, there are four inspection intervals required:

Monthly inspection

This inspection includes:

- Correctly installed at the designated location
- No obstructions to access
- Legible operating instructions on nameplate
- Safety seals and tamper indicators not broken or missing
- Fullness checked by weighing or lifting
- Examination for obvious damage, leakage, or clogged nozzle
- Pressure gauge reads in “good” range
- Condition of wheel cart and wheels good (wheeled units)
- HMIS label in place

Most facilities log the inspection. There is supposed to be a tag on each extinguisher noting the date of the last inspection and who did the inspection.

The field extinguisher covers should be replaced when they are damaged or no longer protect the extinguisher adequately.

Annual inspection

A more thorough annual inspection of extinguishers is required. This inspection includes:

- Complete servicing of the extinguisher
- Recharging
- Must be done by trained personnel

Six-year maintenance

This is required for “stored-pressure” extinguishers, like dry chemicals or halogens (e.g., Halon). The extinguisher is emptied and thoroughly examined. The extinguisher must be hydrotested every 12 years, so every other 6-year inspection must include a hydrotest.

Hydrostatic testing

There is a specific hydrotesting interval defined for types of exchangers:

- Every 5 years for stored-pressure water, water mist, loaded stream, antifreeze, wetting agent, foam, dry chemicals with stainless shells, carbon dioxide, and wet chemicals
- Every 12 years for dry chemicals with stored pressure, halogenated agents, and dry powder with cartridge pressurization

There are hydrotest record requirements also.

A facility needs to define a program to ensure all the extinguisher inspection and testing requirements are satisfied. Often, the operators are asked to inspect extinguishers weekly in addition to the required inspections as a means of identifying problems early.

Concluding Comments

A couple of final words on extinguishers:

- Any time an extinguisher gets used, immediately replace it with an unused extinguisher and get the used one serviced completely. You do not want any of your personnel to try to use an extinguisher, only to find that it is not operable.
- It should be a standard practice that whoever finds a fire must call in the emergency first before they decide to try to use an extinguisher. They will need backup.
- Only personnel trained in the use of an extinguisher should try using it. Improper use can make the situation worse. We will not go into detail on actual extinguisher use here. Many companies, and your own safety or firefighting organization, should be able to provide adequate training. There is also no substitute for actual, hands-on training.

Mobile Firefighting Equipment

In addition to the fixed equipment and extinguishers, there is also usually an array of portable firefighting equipment in a petroleum facility. We will not go into detail on this equipment, but this critical equipment can include:

- Fire pumper trucks
- Fast attack fire trucks – with tanks and monitors or hoses, possibly foam
- Portable monitors – can be hooked to hoses and set to cool equipment
- Foam pumpers
- Emergency medical technical support truck
- Large monitor trucks – some throw 12–15,000 gpm (~45,000–57,000 l/min)

Some of this may be owned by the facility. Some may be from the local fire department. Some may come through mutual aid agreements with nearby facilities.

A facility far-removed from other plants will tend to be more self-sufficient in mobile firefighting equipment and may have more complete integration with the local community firefighting capability.

Fire Protection and Firefighting Plans

We have focused so far on the equipment used for refinery and petroleum processing firefighting. The use of the various parts of the facility fire protection systems is only marginally effective unless there are specific fire protection and firefighting plans in place to manage fire emergencies when they arise.

The emergency management system for most facilities covers other emergencies, in addition to fire. This enables consistent and trained response to all types of emergencies. Here we will describe the standard emergency management system employed commonly in the United States. There may be some local flavors of this, but the basics apply.

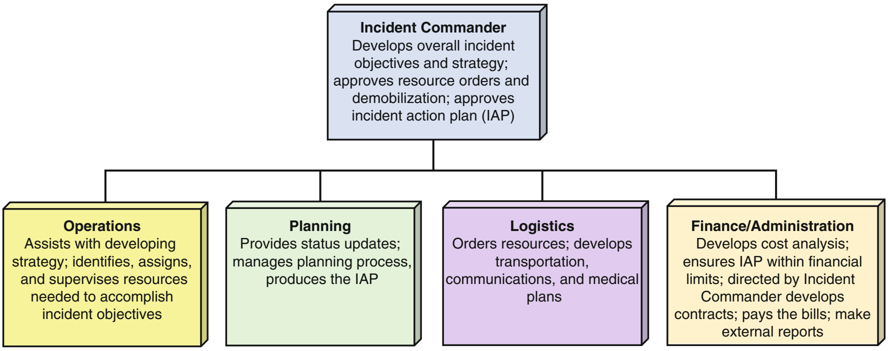


Fig. 3 Simplified incident command system

Incident Command System (ICS)

The most common incident command system (ICS) in petroleum processing facilities looks something like that illustrated in Fig. 3. The ICS is a standardized organization and responsibilities that represents best practices. It is a key feature of the US National Incident Management System (NIMS). This system can be used for fires, releases, medical emergencies, or any other type of situation where fast response is required.

In this system, one person is designated as the incident commander (IC). This is normally a specific person, on-site initially, who has the knowledge, has the training, and is given the authority to develop an attack plan and successfully manage the incident response. If a public emergency response organization (like the city fire department or the Federal government) becomes involved, usually they will assume incident command once they are on-site.

Supporting the IC are organizations to provide:

- Operations support – help decide what to do and execute the plan
- Planning section – manages the planning
- Logistics section – gets the resources needed to execute the plan
- Finance/administration section – tracks costs, keeps plan within financial limits, pays the bills, makes external reports

This system works well with fire and explosion responses, in addition to other emergencies.

Notification Systems and Procedures

One thing we have not mentioned so far is notification of plant personnel when a fire or other emergency has occurred.

All facilities have an emergency notification system (ENS) in the event of a fire, release, or other situation that could place people in danger. The ENS normally is activated by someone activating an alarm or by calling an emergency number that is staffed 100 % of the time.

The nature of the emergency and location is reported. Additional information is provided (usually logged) and then the person receiving the call initiates the alarm, which initiates the incident command system. In medical cases, the general alarm may not be sounded, but the ICS would be activated. In some cases, an alarm will be local to one unit, with an appropriate, less extensive, response. For those with radios and in units with public address systems, the nature of the emergency may be announced in more detail.

Plant alarms are usually audible and may also include visual alarms. The audible alarms may differ for different types of emergencies. Usually there are at least three types of audible notifications, with each having a different sound:

- Fire alarm (for fires, explosions, or other situations that are not otherwise covered)
- Evacuation alarm (for releases primarily)
- All clear

All personnel on site, including contractors and visitors, are trained in how to respond if they hear the alarm. Nonessential personnel, visitors, and contractors are normally cleared off the site or out of the units – avoiding the emergency area. In some cases, however, it may be necessary to “shelter in place” (i.e., go to a building with a specifically designed air handling system to enable isolation). All active permits for maintenance activities are normally canceled by the alarm.

The appropriate first responders will go to the emergency location with the incident commander to assess the problem and begin an attack. Meanwhile, at a safe location, the rest of the ICS assembles to begin their support work.

When the emergency is under control or the condition is eliminated, the “all clear” is called and the all clear notification is sounded.

Periodic practice drills help ensure emergency response runs smoothly so that energy can be focused on the incident.

Conclusion

A well-prepared petroleum processing facility will have:

- Adequately designed, constructed, operated, and maintained equipment
- Well-designed and maintained firefighting system
- Adequate and maintained fire extinguishers
- Appropriate mobile firefighting equipment
- Appropriate and functional alarm system
- Emergency response plan staffed by trained personnel

With these elements in place, a facility should (1) be able to avoid having a fire or explosion and (2) be able to deal with a fire, explosion, or any other emergency if it does occur.

References

National Fire Protection Association, *Guidelines: Fire Extinguishers*, NFPA 10, 2002 edition, IFC 2008. Quincy, MA, USA, (2002)

Texas A&M University, *Fire Extinguishers: Are You Prepared?* (Texas A&M Engineering Extension, Bryan, TX, USA, 2012)

Part V

Reference

Process Equipment for Petroleum Processing

David S. J. Jones and Steven A. Treese

Contents

David S. J. Jones: deceased.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_23

Abstract

This chapter deals with the equipment normally found in the petroleum refining industry. Many of the items that will be described and discussed here are also common to other process industries. Knowledge of these equipment items is essential for good refinery design, operation, and troubleshooting when necessary. The equipment and process design calculations described here include vessels, fractionators, pumps, compressors, heat exchangers, fired heaters, and piping and packed bed pressure drops. Several examples of these calculations are provided.

Keywords
Process equipment • Refinery • Petroleum • Vessel • Tower • Pump • Compressor • Exchanger • Heater piping • Design • Fractionation

Introduction

This chapter deals with the equipment normally found in the petroleum refining industry. Indeed, many of the items that will be described and discussed here are also common to many other process industries. Knowledge of these equipment items is essential for good refinery design, operation, and troubleshooting when necessary. The equipment and design methods described here fall into six categories and will be presented in the following main sections:

- Vessels (columns, towers, fractionators, drums, separators, accumulators, and surge vessels)
- Pumps (variable head-capacity, positive displacement)
- Compressors (centrifugal, axial, reciprocating, rotary)
- Heat exchangers (shell and tube, double-pipe, air coolers, box coolers, direct-contact exchangers)
- Fired heaters (horizontal, vertical)
- Pressure drop calculations (piping, solid beds, single- and two-phase flows)

These sections will include a description of the various equipment types, an in-depth discussion, and review of design features. They will also provide examples of the data sheets usually forwarded to manufacturers for the items required. These data sheets are included as part of the “Mechanical Catalogues” or “Record Data Books” for each unit and supported by narrative specifications, which give details of metallurgy and fabrication codes. These documents are provided by the equipment supplier and are part of the information dossier on each item. Included also are such items as installation details, start-up procedures, routine maintenance procedures, and the like. In most refineries today, the catalogues are maintained on the computer or microfilm. There are also paper copies of the data books maintained.

Vessels and Towers

This section addresses the pressure vessels that are common to most refineries. These include:

- Columns and towers
- Knockout drums and separators
- Accumulators and surge vessels

Storage tanks have been dealt with in the chapter on "off-sites" in this handbook.

Fractionators, Trays, and Packings

Trayed Towers

Columns normally constitute the major cost in any chemical process configuration. Consequently it is necessary to exercise utmost care in handling this item of equipment. This extends to the actual design of the vessel or evaluating a design offered by others. Normally columns are used in a process for fractionation, extraction, or absorption as unit operations. Columns contain internals which may be trays, or packing. Both types of columns will also contain suitable inlet dispersion nozzles, outlet nozzles, instrument nozzles, and access facilities (such as manways or handholes). This item deals primarily with the trayed towers.

Tray Types

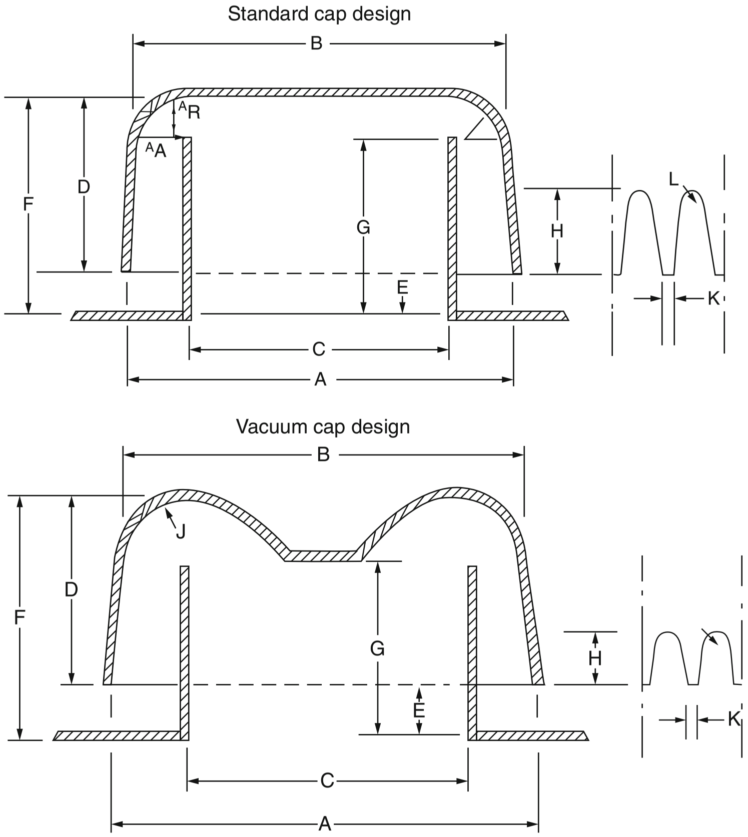
There are three types of trays in common use today:

- Bubble cap
- Sieve
- Valve

Bubble Cap Trays

This type of tray was in wide use up until the mid to late 1950s. Its predominance was displaced by the cheaper sieve and valve trays. The bubble cap tray consists of a series of risers on the tray which are capped by a serrated metal dome. Figure 1 shows two types of caps. One is used in normal fractionation service while the other is designed for vacuum distillation service. Vapor rises up through the risers into the bubble cap. It is then forced down through the serrated edge or, in some cases, slots at the bottom of the cap. A liquid level is maintained on the tray to be above the slots or serrations of the cap. The vapor therefore is forced out in fine bubbles into this liquid phase thereby mixing with the liquid. Mass and heat transfer between vapor and liquid is enhanced by this mixing action to effect the fractionation mechanism.

Capacity. Moderately high with high efficiency.
Efficiency. Very efficient over a wide capacity range.
Entrainment. Much higher than perforated-type trays due to the "jet" action that accompanies the bubbling.
Flexibility. Has the highest flexibility both for vapor and liquid rates. Liquid heads are maintained by weirs.



Dimension	6"	6" raised	4"	6" vacuum
A	6"	6"	4"	6"
B	5¾"	5¾"	3¾"	5¾"
C	4"	4"	2½"	4"
D	2¾"	2¾"	2⅛"	2¾"
E	⅝"	¾"	½"	¾"
F	3⅜"	3½"	2⅝"	3½"
G	2¾"	2½"	2¼"	2½"
H	1⅜"	1⅜"	1"	¾"
J	⅝"	⅝"	⅜"	1"
K	5⁄32"	5⁄32"	5⁄32"	5⁄32"
L	5⁄32"	5⁄32"	⅛"	5⁄32"
Number of slots	28	28	20	28
Total slot area/cap (ft^2)	0.105	0.105	0.047	0.056
Peripheral area under cap (ft^2)	0.082	0.098	0.044	0.098
Total effective slot area (ft^2)	0.187	0.203	0.091	0.154
Chimney area (ft^2)	0.087	0.087	0.034	0.087

Fig. 1 Bubble cap design

Application. May be used for all services except for those conditions where coking or polymer formation occurs. In this case baffle or disc and donut or grid-type trays should be used.

Note: Because of the relatively high liquid level required by this type of tray, it incurs a higher pressure drop than most other types of trays. This is a critical factor in tray selection for vacuum units.

Tray spacing. Usually 18–24″. For vacuum service, this should be about 30–36″.

Sieve Trays

This is the simplest of the various types of trays. It consists of holes suitably arranged and punched out of a metal plate. The vapor from the tray below rises through the holes to mix with the liquid flowing across the tray. Fairly uniform mixing of the liquid and vapor occurs and allows for the heat/mass transfer of the fractionation mechanism to occur. The liquid flows across a weir at one end of the tray through a downcomer to the tray below.

Capacity. As high as or higher than bubble cap trays at design vapor/liquid rates. Performance drops off rapidly at rates below 60 % of design.

Efficiency. High efficiency at design rates to about 120 % of design. The efficiency falls off rapidly at around 50–60 % of design rate. This is due to "weeping" which is the liquid leaking from the tray through the sieve holes.

Entrainment. Only about one-third of that for bubble cap trays.

Flexibility. Not suitable for trays operating at variable loads.

Application. In most mass transfer operations where high capacities in vapor and liquid rates are required. Handles suspended solids and other fouling media well.

Tray spacing. Requires less tray spacing than bubble cap. Usually spacing is rarely less than 15″ although some services can operate at 10″ and 12″. In vacuum service, a spacing of 20–30″ is acceptable.

Valve Trays

These trays have downcomers to handle the liquid traffic and holes with floating caps that handle the vapor traffic. The holes may be round or rectangular and the caps over the holes are moveable within the limits of the length of the "legs" which fit into the holes. Figures 2 and 3 show the type of valves and valve trays offered by Glitsch as their "Ballast" trays.

Valve trays are by far the most common type of tray used in the chemical industry today. The tray has good efficiency and a much better flexibility in terms of turndown than the sieve or bubble cap trays. Its only disadvantage over the sieve tray is that it is slightly more expensive and cannot handle excessive fouling as well as the sieve tray. The remainder of this item will now be dedicated to the sizing and analysis of the valve tray tower.

Trayed Tower Sizing

The height of a trayed tower is determined by the number of trays it contains, the liquid surge level at the bottom of the tower, and the tray spacing. The number of trays is a function of the thermodynamic mechanism for the fractionation or absorption duty required to be performed. This is described in the chapters on atmospheric and vacuum distillation and light ends fractionation of this handbook.

The diameter of the tower is based on allowable vapor and liquid flow in the tower and the type of tray. The next section deals with determining the tower diameter using valve trays.

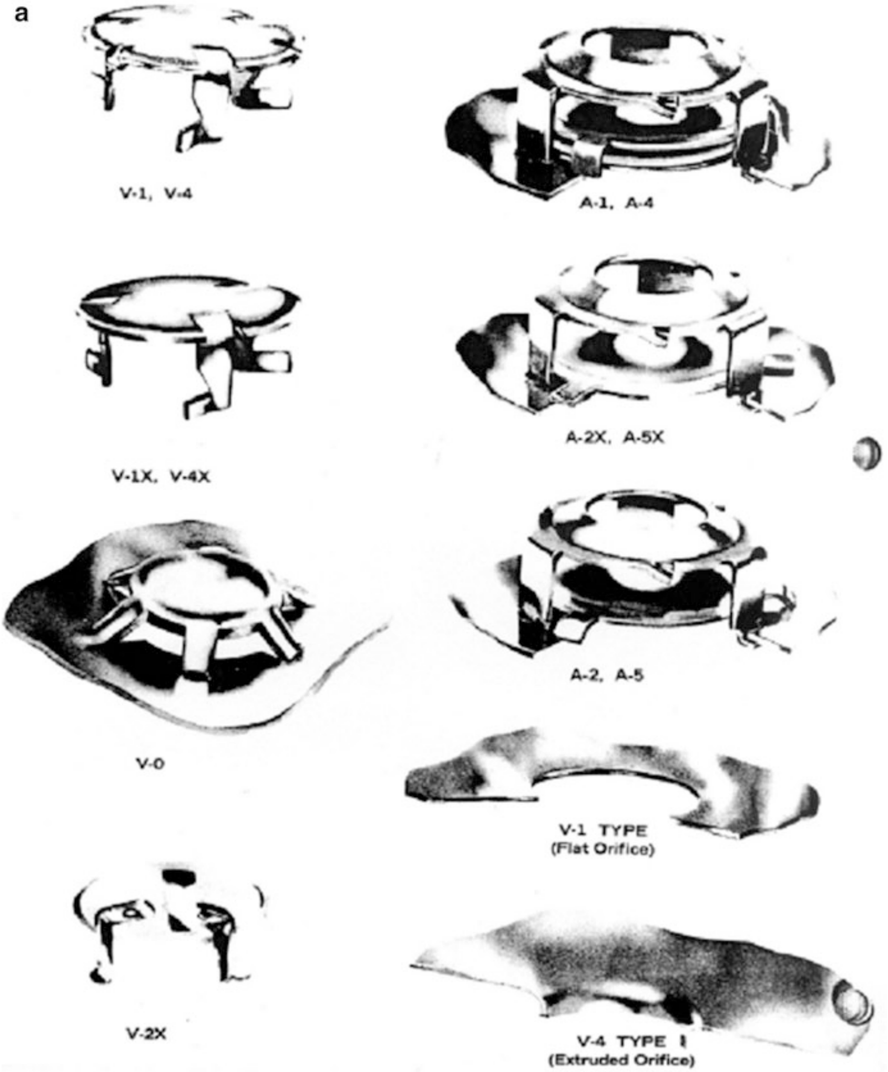
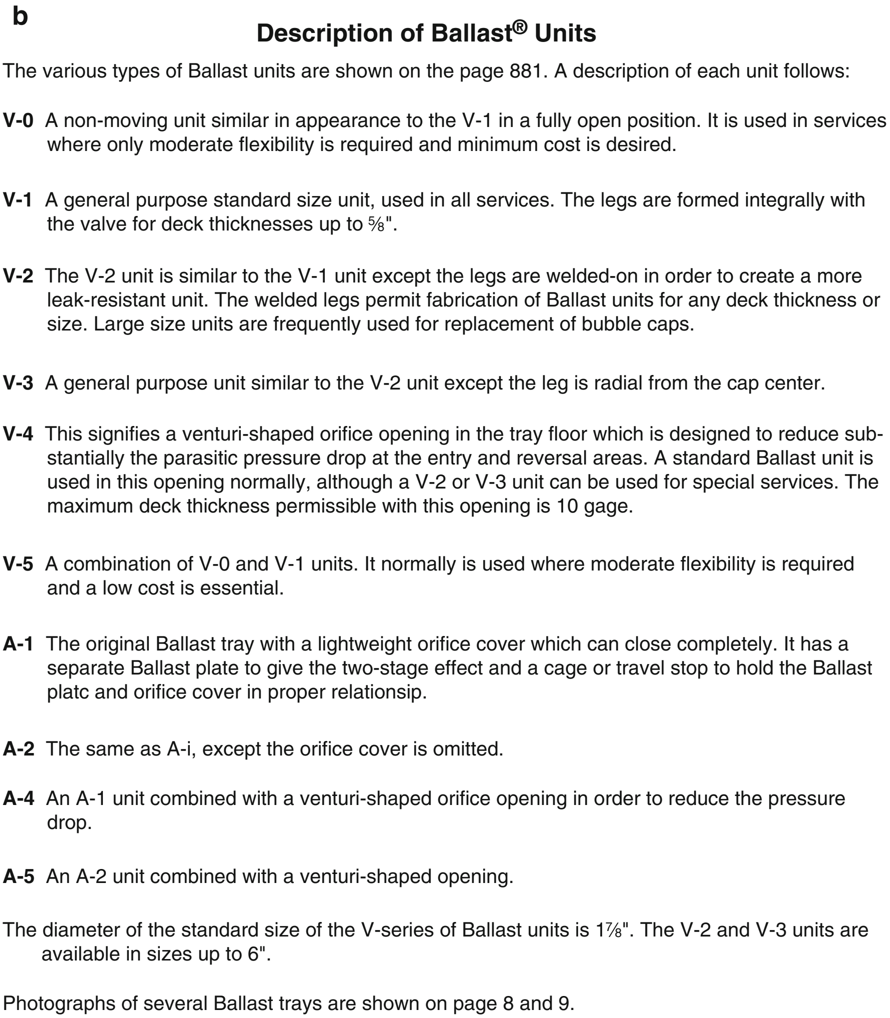


Fig. 2 (continued)



b

Description of Ballast® Units

The various types of Ballast units are shown on the page 881. A description of each unit follows:

V-0 A non-moving unit similar in appearance to the V-1 in a fully open position. It is used in services where only moderate flexibility is required and minimum cost is desired.

V-1 A general purpose standard size unit, used in all services. The legs are formed integrally with the valve for deck thicknesses up to ⅝".

V-2 The V-2 unit is similar to the V-1 unit except the legs are welded-on in order to create a more leak-resistant unit. The welded legs permit fabrication of Ballast units for any deck thickness or size. Large size units are frequently used for replacement of bubble caps.

V-3 A general purpose unit similar to the V-2 unit except the leg is radial from the cap center.

V-4 This signifies a venturi-shaped orifice opening in the tray floor which is designed to reduce substantially the parasitic pressure drop at the entry and reversal areas. A standard Ballast unit is used in this opening normally, although a V-2 or V-3 unit can be used for special services. The maximum deck thickness permissible with this opening is 10 gage.

V-5 A combination of V-0 and V-1 units. It normally is used where moderate flexibility is required and a low cost is essential.

A-1 The original Ballast tray with a lightweight orifice cover which can close completely. It has a separate Ballast plate to give the two-stage effect and a cage or travel stop to hold the Ballast platc and orifice cover in proper relationsip.

A-2 The same as A-i, except the orifice cover is omitted.

A-4 An A-1 unit combined with a venturi-shaped orifice opening in order to reduce the pressure drop.

A-5 An A-2 unit combined with a venturi-shaped opening.

The diameter of the standard size of the V-series of Ballast units is 1⅞". The V-2 and V-3 units are available in sizes up to 6".

Photographs of several Ballast trays are shown on page 8 and 9.

Fig. 2 (**a**, **b**) Valve unit types – Glitsch Ballast

The “Quickie” Method

This method is good enough for a reasonable estimate of a tower diameter which can be used for a budget-type cost estimate or initial plant layout studies. The steps used for this calculation are as follows:

Step 1. Establish the liquid and vapor flows for the critical trays in the section of the tower that will give the maximum values. These are obtained by heat balances (see the chapters on “▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries” and “▶ Distillation of the “Light Ends” from Crude Oil in Petroleum Processing” of this handbook). The critical trays are:

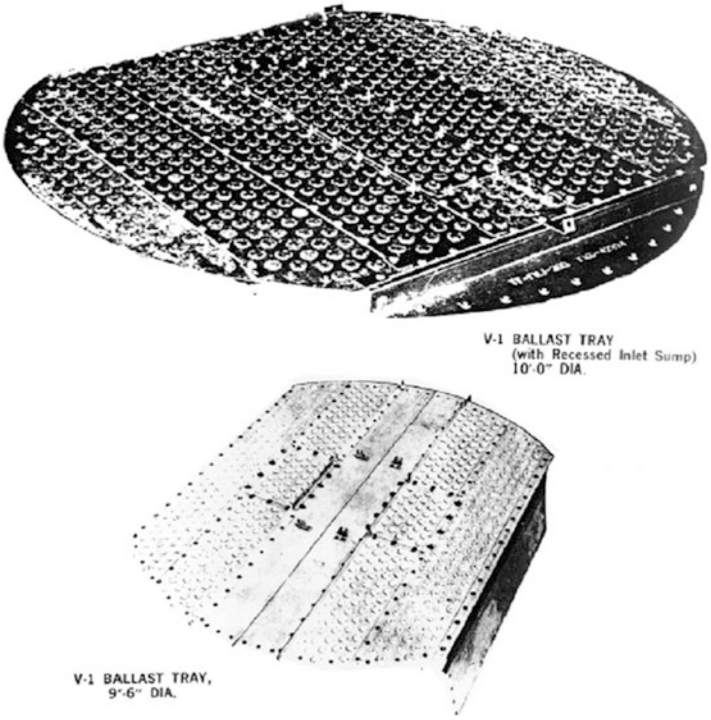


Fig. 3 Valve trays – Glitsch Ballast

The top tray
Any side stream draw-off tray
Any intermediate reflux draw-off tray
The bottom tray

Step 2. Calculate the actual cuft/h at tray conditions of the vapor. Then using the total mass per hour of the vapor, calculate its vapor density in lbs/cuft.

Step 3. From the heat balance, determine the density of the liquid on the tray at tray temperature in lbs/cuft.

Step 4. Select a tray spacing. Start with a 24″ space. Read from Fig. 4 a value for "K" on the flood line, using the equation:

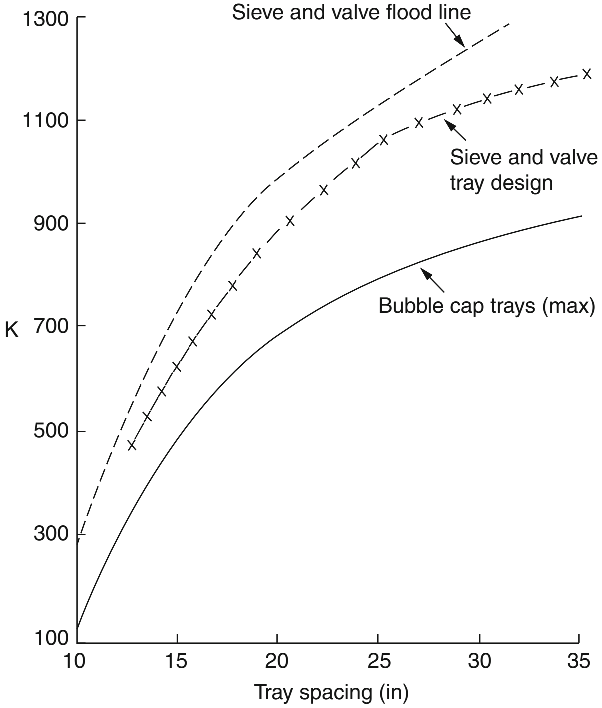
$$G_{\mathrm{f}} = K\sqrt{\rho_{\mathrm{v}} \times (\rho_{\mathrm{l}} - \rho_{v})} \tag{1}$$

where:

G_{f} = mass vapor velocity in lbs/h sqft at flood.
K = the constant read from the flood curve in Fig. 4.
ρ_{v} = density of vapor at tray conditions in lbs/cuft.
ρ_{L} = density of liquid at tray conditions in lbs/cuft.

Step 5. Multiply G_{f} by 0.82 to give mass velocity at 82 % of flood which is the normal recommended design figure. Divide the actual vapor rate in lbs/h by the vapor mass velocity to give the area of the tray. Calculate tray diameter from this area.

Fig. 4 Tray spacing versus "K" factor



An example calculation now follows.

Example Calculation

Calculate the diameter of the tower to handle the liquid and vapor loads as follows:

Vapor to tray	Liquid from tray
lbs/h = 47,700	GPH at 60 = 119.7
moles/h = 929.7	Hot GPH = 153.0
ACFS = 7.83	Hot CFS = 0.339
lbs/cuft ρ_v = 1.69	lbs/h = 33,273
Temp °F = 167	lbs/cuft ρ_L = 27.3
Pressure PSIA = 220	Temp °F = 162

Tray spacing is set at 24″ and the trays are valve type.
From Fig. 4, "K" =1,110 at flood.

$$\rho_v = 1.69\,\text{lbs/cuft at tray conditions.}$$

To calculate ρ of vapor at tray conditions, use

$$\rho = \frac{\text{wt/h} \times 520 \times \text{pressure (psia)}}{378 \times 14.7 \times \text{moles/h} \times \text{Temp}\,^{\circ}\text{R}}$$

where:

Press is tray pressure.
Temp °R is tray temperature in °F + 460.

$$\begin{aligned}\rho_L &= 27.3\ \text{lbs/cuft.}\\ \text{Then } G_f &= 1{,}110\sqrt{1.69\times(27.3-1.69)}\\ &= 7{,}302\ \text{lbs/h sqft}\\ \text{Area of tray at 82 \% of flood} &= \frac{47{,}700}{0.82\times 7{,}302}\text{sqft}\\ &= 7.97\ \text{sqft}\\ &= 3.18\ \text{ft. say } 39''.\end{aligned}$$

The tray dimensions and configuration for design purposes are subject to a much more rigorous examination. This is normally undertaken by the tray manufacturer from data supplied by the purchaser's process engineer. However, this process engineer needs to be able to check the manufacturer's offer before committing to purchase. The following calculation procedure offers a rigorous method for this purpose which establishes tray size and geometry. This calculation is based on a method developed by Glitsch Inc., a major manufacturer of valve and other types of trays and packing. Computer simulation software is also available and used for design checks. Software has largely replaced hand calculations.

The Rigorous Method

A rigorous method used in the design of valve trays is described by the following calculation steps:

Step 1. Establish the liquid and vapor flows as described earlier for the "quickie" method.

Step 2. Calculate the downcomer design velocity V_{dc} using the following equations (or by Fig. 5):

(a)

$$V_{dc} = 250 \times \text{system factor.} \tag{2}$$

(b)

$$V_{dc} = 41 \times \sqrt{(\rho_L - \rho_v)} \times \text{system factor.} \tag{3}$$

(c)

$$V_{dc} = 7.5 \times \sqrt{\text{TS}} \times \sqrt{(\rho_L - \rho_v)} \times \text{system factor} \tag{4}$$

where TS = tray spacing, in inches.
Use the lowest value for the design velocity in gpm/sqft.
Downcomer system factors are given in Table 1.

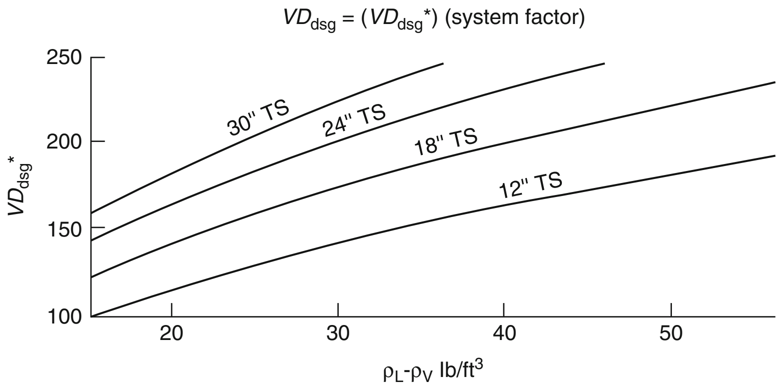


Fig. 5 Downcomer design velocity

Table 1 Downcomer system factors

Service	System factor
Non-foaming, regular system	1.0
Fluorine systems	0.9
Moderate foaming (amine units)	0.85
Heavy foaming (glycol, amine)	0.73
Severe foaming (MEK units)	0.6
Foam stable systems (caustic regen)	0.3

Step 3. Calculate the vapor capacity factor (CAF) using Fig. 6.

$$\mathrm{CAF} = \mathrm{CAF_o} \times \text{system factor}. \tag{5}$$

System factors used for this equation are given in Table 2.

Step 4. Calculate the vapor load using the equation:

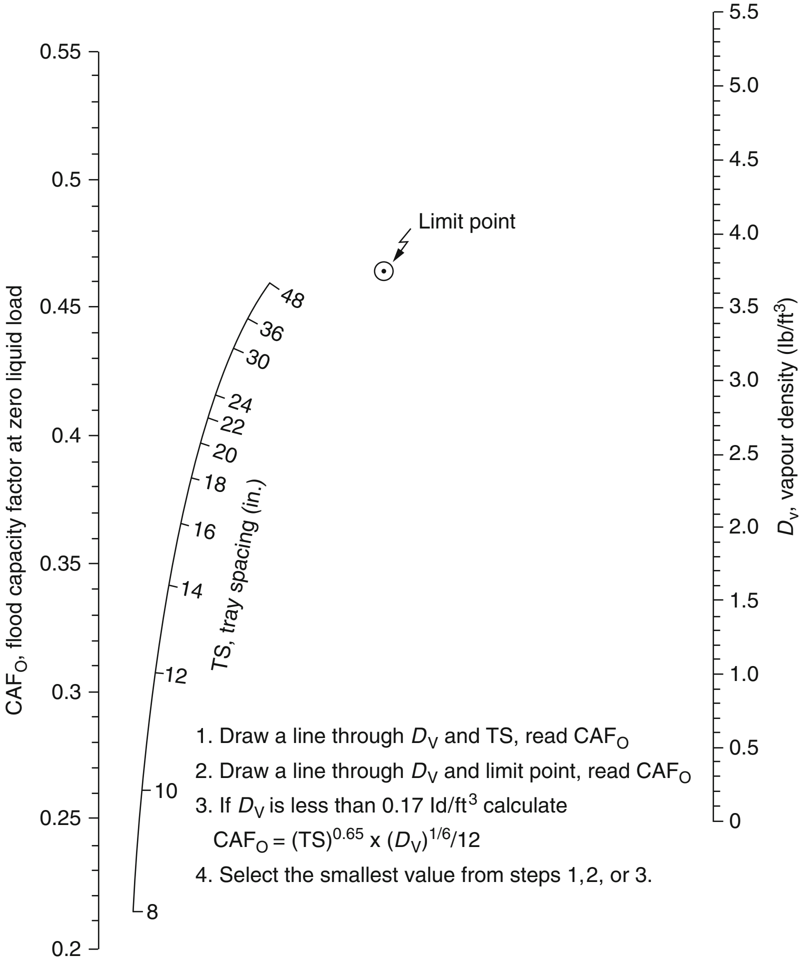
$$V_1 = \mathrm{CFS}\sqrt{\rho_v/(\rho_L - \rho_v)} \tag{6}$$

where CFS = actual vapor flow in cuft/s.

Step 5. Establish tower diameter using Fig. 7. Tray spacing is usually 18″, 24″, or 30″ for normal towers operating at above atmospheric pressures. Large vacuum towers may have tray spacing 30–36″. Note this diameter may be increased if other criteria of tray design are not met.

Step 6. Calculate the approximate flow path length (FPL) based on tower diameter from step 5 using the equation:

$$\mathrm{FPL} = 9 \times \mathrm{DT/NP} \tag{7}$$



1. Draw a line through D_V and TS, read CAF$_O$
2. Draw a line through D_V and limit point, read CAF$_O$
3. If D_V is less than 0.17 Id/ft^3 calculate
   $CAF_O = (TS)^{0.65} \times (D_V)^{1/6}/12$
4. Select the smallest value from steps 1,2, or 3.

Fig. 6 Flood capacities of valve trays

Table 2 Vapor system factors

Service	System factor
Non-foaming, regular	1.0
Fluorine systems	0.9
Moderate foaming	0.85
Heavy foaming	0.73
Severe foaming	0.6
Foam stable system	0.3–0.6

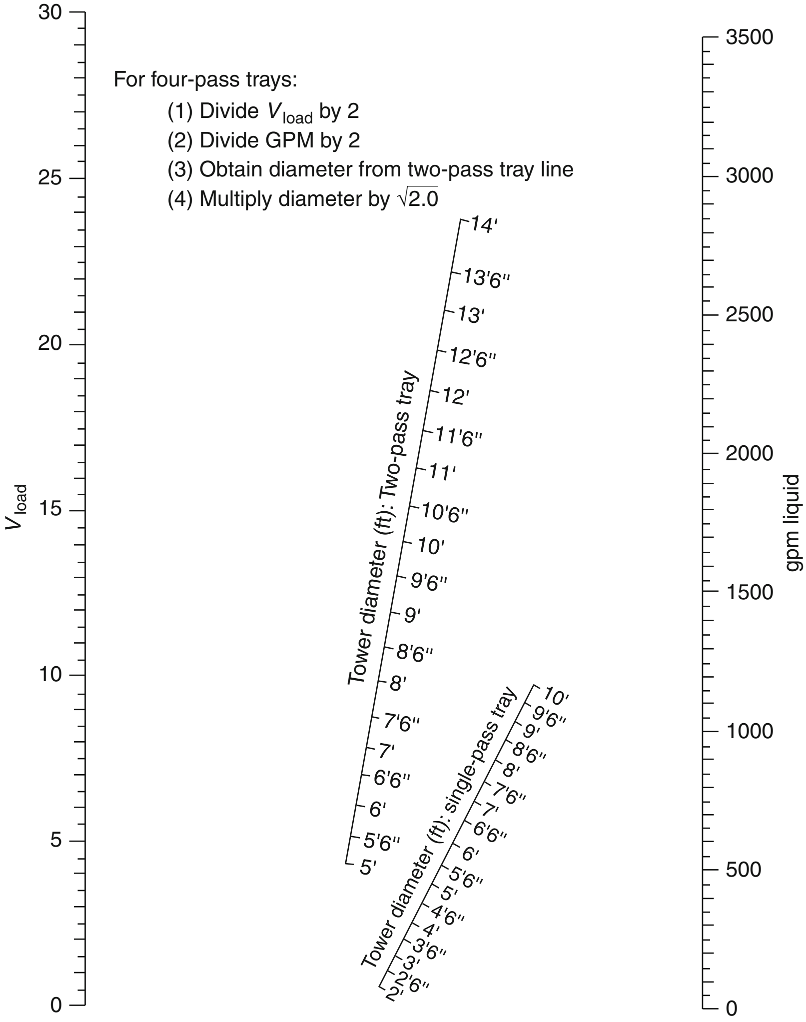


Fig. 7 Tray diameter versus vapor loads

where:

FPL = flow path length in inches.

DT = tower diameter from step 5 in ft.

NP = number of passes. For small towers with moderate liquid flows, this will be 1. For larger towers, this will depend on liquid velocities in the downcomer. The highest number of passes is usually 4.

Step 7. Calculate the *minimum* active area (AA_m) using the expression

$$AA_m = \frac{V_1 + (L \times FPL/13{,}000)}{CAF \times FF} \tag{8}$$

where:

AA_m = minimum active area in sqft.
V_1 = vapor load in CFS.
L = liquid flow in actual gpm.
FPL = flow path length in inches.
CAF = capacity factor from step 3.
FF = Flood Factor usually 80–82 %.

Step 8. Calculate *minimum* downcomer area (AD_m) using the equation

$$AD_m = \frac{L}{V_{dc} \times 0.8} \tag{9}$$

where:

AD_m = minimum downcomer area in sqft.
L = actual liquid flow in gpm.
V_{dc} = design downcomer velocity from step 2.

Note: The downcomer liquid velocity using the calculated minimum downcomer area should be around 0.3–0.4 ft/s.

Step 9. Calculate the *minimum* tower cross-sectional area using the following equations:

$$AT_m = AA_m + 2AD_m \tag{10}$$

or

$$AT_m = \frac{V_1}{0.78 \times CAF \times 0.8} \tag{11}$$

where

AT_m = minimum tower cross-sectional area in sqft.

Step 10. Calculate actual downcomer area using the following equation:

$$AD_c = \frac{AT \times AD_m}{AT_m} \tag{12}$$

where:

AD_c = actual downcomer area in sqft.
AT = tower area in sqft from the diameter calculated in step 5.

Step 11. Determine downcomer width (H_1) (from Appendix 1 of this chapter) for side downcomers. For multi-pass trays, use the following equation with the width factors given in Table 3:

$$H_i = WF \times \frac{AD}{DT} \tag{13}$$

Table 3 Allocation of downcomer area and width factors

←		Fraction of total downcomer area	→	
No of passes	AD1	AD2	AD3	AD4
1	0.5 % each	1.0	–	–
2	0.34 % each	–	0.66	–
3	0.25 % each	0.5	0.5 each	–
4	0.2	–	0.4	0.4
		Width factors (WF)		
Passes	H4	H5	H7	
1	12.0	–	–	
2	–	8.63	–	
3	6.0	6.78 each pass	–	
4	–	5.66	5.5	

where:

H_i = width of individual downcomers in inches.

WF = width factor from Table 3.

AD = total downcomer area in sqft.

DT = actual tower diameter in ft.

See Fig. 8 for allocation of downcomers in multi-pass trays.

Step 12. Calculate the actual FPL from the equation:

$$\text{FPL} = \frac{12 \times \text{DT} - (2\text{H}_1 + \text{H}_3 + 2\text{H}_5 + 2\text{H}_7)}{\text{NP}} \tag{14}$$

where:

H_{1-7} are individual downcomer widths in inches (see Fig. 8).

NP = number of passes.

Step 13. Calculate actual active area (*AA*) using values for H calculated in step 12 and Appendix 1 of this chapter to establish inlet areas of multi-pass tray downcomers.

$$\text{AA} = \text{AT} - (2\text{AD}_1 + \text{AD}_3 + 2\text{AD}_5 + 2\text{AD}_7)$$

where:

AA = actual active area in sqft.

AT = actual tower area in sqft.

AD_{1-7} are individual downcomer areas in sqft for multi-pass trays corresponding to H_{1-7}.

Step 14. From the data now developed, calculate the actual percent of flood or flood factor (FF). The following expression is used for this:

$$\%\,\text{Flood} = \frac{\text{V}_1 + (\text{L} \times \text{FPL}/13{,}000) \times 100}{\text{AA} \times \text{CAF}}. \tag{15}$$

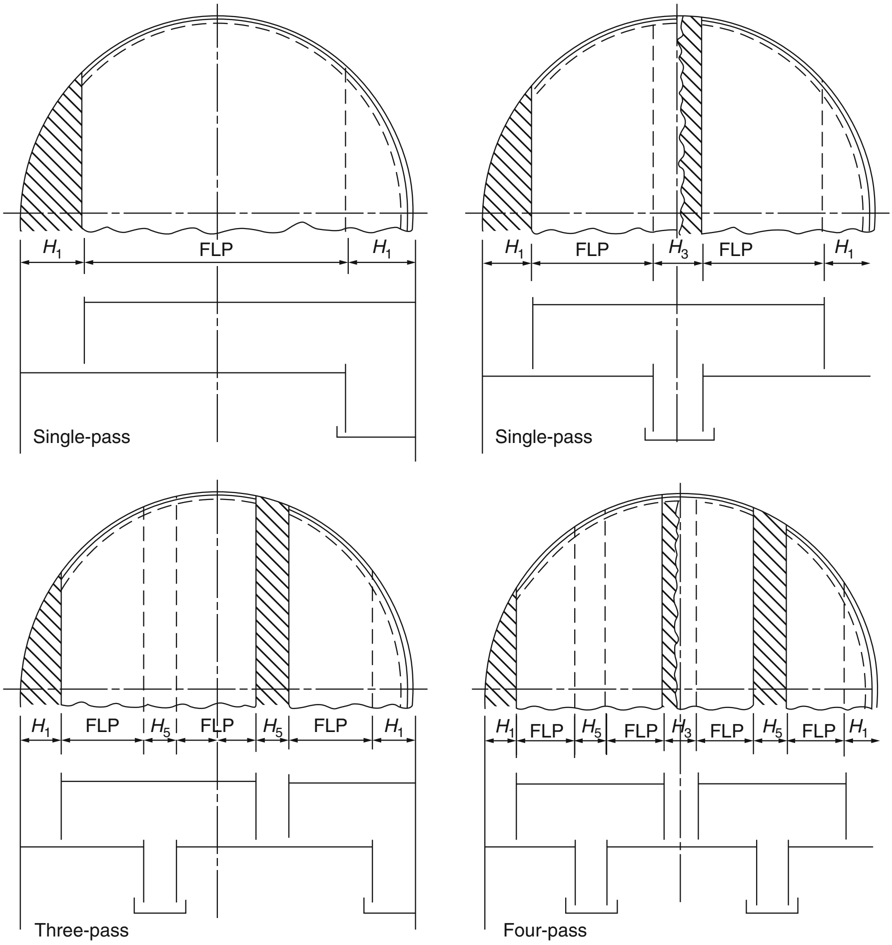


Fig. 8 Types of trays

Step 15. Calculate vapor hole velocity V_h assume 12–14 units (holes) per sqft of AA. Then:

$$V_{\mathrm{h}} = \frac{\mathrm{CFS} \times 78.5}{\mathrm{NU}} \tag{16}$$

where:

V_{h} = hole velocity in ft/s.

CFS = actual cuft/s of the vapor.

NU = total number of units.

Step 16. Calculate dry tray pressure drops from:

$$\text{Valves partly open}: \ \Delta P_{\mathrm{D}} = 1.35\ t_m \rho_m / \rho_{\mathrm{l}} + K_1 (V_{\mathrm{h}})(\rho_{\mathrm{v}}/\rho_{\mathrm{l}}) \tag{17}$$

Table 4 Pressure drop coefficients (Glitch Ballast-type trays)

		← K_2 for deck thickness (in.) →			
Type of unit	K1	0.074	0/104	0.134	0.25
V1	0.2	1.05	0.92	0.82	0.58
V4	0.1	0.68	0.68	0.68	–

← Thickness →		← Densities of valve material →	
Gauge	tm (ins)	Metal	Density (lbs/cuft)
20	0.37	CS	400
18	0.5	SS	500
16	0.6	Ni	553
14	0.074	Monel	550
12	0.104	Titanium	283
10	0.134	Hastelloy	560
		Aluminum	168
		Copper	560
		Lead	708

where:

ΔP_D = dry tray valve pressure drop in inches liquid.
t_m = valve thickness in inches (see Table 4).
ρ_m = valve metal density in lbs/cuft (see Table 4).
K_1 = pressure drop coefficient (see Table 4).

$$\text{Valves fully open}: \ \Delta P_D = K_2 (V_h)^2 \rho_v / \rho_l \tag{18}$$

where K_2 = pressure drop coefficient (see Table 4).

Step 17. Calculate total tray pressure drop.

$$\Delta P = \Delta P_D + 0.4 (L/L_{wi})^{0.87} + 0.4 H_w \tag{19}$$

where:

ΔP = total tray pressure drop in inches of liquid.
L_{wi} = weir length in inches (from Appendix 1).
H_w = weir height in inches (usually 1–2).

Step 18. Calculate height of liquid in downcomer.

First calculate the head loss under the downcomer H_{UD}, where $H_{UD} = 0.65 (V_{UD})^2$. V_{UD} is calculated from the liquid velocity in CFS or gpm/450 divided by the area under the downcomer. Use weir length times weir height for the area. This velocity should be around 0.3–0.6 ft/s for most normal towers.

Then:

$$H_{dc} = H_w + 0.4 (L/L_{wi})^{0.67} + (\Delta P + H_{UD})(\rho_l / (\rho_l - \rho_v)). \tag{20}$$

where:

H_{dc} = height of liquid in downcomer in inches.

For normal design, this should not exceed 50 % of tray spacing.

An example calculation now follows:

Example calculation

In this example, the same liquid and vapor flows and data will be used as in the "quickie calculation." The objective of this calculation will be to determine the tower diameter, tray pressure drop and configuration, and the percent flood for the design flow rates given.

Calculating the downcomer design velocity V_{dc}:

System factor in this case is 1.

$$\begin{aligned} V_{dc} &= 250 \times 1.0 = 250. \\ \text{Or}\ V_{dc} &= 41 \times (\rho_l - \rho_v) \times 1.0 \\ &= 41 \times 5.06 \times 1.0 = 207. \end{aligned} \tag{21}$$

$$\begin{aligned} \text{Or}\, V_{dc} &= 7.5 \times \text{TS} \times (\rho_l - \rho_v) \times 1.0 \\ &= 7.5 \times 4.9 \times 5.06 \times 1.0 = 186\ \text{gpm/sqft}\ (\text{TS} = \text{tray spacing} = 24''). \\ \text{Or}\, V_{dc} &= 188 \text{ from Fig. 5, use}\, V_{dc} = 186\ \text{gpm/sqft}. \end{aligned} \tag{22}$$

Vapor capacity factor CAF:

System factor in this case is 1.

From Fig. 6, CAF = 0.43.

Actual vapor load V_l:

$$\begin{aligned} V_l &= \text{CFS}\sqrt{\rho_v/(\rho_l - \rho_v)} \\ &= 7.83\sqrt{1.69/(27.3 - 1.69)} \\ &= 2.01\ \text{cft/s}. \end{aligned} \tag{23}$$

Approximate tower diameter AT:

Using Fig. 7:

V_l = 2.01 cft/s.

TS = 24″.

L = 153 gpm.

Tower ID = 3.25 ft = 39″.

Area = 8.30 sqft.

Calculate approximate flow path length FPL:

$$\text{FPL} = \frac{9 \times 39}{\text{No. of passes}} \times 12 = 29.25\ \text{in.}$$

Calculate minimum active area AA_m:

$$\begin{aligned}\mathrm{AA_m} &= \frac{V_1 + (L \times \mathrm{FPL}/13{,}000)}{\mathrm{CAF} \times \mathrm{FF}}\\ &= \frac{2.01 + (153 \times 29.25/13{,}000)}{0.43 \times 0.8}\,(\text{using } 80\,\%\,\text{flood})\\ &= 3.01\ \text{sqft.}\end{aligned} \tag{24}$$

Calculating minimum downcomer area AD_m:

$$\begin{aligned}\mathrm{AD_m} &= \frac{\mathrm{L}}{V_{\mathrm{dc}} \times 0.8}\\ &= \frac{153}{186 \times 0.8} = 1.028\ \text{sqft.}\end{aligned} \tag{25}$$

Calculating the minimum tower cross-sectional area:

$$\begin{aligned}\text{Either } \mathrm{AA_m} +\ 2\mathrm{AD_m} &= 3.01 + 2.056\\ &= 5.066\ \text{sqft.}\\ \text{or}\quad \frac{V_1}{0.78 \times \mathrm{CAF} \times 0.8} &= 7.49\ \text{sqft}\end{aligned} \tag{26, 27}$$

Use the larger which is 7.49 sqft.

Min diameter therefore is 3.09 f. say 37″.

Calculating actual downcomer area AD_c:

$$\begin{aligned}\mathrm{AD_c} &= \frac{\mathrm{AT} \times \mathrm{AD_m}}{\mathrm{AT_m}} = \frac{8.3 \times 1.028}{7.49}\\ &= 1.14\,\text{sqft.}\end{aligned}$$

$$\text{Downcomer area/tower area (“A” in Appendix 1)} = \mathrm{AD/AT} = 1.14/8.30 = 0.137. \tag{28}$$

From Appendix 1 “R” = 0.197, then

$$\mathrm{H} = 0.197 \times 3.25 = 0.633\ \text{ft} = 7.6''\ \text{DC width.}$$

Recalculating flow path length FPL:

$$\begin{aligned}\mathrm{FPL} &= 12 \times D_{\mathrm{t}} - (2\,H)\\ &= 12 \times 3.25 - (2 \times 7.6)\\ &= 23.8\ \text{in.}\end{aligned} \tag{29}$$

Recalculating active area based on actual downcomer area:

$$\begin{aligned}\mathrm{AA} &= \mathrm{AT} - (2\mathrm{AD}) \\ &= 8.3 - 2.28 \\ &= 6.02\ \text{sqft, which is greater than min allowed.}\end{aligned} \tag{30}$$

Checking percent of flood:

$$\begin{aligned}\%\ \text{flood} &= \frac{V_1 + (L \times \mathrm{FPL}/13{,}000)}{\mathrm{AA} \times \mathrm{CAF}} \times 100 \\ &= \frac{2.01\ +\ (153 \times 23.8/13{,}000)}{6.02 \times 0.43} \times 100 \\ &= 88.0\% \quad \text{which is a little high for design, but is acceptable.}\end{aligned} \tag{31}$$

Check downcomer velocity:

$$\begin{aligned}&\text{CFS of liquid} = 0.34\ \text{cfs.} \\ &\text{Area of down comer} = 1.14\ \text{sqft.} \\ &\text{Velocity of liquid in downcomer} = \frac{0.34}{1.14} \\ &\qquad = 0.3\ \text{ft/s.}\end{aligned}$$

Calculating pressure drops and downcomer liquid height

- *Dry tray pressure drop*

Partially open valves:

$$\begin{aligned}\Delta P_{\mathrm{D}} &= 1.35\ t_{\mathrm{m}}\rho_{\mathrm{m}}/\rho_1 + K_1(V_{\mathrm{h}})^2(\rho_{\mathrm{v}}/\rho_1). \\ V_{\mathrm{h}} &= \frac{7.83\ \times\ 78.5}{72} \qquad \text{(assumes 12 units per sqft of AA).} \\ &= 8.5\text{ft/s.} \\ \Delta\ P_{\mathrm{D}} &= 1.35 \times 0.74'' \times (490/27.3) + (0.2\ \times\ 72.25\ \times\ 0.062) \\ &= 2.69''\ \text{liquid.}\end{aligned} \tag{32}$$

Fully open valves:

$$\begin{aligned}\Delta P_{\mathrm{D}} &= \mathrm{K}_2\ (\mathrm{V}_{\mathrm{h}})^2 \cdot (\rho_{\mathrm{v}}/\rho_1) \\ &= 0.92 \times 72.25 \times 0.062 \\ &= 4.12''\ \text{liquid. This will be used.}\end{aligned} \tag{33}$$

- *Total tray pressure drop:*

$$\Delta P = \Delta P_D + 0.4\ (L/L_{wi})^{0.67} + (0.4\ \times H_w). \tag{34}$$

H_w (weir height) is fixed at 2″.

L_{wi} (downcomer length) is calculated from Appendix 1 of this chapter as 30.9″.

$$\begin{aligned}\Delta P &= 4.12 + 0.4\ (153/30.9)^{0.67} + 0.89'' \\ &= 6.09'' \text{ of liquid.}\end{aligned}$$

Height of liquid in downcomer:

$$\begin{aligned}H_{\mathrm{dc}} &= H_{\mathrm{w}} + 0.4\ (L/L_{\mathrm{wi}})^{0.67} + (\Delta P\ +\ H_{\mathrm{UD}})(\rho_1/(\rho_1 - \rho_{\mathrm{v}})). \\ H_{\mathrm{dc}} &= 2 + 0.4 \times 1.16 + (6.09\ +\ 0.405)(27.3/25.61) \qquad (35) \\ &= 10.08'' \text{ liquid. This is } 42.0\% \text{ of tray spacing which is acceptable.}\end{aligned}$$

(H_{UD} was calculated using a downcomer outlet area of $L_{\mathrm{wi}} \times 2''$ giving a velocity of 0.339 CFS divided by 0.429 sqft which is 0.79 ft/s. H_{UD} is then 0.65 $(0.79)^2 = 0.405$).

Calculating the actual number of valves for tray layout. With truss lines parallel to liquid flow:

$$\text{Rows} = \left[\frac{\text{FPL} -\ 8.5}{0.5 \times \text{base}} + 1\right]\text{NP} \qquad (36)$$

where:

$$\begin{aligned}\text{Base} &= \text{ spacing of units usually } 3.0'', 3.5'', 4.0'', 4.5'', \text{ or } 6.0''. \\ \text{Units/row} &= \frac{\text{WFP}}{5.75 \times \text{NP}} - (0.8 \times \text{number of beams}) + 1.\end{aligned} \qquad (37)$$

With truss lines perpendicular to liquid flow

$$\begin{aligned}\text{Rows} &= \left[\frac{\text{FPL} - (1.75 \times \text{N}_\text{o}\text{ trusses} - 6.0)}{2.5}\right]\text{NP}. \\ \text{Units/row} &= \frac{\text{WFP}}{\text{base} \times \text{NP}} - (2 \times \text{N}_\text{o}\text{ major beams}) + 1.\end{aligned} \qquad (38, 39)$$

where:

$$\begin{aligned}\text{WFP} &= \text{width of flow path in inches} \\ &= \text{AA} \times 144/\text{FPL}.\end{aligned}$$

Using a base pitch of 3.5″, the number of rows on the trays with trusses parallel to flow was calculated to be 9.7. Units per row were then calculated to be 8.73. This gives a total number of valves over the active area as 84.7. Thus, the number of valves per sqft of AA is 14. The assumption of 12 in the calculation gives a more stringent design; therefore, the assumption is acceptable.

Calculation summary:

Tower diameter = 3.25 ft or 39″.
Downcomer area (ea.) = 1.14 sqft (single pass).
Active area = 6.02 sqft.
Percent of flood = 88 %.
Tray spacing = 24″.
Downcomer backup = 42.0 % of tray spacing.
Number of valves = 85.
Number of rows = 10.
Valve pitch = 3.5″.

Packed Towers and Packed Tower Sizing

Although trayed towers are generally the first choice for fractionation and absorption applications, there are a number of instances where packed towers are preferable. For example, on small-diameter towers (below 3 f. diameter), packed towers are generally cheaper and more practical for maintenance, fabrication, and installation. At the other end of the spectrum, packing in the form of grids and large stacked packed beds have superseded trays in vacuum distillation towers whose diameter range up to 30 f. in some cases. This is because packing offers a much lower pressure drop than trays.

The packing in the tower itself may be stacked in beds on a random basis or in a defined structured basis. For towers up to 10–15 ft, the packing is usually dumped or random packed. Above this tower size and depending on its application, the packing may be installed on a defined stacked or structured manner. For practical reasons and to avoid crushing the packing at the bottom of the bed, the packing is installed in beds. As a rule of thumb, packed beds should be around 15 f. in height. About 20 f. should be a maximum for most packed sections.

Properties of good packing are as follows:

- Should have high surface area per unit volume.
- The shape of the packing should be such as to give a high percentage of area in active contact with the liquid and the gas or in the two liquid phases in the case of extractors.
- The packing should have favorable liquid distribution qualities.
- Should have low weight but high unit strength.
- Should have low pressure drop but high coefficients of mass transfer.

Some data on the various common packing available commercially are given in Tables 5, 6, and 7. Figure 9 shows a sectional layout of a typical packed tower. Note this tower has bed supports designed for gas distribution and includes intermediate weir liquid distributors between some of the beds.

Table 5 Physical properties of some common packing

Packing type	Size (in.)	Wall thickness (in.)	OD and length	Approx. no./per ft^3	Approx. wt/per ft^3	Approx. surface area (ft^2 ft^3)	% void volume
Raschig rings (ceramic)	1/4	1/32	1/4	88,000	46	240	73
	5/16	1/16	5/16	40,000	56	145	64
	3/8	1/16	3/8	24,000	52	155	68
	1/2	1/32	1/3	10,600	54	111	63
	1/2	1/16	1/2	10,600	48	114	74
	5/8	3/32	3/8	5,600	48	100	68
	3/4	3/32	3/4	3,140	44	80	73
	1	1/3	1	1,350	40	58	73
	1-1/4	3/16	1-1/2	680	43	45	74
	1-1/2	1/4	1-2/3	375	46	35	68
	1-1/2	3/16	1-1/2	385	42	38	71
	2	1/4	2	162	38	28	74
	2	3/16	2	164	35	29	78
	3	3/8	3	48	40	19	74
Raschig rings (metal)	1/4	1/32	1/4	88,000	150	236	69
	5/16	1/32	5/6	45,000	120	190	75
	5/16	1/16	5/16	43,000	198	176	60
	1/2	1/32	4/2	11,800	77	128	84
	1/2	1/16	1/2	11,000	132	118	73
	19/32	1/32	19/32	7,300	66	112	86
	19/32	1/32	19/32	7,000	120	106	75
	3/4	1/32	3/4	3,400	55	84	88
	3/4	1/16	3/4	3,190	100	72	78
	1	1/32	1	1,440	40	63	92
	1	1/16	1	1,345	73	57	85
	1-1/4	1/16	1-1/2	725	62	49	87
	1-1/2	1/16	1-1/2	420	50	41	90
	2	1/16	2	180	38	31	92
	3	1/16	3	53	25	20	95
Raschig rings (carbon)	1/4	1/16	1/4	85,000	46	212	55
	1/2	1/16	1/2	10,600	27	114	74
	3/4	1/8	3/4	3,140	34	75	67
	1	1/3	1	1,325	27	57	74
	1-1/4	1/16	1-1/4	678	31	45	69
	1-1/2	1/2	1-1/2	392	34	37	67
	2	1/5	2	166	27	28	74
	3	5/16	3	49	33	19	78
Berl saddles (ceramic)	1/4	–	–	113,000	56	274	60
	1/2	–	–	16,200	54	142	63
	3/4	–	–	5,000	48	82	66

(*continued*)

Table 5 (continued)

Packing type	Size (in.)	Wall thickness (in.)	OD and length	Approx. no./per ft^3	Approx. wt/per ft^3	Approx. surface area (ft^2 ft^3)	% void volume
	1	–	–	2,200	45	76	69
	1-1/2	–	–	580	38	44	75
	2	–	–	250	40	32	72
Intalox saddles (ceramic)	1/4	–	–	117,500	54	300	75
	1/2	–	–	20,700	47	190	78
	3/4	–	–	6,500	44	102	77
	1	–	–	2,385	42	78	77
	1-1/2	–	–	709	37	60	81
	2	–	–	265	38	36	79

Table 6 Coefficients for use in the HETP equation

Packing type	Packing size (in.)	K_1	K_2	K_3
Raschig rings	0.375	2.10	−0.37	1.24
	0.500	0.853	−0.24	1.24
	1.000	0.57	−0.10	1.24
	2.000	0.52	0.00	1.24
Saddles	0.500	5.62	−0.45	1.11
	1.000	0.76	−0.14	1.11
	2.000	0.56	−0.02	1.11

Table 7 Recommended packing sizes

	← Tower diameter ft →				
Packing type	1.0	2.0	3.0	4.0	+ 5.0
Raschig rings	0.5	0.75	1.00	1.5	3.00
Berl saddles	0.75	1.50	2.00	2.00	3.00
Intalox saddles	0.75	1.50	2.00	2.00	3.00
Pall rings	1.00	1.50	2.00	2.00	3.00

Other salient points concerning packed towers are as follows:

1. Reflux ratios, flow quantities, and number of theoretical trays or transfer units are calculated in the same manner as for trayed columns.
2. Internal liquid distributors are required in packed towers to ensure good distribution of the liquid over the beds throughout the tower.

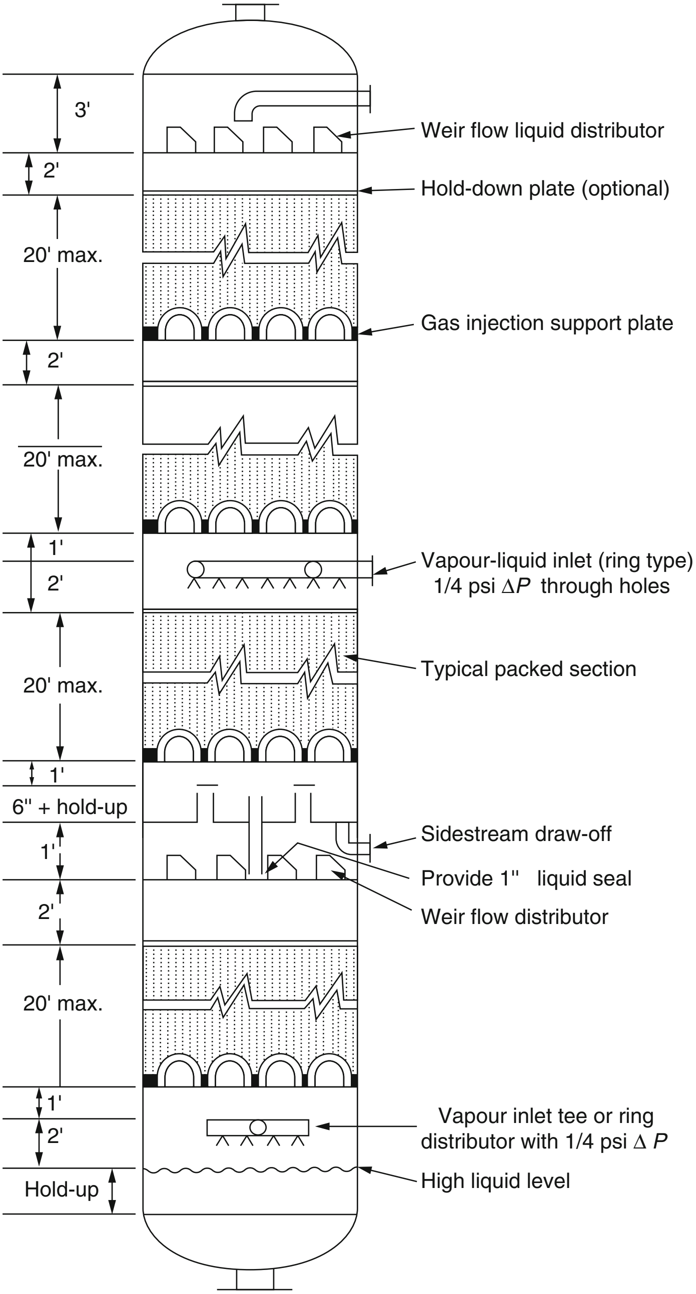


Fig. 9 A typical packed tower

3. The packed beds are supported by grids. These are specially designed to ensure good flows of the liquid and the gas phases.
4. Every care must be taken in the design of the packed tower that the packing is always properly "wetted" by the liquid phase. Packing manufacturers usually quote a minimum wetting rate for their packing. This is usually around 2.0–2.5 gpm of liquid per sqft of tower cross section. Most companies prefer this minimum to be around 3.0–3.5 gpm/sqft (Tables 5 and 6).

Sizing a Packed Tower

The height of the tower is determined by the methods used to calculate the number of theoretical trays required to perform a specific separation. These have been discussed earlier in the introductory chapter to this handbook. Normally, this calculation is done by process simulation software. A figure equivalent to the height of a theoretical tray is then calculated to determine the height of packing required. This is used as the basis to determine the overall height of the tower by adding in the space required for distributors, support trays, and the like.

The diameter of the tower is calculated using a method which allows for good mass and heat transfer while minimizing entrainment. The same principle of tower flooding is applicable to packed towers as for trayed towers. A calculation procedure for determining a packed tower diameter and the height of packed beds now follows:

Step 1. From examination of the flows of vapor and liquid in the tower, determine the critical section of the tower where the loads are greatest. Usually this is at the bottom of an absorption unit and either the top or bottom of a fractionator.

Step 2. Determine the conditions of temperature and pressure at the critical tower section. This is usually accomplished by bubble and dew point calculations as described in the introductory chapter to this handbook. That is, bubble point of the bottoms liquid (either in a fractionator or an absorber) determines the bottom of the tower conditions, and dew point calculation of the overhead vapor determines the tower top conditions.

Step 3. Establish the liquid and vapor stream compositions at the critical tray conditions. See the chapter on "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook for determining vapor/liquid streams in absorption and fractionation towers. Calculate the properties of these streams such as densities, mass/unit time, moles/unit time, viscosity, etc. at the conditions of the critical tower section. You can use process simulation software for this, too. Next select a packing type and size. Use Table 7 for this.

Step 4. Commence the tower sizing by calculating the diameter. First calculate a value for

$$(L/G)\sqrt{(\rho_{\mathrm{v}}/\rho_{1})} \tag{40}$$

where:

L = mass liquid load in lbs/s sqft.

G = mass vapor load in lbs/s sqft.

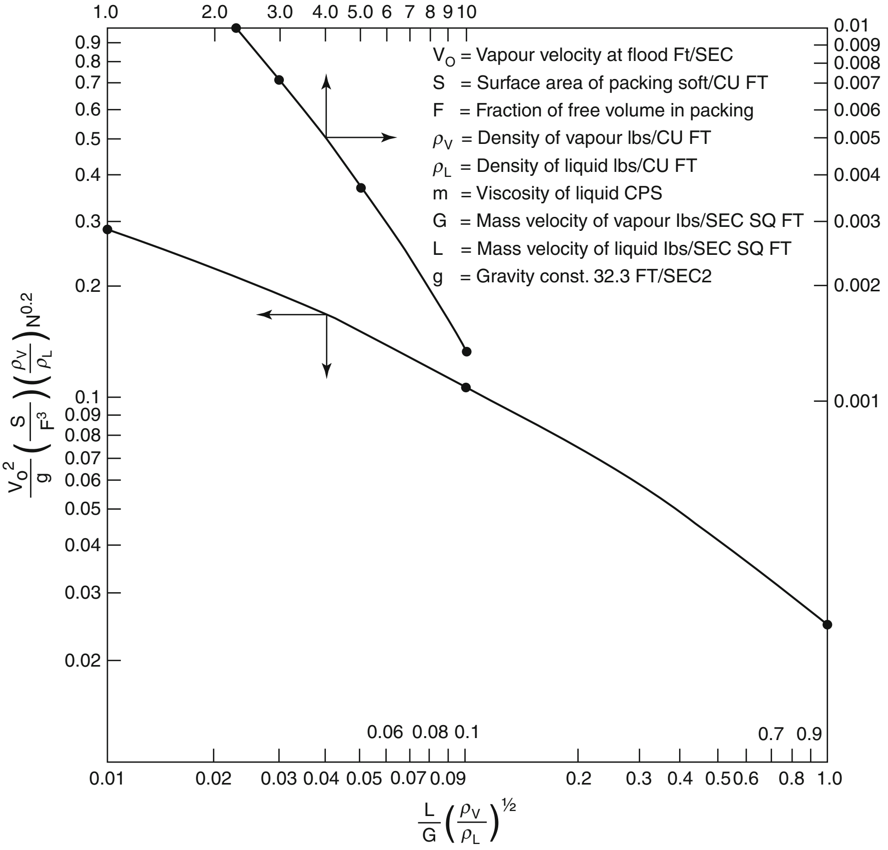


Fig. 10 Packed tower flooding criteria

ρ_v = density of vapor in lbs/cuft at tower conditions.
ρ_1 = density of liquid in lbs/cuft at tower conditions.
Then, using Fig. 10, read off a value for the equation:

$$(L/G)\sqrt{(\rho_v/\rho_1)} = \frac{V^2 \cdot S \cdot \rho_v \cdot \mu^{0.2}}{g(F)^3 \rho_1} \tag{41}$$

where:

V = the vapor velocity at flood in ft/s.
g = 32.2 ft/s/s.
S = surface area of packing in sqft/cuft of packing (see Table 5).
F = fraction of void (see Table 5).
μ = viscosity of liquid in cPs.

Step 5. Solve the equation from step 4 to give a value for V. This is the superficial velocity of the vapor at flood. Designing for 80 % of flood, multiply V by 0.8.

Step 6. Divide the total cuft/s of the vapor flowing in the tower by 0.8 V to give the tower cross-sectional area in sqft. Calculate the tower diameter from this area.

Step 7. The next part of the calculation is to determine the height of the tower. The number of theoretical trays has been determined by either the fractionation or absorption calculation described in the handbook chapter entitled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" or by computer simulation. It is now required to establish either the actual number of trays for a trayed tower or the height of packing in the case of a packed tower. This calculation deals with the second of these.

The next step sets out to establish the HETP which is the height equivalent to a theoretical tray.

Step 8. The HETP is calculated from the following equation:

$$\mathrm{HETP} = K_1 \cdot G_{\mathrm{h}}^{K_2} \cdot D^{K_3} \cdot \frac{62.4 \times \alpha \times \mu^2}{\rho_1} \tag{42}$$

where:

$K_{1,2,3}$ = factors from Table 6.

D = tower diameter in inches.

α = relative volatility of the more volatile component in the liquid phase (see step 9 below).

μ = viscosity in cPs.

G_{h} = mass velocity of the vapor in lbs/h sqft.

Step 9. To determine the relative volatility α, select a key light component that is in the lean liquid and the wet gas. The relative volatility is the equilibrium constant of the lightest significant component in the rich liquid divided by the equilibrium constant of the light key component. Solve for a value of HETP and multiply this by the number of theoretical stages to give the total packed height. Software can also perform this calculation.

Step 10. Determine the number of beds to accommodate the packed height. Allow space between the beds for vapor/liquid redistribution and holdup plates. Use Fig. 9 as a guide for this. The tower height will be the sum of beds, internal distributors packing support trays, liquid holdup, and vapor disengaging space.

An example calculation now follows.

Example calculation

In this example, the number of theoretical trays for an absorption unit has been fixed as 4. The compositions of the "wet" gas and the lean liquid have been given and used to determine the composition and quantities of the rich liquid and the lean gas. The quantities to be used in the following calculation are as follows:

Rich liquid leaving the bottom of the absorber = 452.66 moles/h.

Wet gas entering the bottom of the tower = 1,018.35 moles/h.

Their respective compositions and conditions are as follows:

Wet gas

	Mole frac	Mole wt	Weight
H_2	0.467	2.0	0.93
C_1	0.190	16.0	3.40
C_2	0.059	30.0	1.77
H_2S	0.242	34.0	8.24
C_3	0.604	44.0	1.32
iC_4	0.006	58.0	0.35
nC_4	0.006	58.0	0.35
Total	1.000	16.0	16.00

$$\text{Temperature} = 95\,^{\circ}\text{F; pressure} = 175 \text{ psia.}$$

$$\text{Cuft} = \frac{378 \times 14.7 \times 555}{175 \times 520} = 33.89.$$

$$\rho_v = 16/33.89 = 0.473 \text{ lbs/cuft.}$$

Rich liquid

	Mole frac	Mole wt	wt fact	lbs/Gal	vol fact
H_2	0.004	2.0	0.002	–	–
C_1	0.013	16.0	0.208	2.5	0.083
C_2	0.016	30.0	0.480	2.97	0.162
H_2S	0.092	34.0	3.128	6.56	0.477
C_3	0.028	44.0	1.232	4.23	0.291
iC_4	0.011	58.0	0.638	4.68	0.136
nC_4	0.013	58.0	0.754	4.86	0.155
C_9	0.823	128.0	105.344	6.02	17.499
Total	1.000		111.786	5.95	18.803

Temperature = 95 °F
SG at 60°F = 0.715
SG at 95°F = 0.696
ρ_1 at 95°F = 43.3 lbs/cuft

$$(L/G)\sqrt{(\rho_v/\rho_1)} = \frac{V^2 \cdot S \cdot \rho_v \cdot \mu^{0.3}}{gF^3\rho_1} \tag{43}$$

where:

V = the vapor velocity at flood in ft/s.
g = 32.2 ft/s.
S = surface area of packing in sqft/cuft of packing (see Table 5).
= 36 sqft/cuft.
F = fraction of void (see Table 5) = 0.79.

μ = viscosity of liquid in cps. = 0.56 cPs.

$$(L/G)\sqrt{(\rho_{\rm v}/\rho_1)} = \frac{50,670}{16,325} \times \left[\frac{0.473}{43.3}\right]^{1/2} = 0.324.$$

From Fig. 10, y value is = 0.055 for x = 0.324.

Then:

$$\frac{V^2 \times S \times \rho_{\rm v} \times \mu}{g \times F^3 \times \rho_1} = 0.055.$$

$$\begin{aligned}
V^2 &= \frac{0.055}{0.022} = 2.5\ .\\
V &= 1.58\ \text{ft/s.}\\
\text{at } 80\,\%\text{ of flood } V &= 1.58\ \times 0.8\\
&= 1.26\ \text{ft/s.}\\
\text{Total vapor flow} &= 16,325\ \text{lbs/h}\\
&= \frac{16,325}{0.473} = 34,514\ \text{cuft/h.}\\
&= 9.59\ \text{cuft/s}\\
\text{Cross} - \text{sectional area} &= \frac{9.59}{1.26} = 7.6\ \text{sqft.}\\
\text{Tower diameter}\ &=\ 3.1\ \text{ft say } 3.25\ \text{ft or } 39''.
\end{aligned}$$

To calculate HETP, use 2″ Berl saddles.

$$\text{HETP} = K_1 \cdot G_{\rm H}^{\rm K_2} \cdot D^{\rm K_3} \cdot \frac{62.4 \times \alpha \times \mu_1}{\rho_1} \tag{44}$$

where:

K_1 = 0.56.
K_2 = −0.2.
K_3 = 1.11.
α = relative volatility (neglect H_2 and C_1 in liquid composition as noncondensable). The key component is C_3 then is KC_2/KC_3, which is 4.6/1.0 = 4.6.
G_H = 16,325/7.6 = 2,148 lbs/h·sqft.
D = tower diam = 39″.

$$\begin{aligned}
\text{HETP} &= \frac{0.56 \times 39 \times 62.4 \times 4.6 \times 0.56}{(2,148)^{0.02} \times 43.3}\\
&= 25.83\ \text{ft per theoretical tray.}
\end{aligned}$$

The number of theoretical trays was fixed at four for this separation. Then using four theoretical trays, the total height of packing = 4 × 25.83 ft = 103 ft call it 100 ft. Five packed beds each 20 f. would satisfy the required duty. Using Fig. 9 as a guide, the tower height is developed as follows:

Bottom tan to HLL (*holdup*). Liquid is fed to a stripping column; therefore, let the holdup time be 3 min to NLL. Then NLL = 6.9 f. say 7.0 f. and HLL = 10 ft.

HLL to vapor inlet distributor. This will be set at 2.0 ft.

Distributor to bottom bed packing support. This will be set at 1.0 ft.

Bottom packed bed support to top of packed bed. Packed height is 20 ft.

Top of bottom bed to bottom of next bed. Set this at 3.0 f. to allow for a liquid weir-type distributor.

Height to top of top bed.

Packed height which is 4 × 20 ft = 80.

4 distributors ⇒ 12 ft.

Total = 92 ft.

Top of top bed to top tan (*tangent*). Make this 5 f. to allow for liquid distribution tray and liquid inlet pipe.

Total height tan to tan = 130 ft.

Drums and Drum Design

Drums may be horizontal vessels or vertical. Generally drums do not contain complex internals such as fractionating trays or packing as in the case of towers. They are used however for removing material from a bulk material stream and often use simple baffle plates or wire mesh to maximize efficiency in achieving this. Drums are used in a process principally for:

- Removing liquid droplets from a gas stream (knockout pot)
- Separating vapor and liquid streams
- Separating a light from a heavy liquid stream (separators and decanters)
- Surge drums to provide suitable liquid holdup time within a process
- To reduce pulsation in the case of reciprocating compressors

Drums are also used as small intermediate storage vessels in a process.

Vapor Disengaging Drums

One of the most common examples of the use of a drum for the disengaging of vapor from a liquid stream is the steam drum of a boiler or a waste heat steam generator. Here the water is circulated through a heater where it is raised to its boiling point temperature and then routed to a disengaging drum. Steam is flashed off in this drum to be separated from the liquid by its superficial velocity across the area above the water level in the drum. The steam is then routed to a superheater and thus to the steam main. The performance of the steam superheater depends on receiving fairly “dry” saturated steam, that is, steam containing little or no water droplets. The separation mechanism of the steam drum is therefore critical. The design of a vapor disengaging drum depends on the velocity of the vapor and the area of disengagement. This is expressed by the equation:

$$V_c = 0.157\sqrt{\frac{\rho_1 - \rho_v}{\rho_v}} \tag{45}$$

where:

V_c = critical velocity of vapor in ft/s.
ρ_1 = density of liquid phase in lbs/cuft.
ρ_v = density of vapor phase in lbs/cuft.

The area used for calculating the linear velocity of the vapor is:

- The vertical cross-sectional area above the high liquid level in a horizontal drum
- The horizontal area of the drum in the case of vertical drums

The allowable vapor velocity may exceed the critical, and normally design velocities will vary between 80 % and 170 % of critical. Severe entrainment occurs however above 250 % of critical. Table 8 gives the recommended design velocities for the various services. The minimum vapor space above the liquid level in a horizontal drum should not be less than 20 % of drum diameter or 12″, whichever is greater.

Crinkled wire mesh screens (*CWMS*) screens are effective entrainment separators and are often used in separator drums for that purpose. When installed they improve the separation efficiency so vapor velocities much above critical can be tolerated. They are also a safeguard in processes where even moderate liquid entrainment cannot be tolerated.

CWMS are now readily available as packages that include support plates and installation fixtures. Normally for drums larger than 3 f. in diameter 6″, thick open mesh-type screen is used.

Liquid Separation Drums

The design of a drum to perform this duty is based on one of the following laws of settling:

Stoke's law

$$V = 8.3 \times 10^5 \times \frac{d^2 \Delta S}{\mu} \tag{46}$$

when the Re number is <2.0.
Intermediate law

$$V = 1.04 \times 10^4 \times \frac{d^{1.14} \Delta S^{0.71}}{S_c^{0.29} \times \mu^{0.43}} \tag{47}$$

when the Re number is 2–500.
Newton's law

$$V = 2.05 \times 10^3 \times \left[\frac{d\Delta S}{S_c}\right]^{1/2} \tag{48}$$

Table 8 Some typical drum applications

Service	Liquid surge and distillate	Settling drums	Compressor suction		Fuel gas KO drams	Steam drums	Water disengaging drums
			Cent	Recip			
Allowable vapor velocity without CWMS, % V_c	170		80	80	170	–	170
Allowable vap velocity with one CWMS, % V_c			150	120		100	
Allowable vap velocity with two CWMS, % V_c			–	–		150	
Liquid holdup set by:	Water settling	Settling requirements	10 min liquid spill		Should be at least volume of a 20 f. slug of condensate	1/3 the heater and steam piping volume	50 in. per minimum settling rate for hydrocarbon vapors from water
	Minimum instrument	Minimum instrument	When taking suction from absorbers		Following an absorber – 5 min on total lean oil circulation		Minimum height to low level 1.5 ft
	Controlling Process	Controlling process	For refrigerators – 5 min based on largest cooling unit				
	Inventory requirement						
Normal drum position	Horizontal	Horizontal	Vertical		Vertical	Vertical	Horizontal
Type of nozzle inlet	90° bend	90° bend	Tee dist		Flush	Tee Dist or proprietary	90° bend
Outlet vapor	Flush	–	Flush		Flush	Flush	Flush
Outlet liquid	Flush	Flush	Flush		Flush	Flush	Flush

Table 9 Typical droplet sizes for liquid-liquid separation calculations

Lighter phase	Heavy phase	Minimum droplet size
0.850 SG and lighter	Water	0.008 in.
Heavier than 0.850	Water	0.005 in.

when the Re number is >500

where:

$$\text{Re number} = \frac{10.7 \times d \cdot V \cdot S_c}{\mu}. \tag{49}$$

V = settling rate in inches per minute.
d = droplet diameter in inches.
S = droplet specific gravity.
S_c = continuous phase specific gravity.
ΔS = specific gravity differential between the two phases.
μ = viscosity of the continuous phase in cPs.

Table 9 may be used as a guide to estimating droplet size.

The holdup time required for settling is the vertical distance in the drum allocated to settling divided by the settling rate. Some typical applications of drums for this service are given in Table 8.

Settling baffles are often used to reduce the holdup time and the height of the liquid level.

Surge drums

This type of drum, the calculation of holdup time, and surge control have been described in section "Overall Pressure Drop, Including Elevation and Velocity Changes" of the handbook chapter entitled "▶ Process Controls in Petroleum Processing."

Pulsation drums or pots

This type of drum will be described in some detail in part 3 of this chapter in the section on reciprocating compressors.

An example calculation of drum sizing now follows.

Example Calculation

It is required to provide the dimensions and process data for the design of a reflux drum receiving the hydrocarbon distillate, water, and uncondensed hydrocarbon vapor from a distillation column. Details of flow and drum conditions are as follows:

Vapor: 12,000 lbs/h, 40 mole wt, 300 moles/h.
Distillate product: 76,650 lbs/h, SG at 100°F=0.682.
Reflux liquid: 61,318 lbs/h, SG at 100°F=0.682.
Water: 17,381 lbs/h.
Temperature of drum: 100°F.
Pressure of drum: 30 psia.

The drum is to be a horizontal vessel located on a structure 45 f. above grade. The liquid product is to feed another fractionating unit and therefore requires a holdup time of 15 min between LLL and HLL. The vapor leaving the drum is to be routed to fuel gas via a compressor; therefore, complete disengaging of liquid droplets is required. Complete separation of water from the oil is required. However, as the water is routed to a desalter separator from the drum, separation of oil from the water is not critical.

In all probability, the surge volume required by the product will be the determining feature of this design. Setting the liquid levels in the drum will depend on the settling of the water from the hydrocarbon phase. The design will be checked for satisfactory vapor disengaging.

The Design

Step 1 – Calculating the surge volume for the distillate product

$$\begin{aligned}\text{Holdup time} &= 15\ \text{min.}\\ \text{Product rate} &= \frac{76{,}650\ \text{lbs/h}}{0.682 \times 62.2} = 1{,}807\ \text{cuft/h.}\\ \text{Holdup volume} &= \frac{1{,}807 \times 15}{60} = 452\ \text{cuft.}\end{aligned}$$

Then the volume of liquid between HLL and LLL is 452 cuft. Let this be 60 % of the total drum volume. Then drum volume 452/0.60 = 753 cuft.

Using a length-to-diameter ratio (*L*/*D*) of 3, diameter and length are calculated as follows:

$$\begin{aligned}753\ \text{cuft} &= \frac{\pi \cdot D^2}{4} \times 3D\,.\\ D &= \sqrt[3]{\frac{753 \times 4}{3\pi}} \;=\; 6.8\ \text{ft make it 7.0 ft.}\\ L &= 3 \times 7.0\ \text{ft} = 21.0\ \text{ft.}\end{aligned} \tag{50}$$

Step 2 – Calculating water settling rate

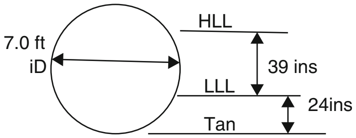
Using "intermediate law" then:

$$\begin{aligned}V &= 1.04 \times 10^4 \times \frac{d^{1.14}\Delta S^{0.71}}{S_c^{0.29} \times \mu^{0.43}}.\\ V &= \text{settling rate in ins/min.}\\ d &= \text{droplet size in ins} = 0.008''.\\ S_\text{c} &= \text{SG of continuous phase} = 0.682.\\ S_\text{w} &= \text{SG of water} = 0.993.\\ \Delta S &= 0.311.\\ V &= 1.04 \times 10^4 \times \frac{0.004 \times 0.44}{0.895 \times 0.78}\\ &= 29.2\ \text{in./min.}\end{aligned} \tag{51}$$

Check Re number:

$$\mathrm{Re} = \frac{10.7 \times 0.008 \times 29.2 \times 0.682}{0.56}$$
$$= 3.0 \text{ so use of “intermediate law” is correct.}$$

Step 3 – Setting the distance between bottom tan and LLL



Sufficient distance or surge should be allowed below LLL to provide a LLL alarm at a point about 10 % below LLL and bottom tangent. The remaining surge should be sufficient to provide the operator with some time to take emergency action (such as shutting down pumps).

Let LLL be 2 f. above bottom tan. Then the surge volume in this section is as follows:

$\mathrm{R} = 2/7 = 0.286$. From Appendix 1 at 0.237, area of section $= 0.237 \times 38.48 = 9.1$ sqft and volume $= 21 \times 9.1 = 191$ cuft.

$$\text{Total flow rate} = \text{product} + \text{reflux} + \text{water}$$
$$= 3{,}531.4 \text{ cuft/h} = 58.86 \text{ cuft/min}.$$

Minutes of holdup below LLL = 3.25 min.

By the same calculation, holdup after alarm = 2.9 min, which is satisfactory.

Step 4 – Checking settling time for the water

At the LLL, a distance of 2 f. from tan.

Residence time for liquid below LLL = 3.25 min.

Minimum settling time required:

$$\frac{\text{Vert distance to bottom of drum}}{\text{Settling rate}} = \frac{24''}{29.2 \text{ in./min}} = 0.82 \text{ min}, \tag{52}$$

which is adequate.

Step 5 – Calculating height of HLL above LLL

$$\text{Total volume to HLL} = 191 + 452 = 643 \text{ cuft}$$
$$\text{Area above HLL} = \frac{808 \text{ cuft} - 643 \text{ cuft}}{21 \text{ ft}} = 7.58 \text{ sqft}.$$

Using table in Appendix 1 of this chapter:

$$\frac{A_D}{A_s} = \frac{7.58}{38.48} = 0.197 \quad R = 0.251.$$
$$r = 0.251 \times 7.0 = 1.76 \text{ ft.}$$
$$\text{Height of HLL above LLL} = 7 - (1.76 + 2.0)$$
$$= 3.25 \text{ ft. (39 in.).}$$

Step 6 – Checking the vapor disengaging space

$$V_c = 0.157\sqrt{\frac{\rho_1 - \rho_v}{\rho_v}} \tag{53}$$

where:

V_c = critical velocity of vapor in ft/s.
ρ_l = density of liquid phase in lbs/cuft = 42.42.
ρ_v = density of vapor phase in lbs/cuft = 0.216.
V_c = 2.28 ft/s.

Actual velocity of vapor is as follows:

$$\text{Cross} - \text{sectional area of vapor space above HLL} = 7.58 \text{ sqft}$$
$$\text{Vapor linear velocity} = \frac{59,840 \text{ cuft/h}}{7.58 \times 3,600} = 2.19 \text{ ft/s}$$

which is 96 % of critical.

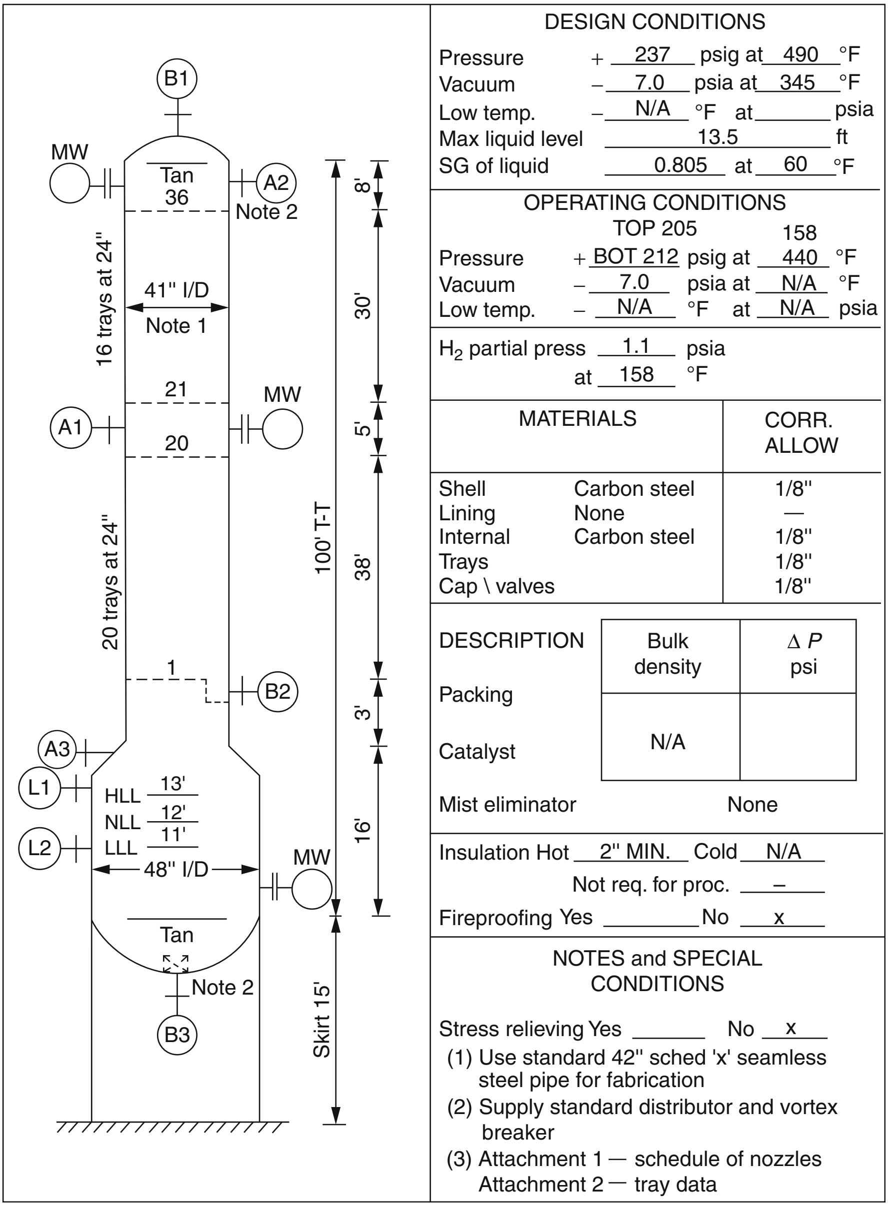
The drum design meets all necessary criteria.

Specifying Pressure Vessels

The process engineer's responsibility extends to defining the basic design requirements for all vessels. These data include:

- The overall vessel dimensions
- The type of material to be used in its fabrication
- The design and operating conditions of temperature and pressure
- The need for insulation for process reasons
- Corrosion allowance and the need for stress relieving to meet process conditions
- Process data for internals such as trays, packing, etc.
- Skirt height above grade
- Nozzle sizes, ratings, and location (not orientation)

Typical process data sheets used for specifying columns and horizontal drums are given in Figs. 11 and 12 (with their attachments in Fig. 13), respectively. These data sheets have been completed to reflect the examples calculated in this chapter. The following paragraphs describe and discuss the contents of these data sheets.



DESIGN CONDITIONS

Pressure + 237 psig at 490 °F
Vacuum – 7.0 psia at 345 °F
Low temp. – N/A °F at psia
Max liquid level 13.5 ft
SG of liquid 0.805 at 60 °F

OPERATING CONDITIONS

Pressure + TOP 205 BOT 212 psig at 158 440 °F
Vacuum – 7.0 psia at N/A °F
Low temp. – N/A °F at N/A psia

H_2 partial press 1.1 psia
at 158 °F

MATERIALS		CORR. ALLOW
Shell	Carbon steel	1/8"
Lining	None	—
Internal	Carbon steel	1/8"
Trays		1/8"
Cap \ valves		1/8"

DESCRIPTION	Bulk density	Δ *P* psi
Packing	N/A	
Catalyst		

Mist eliminator None

Insulation Hot 2" MIN. Cold N/A
Not req. for proc. –
Fireproofing Yes No x

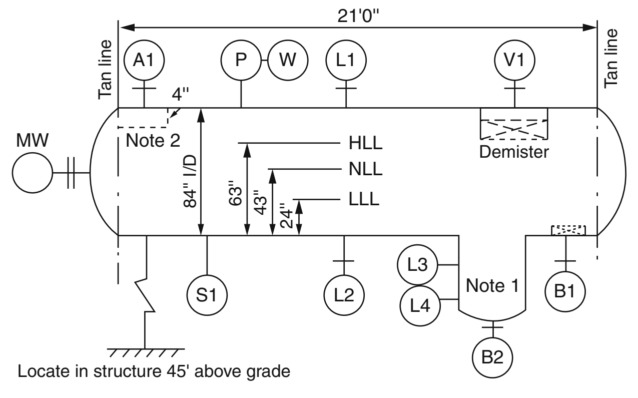
NOTES and SPECIAL CONDITIONS

Stress relieving Yes No x
(1) Use standard 42" sched 'x' seamless steel pipe for fabrication
(2) Supply standard distributor and vortex breaker
(3) Attachment 1 — schedule of nozzles
Attachment 2 — tray data

Fig. 11 A typical process data sheet for columns

The Vessel Sketch

This particular vessel (Fig. 11) is a light ends' fractionator and has a single tray diameter (i.e., it is not swaged). The tower contains 36 valve trays on a 24″ tray spacing and has a calculated diameter of 39″ for the trayed section.



DESIGN CONDITIONS	Pressure 50 psig H_2 Par press NIL psi Max liquid level 70 in.	Vacuum 7.5 psia Temperature 250 °F Design for steam out Yes x No
OPERATING CONDITIONS	Pressure 15 psig Normal liquid level 43 ins.	Temperature 100 °F
CORROSION ALLOWANCES	Shell ⅛ in., water boot ¼ in.	
MATERIALS	Shell CS Lining (Note 3) Mist eliminator: Yes	Internals CS Packing None
Type of packing	None	
Type of mist eliminator	Wire mesh min, 4 in. thick	Insulation Yes No x Fireproffing Yes x No
SG of liquid(s)	0.682 at 100 °F	Stress relieve Yes No x

Notes and ref. drawings

1. Supply 36" T-T x 24" I/D boot as shown
2. Splash distribution 8" SQ x 4" deep
3. Gunnite line to HLL (1½" thick) shell only. No lining in boot

Fig. 12 A typical process data sheet for horizontal vessels (drums)

This diameter will be specified as 41″ ID, however. This can be met by a standard 42″ schedule “X” pipe and this will reduce the cost of the vessel. The overall dimension for the tower is completed by setting the height of the tower from tan to tan. In the example here, this has been done as follows:

$$\text{Height of trayed section} = (\text{No. of trays} - 1.0) \times \text{tray spacing}. \qquad (55)$$

a

Ref	Description	Size, in inch	RTG
A 1	Feed inlet nozzle	6	150 RF
A 2	Reflux inlet nozzle	4	150 RF
A 3	Inlet from reboiler	6	300 RF
B 1	O/Head vapor outlet	8	150 RF
B 2	Outlet to reboiler	4	300 RF
B 3	Bottom product outlet	3	300 RF
L1 L2	Instrument nozzles	¾	300 RF
MW	Manways	24	150 RF

b

Vessel no	C401	
Vessel name	Reformate stabilizer	
Description of material	Unstabilized light hydrocarbons	
Section	Top trays 21–36	Bottom trays 1–20
Total trays in section	16	20
Max ΔP per tray, psi	0.25	0.25
Conditions on tray	Top Tray No 30	Bottom Tray No 1
Vapor		
Temp, °F	167	440
Pressure, psig	205	212
Density, lbs/cuft	1.69	2.0
Rate, lbs/hr	47,700	71,021
ACFS	7.83	9.81
Liquid		
Temp, °F	162	430
Viscosity, Cps	0.3	0.85
Density, lbs/cuft	27.3	38.2
Mole weight	57	100
Rate, lbs/hr	33,273	104,950
Rate, cuft/min	20.34	45.79
Tower diameter, ft	3′ 5″	
Number of tray passes,	One	
Type of tray	Valve	
Tray spacing, ins	24	

Fig. 13 (**a**, **b**) Attachments 1 and 2. Nozzle schedule and tray data sheet

The fractionation calculation has determined 36 actual trays for this tower. Thus, the trayed height is $(36 - 1) \times 24'' = 70$ ft.

Add another 3 f. to accommodate the feed inlet distributor on tray 20. Then total trayed height is 73 ft.

The bottom of the tower must accommodate the liquid surge requirement. As the tower diameter is relatively small, a swaged section of 4 f. diameter will be considered below the bottom tray for surge. The liquid product goes to storage; therefore, the surge requirement need not be more than 3 min on product.

From the unit's material balance, the bottom product is as follows:

Weight per hour = 117,513 lbs.
Temperature = 440°F.
Density at 440°F = 40 lbs/cuft.

Then hot cuft/min of product = 48.96.

The product goes to storage; therefore, only 2–3 min surge is required. This will be set at 3 min surge to NLL.

$$\begin{aligned} \text{Total surge to NLL} &= 48.96 \times 3 = 146.9 \text{ cuft.} \\ \text{Cross} - \text{sectional area of surge section} &= \pi/4 \times 4^2 \\ &= 12.6 \text{ sqft.} \\ \text{Height of NLL above tan} &= \frac{146.9}{12.6} \\ &= 11.7 \text{ ft, make it 12 ft.} \end{aligned}$$

Level range will be 24″; then, HLL will be 12 + 1 = 13 f. above NLL.

Let the reboiler inlet nozzle be 3 f. above HLL = 16 f. above tan.

Allow another 3 f. between reboiler inlet nozzle and bottom tray. This provides adequate space for vapor separation from the high liquid level.

At the top of the column space must be provided between the top tray and the top vapor outlet nozzle to accommodate the reflux return distributor and vapor disengaging from the top tray. Let this be 8 f. from top tray to the tower top tan line. Then,

Total tower height:

$$\begin{aligned} \text{From bottom tan to bottom tray} &= 19.0 \text{ ft.} \\ \text{The trayed section} &= 73.0 \text{ ft.} \\ \text{From top tray to top tan} &= 8.0 \text{ ft.} \\ \text{Total} &= 100.0 \text{ ft tan to tan.} \end{aligned}$$

These overall dimensions are now inserted on the vessel diagram as shown in Fig. 11. An attached sheet will be included to give the nozzle description, size, and flange rating referring to those shown in the small circles on the sketch. A schedule of flange ratings for carbon steel is given in Table 10. It is advisable to verify these values with the most recent code information.

Table 10 Schedule of flange ratings for carbon steel

Flange class, #	150#	300#	400#	600#	900#
Service temp, °F	Max operating pressure, psig				
100	275	720	960	1,440	2,160
150	255	710	945	1,420	2,130
200	240	700	930	1,400	2,100
250	225	690	920	1,380	2,070
300	210	680	910	1,365	2,050
350	195	675	900	1,350	2,025
400	180	665	890	1,330	2,000
450	165	650	870	1,305	1,955
500	150	625	835	1,250	1,875
550	140	590	790	1,180	1,775
600	130	555	740	1,110	1,660
650	120	515	690	1,030	1,550
700	100	470	635	940	1,410
750	100	425	575	850	1,275
800	92	365	490	730	1,100
850	82	300	400	600	900
900	70	225	295	445	670
950	55	155	205	310	465
1,000	40	85	115	170	255

The only other dimension that will be shown on the sketch is that of the skirt. Now the vessel is installed on-site supported by a metal skirt fixed to the concrete foundation of the vessel. The height of this skirt is fixed by a few criteria. If the product from the bottom of the tower is to be pumped (as is usual), the skirt height must be such as to accommodate the suction conditions for the pump. The most important of these conditions is the head required to meet the pump's net positive suction head (NPSH). See section "Pumps" of this chapter for details. Usually a skirt height of 15 f. meets most NPSH requirements. The second consideration dictating skirt height may be the head required by a thermosiphon reboiler. If the vessel is new and being designed, the skirt height of 15 f. remains adequate with properly designed piping to and from the reboiler.

Design Conditions

This particular tower operates at 212 psig and 440°F in the bottom and 205 psig and 158°F at the top. It is therefore classed as a pressure vessel and will be fabricated to meet a pressure vessel code. The most common of these codes is the ASME code either Section 1 or Section 8. Most vessels in the chemical industry are fabricated to ASME Section 8. When fabricated, inspected, and approved, it will be stamped to certify that its construction conforms to this pressure vessel code.

Among the data required by the code and for complete vessel engineering and fabrication are the design conditions of temperature and pressure for the vessel.

Table 11 Typical operating versus design pressures for vessels

Maximum:	
Operating pressure, psig	Design pressure, psig
Full or partial vacuum	50
0–5	50
6–35	50
36–100	Operating + 15
101–250	Operating + 25
251–500	Operating + 10 %
501–1,000	Operating + 50
Over 1,000	Operating + 5 %

Table 12 Typical operating versus design temperatures for vessels

Maximum:	
Operating temperature, °F	Design temperature, °F
Ambient −200	250
201–450	Operating + 50
Over 450	Divide into zones add 50 to each operating zone
Vessels	
Up to 225	250
226–600	Operating + 25
Over 600	Operating + 50
Minimum:	Minimum:
Operating temperatures, °F	Design temperatures, °F
15 to Ambient	Operating – 25
14–10	Operating−20
−10–80	Operating – 10
Below −80	Operating

Design Pressure

The design pressure is based on the maximum operating pressure at which the relief valve will open plus a suitable safety increment. Table 11 provides a guide to this increment.

In cases where vessels relieve to a flare header, it may be necessary to add a little more to the differential between operating and design pressures to accommodate for the flare back pressure.

Design Temperatures

Table 12 may be used as a guide to the max and min design temperatures. Some companies may use the maximum temperature which does not reduce the allowable stress values for design purposes. This avoids having to re-rate a vessel later.

Note: Very often companies will have their own standards for these design criteria. The table given here may be used if there are no company standards.

A vacuum condition can exist in a tower during normal steam out if the tower is accidentally shut in and the steam valve closed. Normally a design vacuum pressure of 7 psia is specified at the steam saturated temperature to cover this contingency. Some companies may also specify full vacuum rating if it does not create any other problems.

Low Temperature

This applies to towers in cryogenic services (such as demethanizers and LNG plants). There may be a situation in a non-cryogenic service where rapid depressurizing causes subzero temperatures to exist. If this is a situation that can exist for several hours and occurs frequently, this condition should be entered. Otherwise make an appropriate remark in “Notes and Special Conditions.”

Max Liquid Level

This is the liquid level under operating conditions that will:

Either activate the high liquid level alarm
Or shut down the feed pump.

Whichever system is applicable to protect the plant operation. Usually this is quoted as the HLL and 1–2 % of surge.

SG of Liquid

Quote this as the SG of the liquid on which the surge volume was based. This SG is usually quoted at 60 °F. If another temperature is used, be sure to include that temperature.

Operating Conditions

In most fractionation towers, there will be two distinctly different conditions of temperature and pressure – those for the tower top and those for the bottom of the tower. Both these conditions must be quoted in this case. The same situation may not necessarily arise in an absorption column.

Operating Temperatures and Pressures

Quote the calculated data as they will appear also on the process flow diagram. Show the tower top pressure and temperature first, followed by the bottom set of conditions. If the tower has been sized on data for more than one design case, show the highest numbers calculated for top and bottom. Also make a note in the “Notes and Special Conditions” section of the cases used as a basis.

Other Operating Data

Vacuum conditions in this case only apply if the tower operates normally at subatmospheric pressure. In this case, quote the lowest pressure the tower will be operated on together with the normal operating temperature(s). Note in many vacuum fractionators, there will be a spectrum of these conditions along the tower; these should be quoted for critical locations in the tower. Such locations would be feed inlet (flash zone), side stream, and pump-around, draw off, tower top.

Low temperatures and the associated pressure apply only to cryogenic plants in this case.

Hydrogen Partial Pressure

This item is important to the metallurgist who will select the grade of metal to be used in fabrication of the vessel. Generally the hydrogen partial pressure that will be quoted will be the one that exists at the tower top under normal operating conditions. For example, the dew point calculation used in the sizing of the tower given in Fig. 11 was based on the following tower top vapor composition.

	Mole fraction
H_2	0.005
C_1	0.021
C_2	0.117
C_3	0.378
iC_4	0.207
nC_4	0.268
iC_5	0.004
Total	1.000

The tower top pressure is 220 psia and the temperature is 158 °F.

$$\begin{aligned}\text{Hydrogen partial pressure} &= \frac{\text{moles } H_2}{\text{total moles gas}} \times \text{system pressure} \\ &= \frac{0.005}{1.0} \times 220 = 1.1\,\text{psia.}\end{aligned} \tag{56}$$

Materials and Corrosion Allowance

The process engineer, working with the materials engineer, will make an initial specification for the types of materials required to meet the process conditions. For example, where carbon steel only is to be used, the process engineer indicates “CS.” He is not normally required to state the grade of steel to be used; this is the responsibility of the vessel specialist or the metallurgist. However, if the process engineer has a special knowledge of the material to be used and its specifics, he should note it on the data sheet.

The same applies to the corrosion allowance. Normally 1/8″ is used for this allowance; however, there may be some mild corrosive condition existing which may justify using a higher number.

Description of Internals

This is self-explanatory when it refers to packed columns. In the case of trayed towers, a separate data sheet giving sufficient data for tray rating and sizing is attached to the process data sheet front page. This is shown in the attachments to Fig. 13.

Other common internals, such as distributors, vortex breakers, and the like, are not normally shown on this data sheet. These are normally standard to a particular design office and will be added to the engineering drawings developed from this process data sheet later.

Insulation and Fireproofing

The insulation requirement for heat conservation is specified by the process engineer as required. An approximate thickness is shown. This will be checked later by the vessel specialist. In the case of fireproofing, the process engineer indicates whether or not it is needed. The process engineer's relief valve sizing based on a fire condition takes into consideration any fireproofing specified.

Notes and Special Conditions

This item is a "catch all" and is used to make note of whatever other information the process engineer may wish to add to the data sheet to ensure the equipment item will meet the process requirements. The question of stress relieving of the vessel is an item which is most important to the proper fabrication of the vessel and to its cost. The process engineer usually has knowledge whether this is needed or not to handle the process material at the conditions specified. He must therefore indicate this in this section of the data sheet. Other entries in this item should be a list of the attachments to the data sheet.

Most of the process data used to define the requirements for a horizontal drum are the same as those applied to a column, and these have already been discussed for Fig. 11. The data included in the example given in Fig. 12 have been calculated earlier in this chapter. In the data sheet however, a "boot" measuring 2 f. ID × 3 f. high has been added to the outlet end of the vessel to accumulate the water phase for better control of its level and to allow the disengaging of the hydrocarbon from the water.

Pumps

Pumps in the petroleum and other process industries are divided into two general classifications which are

- Variable head-capacity
- Positive displacement

The variable head-capacity types include centrifugal and turbine pumps while the positive displacement types cover reciprocating and rotary pumps. Brief descriptions and some examples of each pump type follow.

The centrifugal pump

Centrifugal pumps comprise a very wide class of pumps in which pumping of liquids or generation of pressure is effected by a rotary motion of one or more impellers. The impeller or impellers force the liquid into a rotary motion by impelling action, and the pump casing directs the liquid to the impeller at low pressure and leads it away under a higher pressure. There are no valves in centrifugal-type pumps (except, of course, isolation valves for maintenance and check valves for backflow prevention); flow is uniform and devoid of pulsation. Since this type of pump operates by converting velocity head to static head, a pump impeller operating at a fixed speed will develop the same theoretical head in feet of fluid flowing regardless of the density of the fluid. A wide range of heads can be handled. The maximum head (in ft of fluid) that a centrifugal pump can develop is determined primarily by the pump speed (rpm), impeller diameter, and number of impellers in series. Refinements in impeller design and the impeller blade angle primarily affect the slope and shape of the head-capacity curve and have a minor effect on the developed head. Multistage pumps are available which will develop very high heads. This versatility in handling high-pressure head makes the centrifugal pump the most commonly used type in the process industry.

The turbine pump

A turbine or (regenerative turbine) pump is a type of centrifugal pump that uses an impeller with multiple, small blades running in an annular channel around the outside of a rotating wheel. Pumping is achieved by head impulses created by the rapidly spinning blades. This type of pump can also be used for pressure letdown or reduction and power recovery from high pressure systems. The actual energy that can be recovered in a power recovery service is about half the available horsepower. This type of pump is expensive and maintenance intensive, and is therefore not as widely used as the centrifugal pump.

The rotary pumps

Rotary pumps are positive displacement pumps. Unlike the centrifugal-type pump, these types do not throw the pumping fluid against the casing but push the fluid forward in a positive manner similar to the action of a piston. These pumps however do produce a fairly smooth discharge flow unlike that associated with a reciprocating pump. The types of rotary pumps commonly used in a process plant are:

- *The gear pump*. This pump consists of two or more gears enclosed in a closely fitted casing. The arrangement is such that when the gear teeth are rotated, they are unmeshed on one side of the casing. This allows the fluid to enter the void between gear and casing. The fluid is then carried around to the discharge side by the gear teeth, which then push the fluid into the discharge outlet as the teeth again mesh.
- *Screw pumps*. These have from one to three suitably threaded screwed rotors of various designs in a fixed casing. As the rotors turn, liquid fills the space between the screw threads and is displaced axially as the threads mesh.
- *Lobular pumps*. The lobular pump consists of two or more rotors cut with two, three, or more lobes on each rotor. The rotors are synchronized for positive rotation by external gears. The action of these pumps is similar to that of gear pumps, but the flow is usually more pulsating than that from the gear pumps.

- *Vane pumps*. There are two types of vane pumps: those that have swinging vanes and those that have sliding vanes. The swinging vane type consists of a series of hinged vanes which swing out as the rotor turns. This action traps the pumped fluid and forces it into the pump discharge. The sliding vane pump employs vanes that are held against the casing by the centrifugal force of the pumped fluid as the rotor turns. Liquid trapped between two vanes is carried around the casing from the inlet and forced out of the discharge.

Reciprocating pumps

These are positive displacement pumps and use a piston within a fixed cylinder to pump a constant volume of fluid for each stroke of the piston. The discharge from reciprocating pumps is pulsating. Reciprocating pumps fall into two general categories. These are the simplex type and the duplex type. In the case of the simplex pump, there is only one cylinder which draws in the fluid to be pumped on the back stroke and discharges it on the forward stroke. External valves open and close to enable the pumping action to proceed in the manner described. The duplex pump has a similar pumping action to the simplex pump. In this case however there are two parallel cylinders which operate on alternate stroke to one another. That is, when the first cylinder is on the suction stroke, the second is on the discharge stroke. In addition to duplex pumps, there are also reciprocating pumps with 3 or more cylinders.

Reciprocating pumps may have direct acting drives or may be driven through a crankcase and gearbox. In the case of the direct acting drive the pump piston is connected to a steam drive piston by a common piston rod. The pump piston therefore is actuated by the steam piston directly. Reciprocating pumps driven by electric motors, turbines, etc. are connected to the prime mover through a gearbox and crankcase.

Other positive displacement pumps

There are other positive displacement pumps commonly used in the process industry for special services. Some of these are:

Metering or proportioning pumps. These are small reciprocating plunger-type pumps with an adjustable stroke. These are used to inject fixed amounts of fluids into a larger stream or vessel.

Diaphragm pumps. These pumps are used for handling thick pulps, sludge, acid or alkaline solutions, and fluids containing gritty solid suspensions. They are particularly suited to this kind of service because the working parts are associated with moving a diaphragm back and forth to cause the pumping action. The working parts therefore do not come into contact with this type of fluid which would be harmful to them.

Characteristic curves

Pump action and the performance of a pump are defined in terms of their *characteristic curves*. These curves correlate the capacity of the pump in unit volume per unit time versus discharge or differential pressures. Typical curves are shown in Figs. 14, 15, and 16. Figure 14 is a characteristic curve for a reciprocating simplex pump which is direct driven. Included also is this reciprocating pump on a power drive.

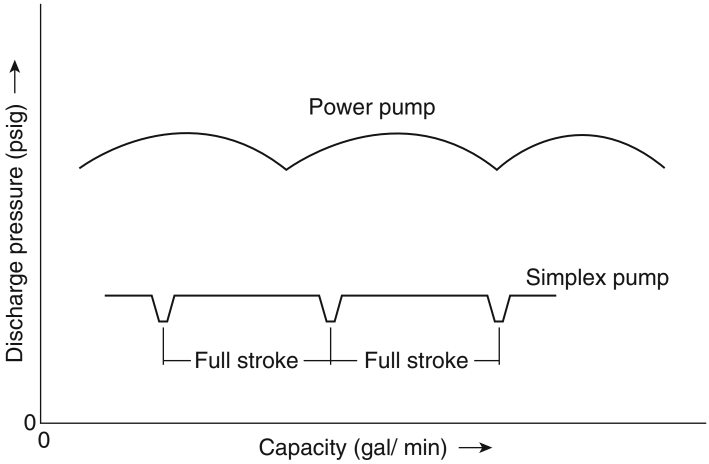


Fig. 14 Characteristic curves for a reciprocating pump

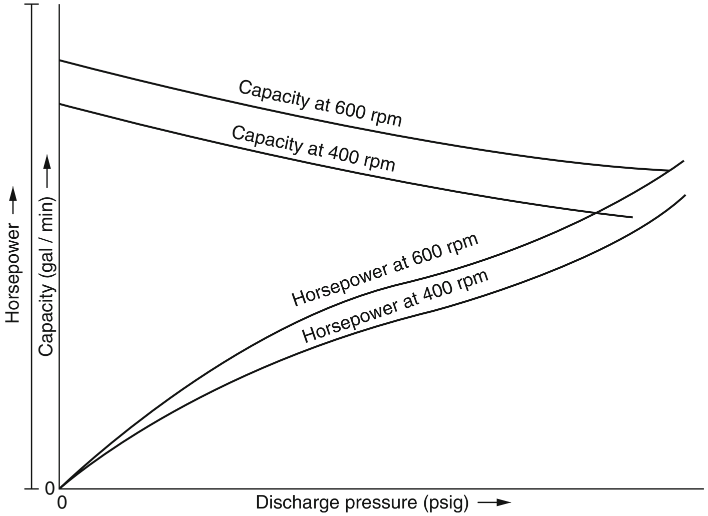


Fig. 15 Characteristic curves for a rotary pump

Figure 15 gives typical curves for a rotary pump. Here the capacity of the pump is plotted against discharge pressure for two levels of pump speed. The curves also show the plot of brake horsepower versus discharge pressure for the two pump speed levels.

Figure 16 is a typical characteristic curve for a centrifugal pump. This curve usually shows four pump relationships in four plots. These are:

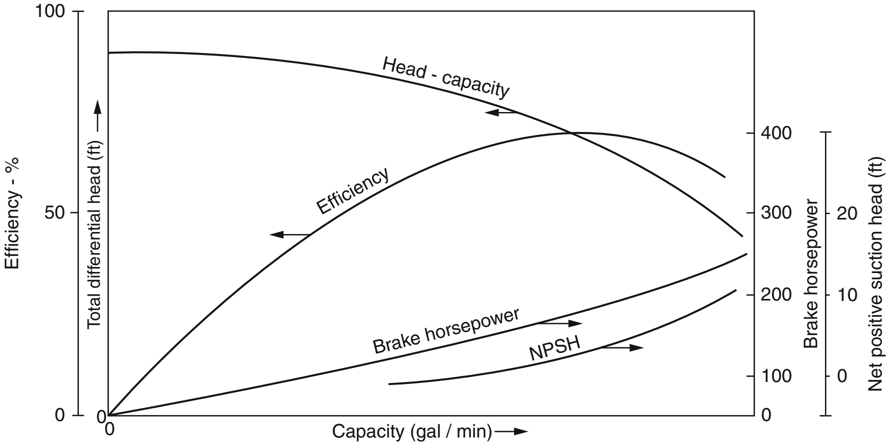


Fig. 16 Characteristic curves for a centrifugal-type pump

- A plot of capacity versus differential head. The differential head is the difference in pressure between the suction and discharge.
- The pump efficiency as a percentage versus capacity.
- The brake horsepower of the pump versus capacity.
- The net positive suction head (NPSH) required by the pump versus capacity. The required NPSH for the pump is a characteristic determined by the manufacturer.

Pump Selection

Most industrial pumping applications favor the use of centrifugal pumps. The prominence of this type of pump stems from its ability to handle a very wide spectrum of fluids at a large range of pumping conditions. It is fitting that in considering pump selection, the first choice has to be the centrifugal pump and all others become a selection by exception. Centrifugal pumps are generally the simplest in construction, lowest initial cost, and simplest to operate and to maintain. This discussion begins with the selection characteristics of the centrifugal-type pump.

The Centrifugal Pump

Before looking at the selection of the centrifugal pump, it is necessary to define the following terminology associated with pumps in general. These are:

- Capacity
- Differential head
- Available NPSH
- Required NPSH

Capacity. This can be defined as the amount of fluid the pump can handle per unit time and at a differential pressure or head. This is usually expressed as gallons per minute at a differential head of so many pounds per square inch or so many feet.

Differential head. This is the difference in pressure between the suction of the pump and the discharge. It is usually expressed as PSI and FEET in specifying a pump. The following formula is the conversion from PSI to feet:

$$\Delta H = \frac{2.31 \times \Delta P}{\mathrm{SG}} \tag{57}$$

where:

H = the differential head in feet of fluid being pumped.
ΔP = the differential pressure of the fluid across the pump measured in pounds per square inch.
SG = the specific gravity of the fluid at the pumping temperature.

Available NPSH. The available NPSH is the static head available (in feet or meters) above the vapor pressure of the fluid at the pumping temperature. This is a feature of the design of the system which includes the pump.

Required NPSH. Is the static head above the vapor pressure of the fluid required by the pump design to function properly? The required NPSH must always be less than the available NPSH.

Selection Characteristics

Selection of any pump must depend on its ability to handle a particular fluid effectively and the efficiency of the pump under normal operating conditions. The second of these primary requirements can be determined by the pump's characteristic curves. These have already been described earlier in this part of the chapter, and a further discussion on these now follows.

Capacity range

Normal

Figures 17 and 18 show the normal capacity range for various types of centrifugal pumps in two different speed ranges, 3,550 rpm and 2,950 rpm.

These values correspond to motor full load speeds available with current at 60 and 50 cycles, respectively. Most process applications call for these speed ranges. Lower speeds are for low or medium head and high-capacity requirements and for special abrasive slurries or corrosive liquids. Low-capacity centrifugal pump applications may require special recirculation provisions in the process design to maintain a minimum flow through the pump. Because of practical considerations in impeller construction, the smallest available process-type centrifugal pumps are rated at about 50 gpm.

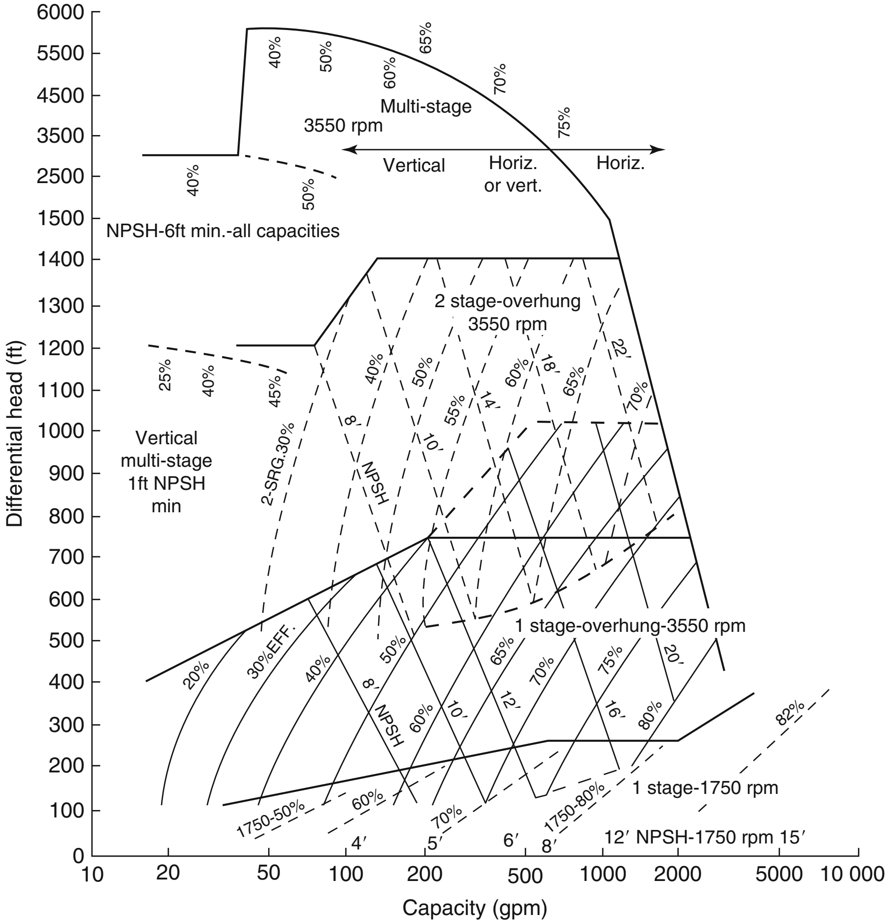


Fig. 17 Centrifugal pumps at 3,550 rpm

High- and low-capacity ranges

Pumps above the limits shown in Figs. 17 and 18 will normally require large horsepower drivers. Special investigation of efficiency, speed, NPSH requirements, etc., will normally be justified. As an example, heads at or above the limits shown for multistage pumps at standard motor speed may be obtained by speed-increasing gears (motor drive) or turbines to give pump operating speeds above maximum motor speeds (NPSH requirements increase with speed).

In general, centrifugal pumps should not be operated continuously at flows less than approximately 20 % of the normal rating of the pump. The normal rating for the pump is the capacity corresponding to the maximum efficiency point. Table 13 lists minimum desirable flow rates which should be maintained by continuous recirculation, if the required process flow conditions are of lower magnitude:

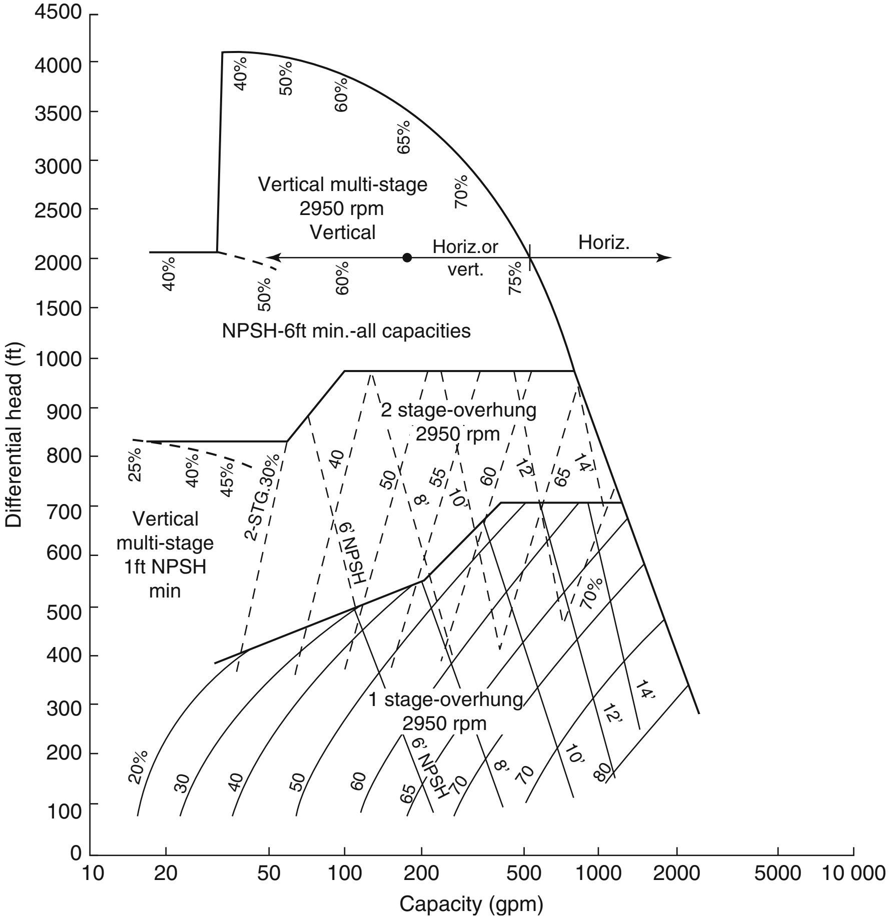


Fig. 18 Centrifugal pumps at 2,950 rpm. High- and low-capacity ranges

Care must be exercised in the design of any recirculation system to insure that the recirculated flow does not increase the temperature of pump suction and cause increased vapor pressure and reduction of available NPSH.

For low-head pumps that can operate at 1,750 or 1,450 rpm, the above-normal and minimum continuous capacities are reduced by 50 %.

Effect of liquid viscosity

When suitably designed, centrifugal pumps can satisfactorily handle liquids containing solids, dirt, grit, and corrosive compounds. Though fluids with viscosities up to 20,000 SSU (440 cSt) can be handled, 3,000 SSU (650 cSt) is usually the practical limitation from an economical operating standpoint.

Effect of suction head

An important requirement is that there be sufficient NPSH at the eye of the first-stage impeller. This is static pressure above the vapor pressure of the

Table 13 Centrifugal pump typical operating limits

Head range feet	Pump type	Minimum continuous capacity rating, gpm	Normal rating of pump, gpm
60 cycle speed (3,550 rpm)			
To 100	1 stg	10	60
100–350	1 stg	15	75–100
350–650	2 stg	30	150
650–1,100	2 stg	40	160
400–1,200	Multistg	15	50
1,200–5,500	Multistg	40	100–120
50 cycle speed (2,950 rpm)			
To 75	1 stg	10	50
75–250	1 stg	15	60–80
250–450	2 stg	25	120
450–775	2 stg	30	130
250–850	Multistg	10	40
850–3,800	Multistg	30	80–100

fluid handled to prevent vaporization at the impeller eye. Flashing of the fluid produces a shock or cavitation effect at the impeller which results in metal loss, noise, lowered capacity and discharge pressure, and rapid damage to the pump. NPSH requirements for various centrifugal pumps will normally vary from 6 to over 20 (in feet of fluid) depending on type, size, and speed. Vertical pumps can be built for practically no NPSH at all at the nozzle. These will have extended barrels in order to provide the required NPSH at the eye of the first-stage impeller.

Efficiency

The efficiency of centrifugal pumps varies from about 20 % for low-capacity (<20 gpm) pumps to a range of 70–80 % for high-capacity (>500 gpm) pumps. Extremely large capacity pumps (several thousand gpm) may have efficiencies up to nearly 90 %.

The rotary pumps

Rotary pumps deliver constant capacity against variable discharge pressure. This is a feature for all positive displacement pumps. Rotary pumps are available for process application over a range of 1–5,000 gpm capacity and a differential pressure up to about 700 psi. Displacement of the pump varies directly as the speed, except in the case where the capacity may be influenced by the viscosity of the fluid. In this case, thick viscous liquids may limit capacity because they cannot flow into the cylinder fast enough to keep it completely filled. Rotary pumps are used mostly in low-capacity service where the efficiency of a centrifugal pump would be very low.

Reciprocating pumps

The liquid discharge from reciprocating pumps is pulsating. The degree of pulsation is higher for simplex pumps than for the duplex type. The pulsation is also higher for direct-driven pumps than for those driven by motor or turbine through a gearbox.

Pulsation is generally not a problem in the case of small low speed pumps of this type. It affects only the associated instrumentation which can be compensated for by local dampeners. However, as the pump speed is increased, the pulsation effect becomes more serious affecting the piping design of the system. Under these conditions of high pulsation, instantaneous piping pressures may often exceed the design pressure of the piping. The piping must then be designed to meet this higher-pressure requirement which invariably results in a higher cost. As an alternative, discharge dampeners are often considered but these too add to the cost of the pump installation.

Reciprocating pumps are used mostly in situations where their low piston speeds will withstand corrosive and abrasive conditions. They are ideal also for pumping at low capacity against high differential head and where it is necessary to maintain a constant flow rate against a gradually increasing discharge pressure.

Evaluating Pump Performance

Many process engineers are involved with the day-to-day operation of process plants. Many of their duties in this respect are concerned with maintaining plant efficiency, locating trouble areas, and solving operational problems. This discussion is directed to these engineers and presents the calculation methods to check pump performance in terms of the pump horsepower and the available NPSH for a pump.

Brake Horsepower Efficiency

Actual running efficiency can be calculated from plant data. This may be compared with a typical expected efficiency to evaluate the pump performance. The steps below are followed to arrive at this efficiency figure.

Step 1. Obtain flow rate from plant readings. Also read discharge pressure and, if available, suction pressure. If this later reading is not available, calculate it from source pressure, height of liquid above pump suction, and frictional loss.

Step 2. Read stream temperature and obtain SG of stream from lab data. Calculate SG at flow conditions.

Step 3. Calculate differential head which is discharge pressure in PSIA − suction pressure in PSIA. Convert to differential head in feet by

$$\frac{\Delta P \times 144}{62.2 \times \mathrm{SG(at\ flow\ cond)}}. \tag{58}$$

Step 4. Convert feed rate to pounds per hour. Then calculate hydraulic horsepower from the expression

$$\frac{\mathrm{Head(ft)} \times \mathrm{rate(lbs/h)}}{60\,(\mathrm{min}) \times 33{,}000(\mathrm{ft-lbs/min})}. \tag{59}$$

Step 5. From motor data sheet, obtain pump motor running efficiency. From plant data read power usage in kW.

Step 6. Convert pump power to HP by dividing kW by 0.746. Multiply this by pump efficiency expressed as a fraction. This is the brake horsepower.

Step 7. Divide hydraulic horsepower by brake horsepower and multiply by 100 to give efficiency as a percentage.

Step 8. Check against Fig. 17 or 18 to evaluate pump performance. That is, the calculated efficiency within a reasonable agreement with the expected efficiency given by Fig. 17 or 18. You can also compare to the pump curve provided by the vendor, if available. Should there be a large discrepancy, the appropriate mechanical or maintenance engineers should be informed.

Checking Available NPSH

This needs to be done if the pump is showing signs of vibration and losing suction under normal operations.

Step 1. Obtain details of the fluid being pumped (temperature, SG, flow rate, source pressure, and vapor pressure of fluid).

Step 2. Calculate the frictional pressure drop in the suction line.

Step 3. Calculate the suction pressure of the pump by taking source pressure and adding in the static head. For this calculation, take static head as being from the bottom of the vessel (not from the liquid level).

Step 4. From the suction pressure calculated in step 3, take out loss through friction.

Step 5. Calculate NPSH available as being net suction pressure less vapor pressure. This is usually quoted in feet (or meters), so convert using

$$\frac{\mathrm{PSI} \times 144}{62.2 \times \mathrm{SG}} \tag{60}$$

Step 6. Check against manufacturer's data sheet for required NPSH. If the available NPSH is less than the required, the pump will continue to cavitate. Fill tank to a level that the vibration stops and maintain it at that level.

If the problem is really troublesome and maintaining a liquid level as suggested in step 6 above is not practical, contact the pump manufacturer. Very often he is able to make some minor changes to the pump design that will solve the problem.

Example Calculations

Example calculation No. 1 – pump brake HP efficiency:

$$\text{Flow capacity of pump at flow conditions} = 200\ \text{gpm}.$$
$$(\text{From plant data}) = 82,632\ \text{lbs/h}.$$

$$\begin{aligned}
\text{Suction pressure (plant data)} &= 120\ \text{psig.}\\
\text{Discharge pressure} &= 450\ \text{psig.}\\
\Delta\text{pressure} &= 330\ \text{psi.}\\
\text{SG at flow conditions} &= 0.827.\\
\text{Differential head ft} &= \frac{330 \times 144}{62.2 \times 0.827} = 924\,\text{ft.}\\
\text{Hydraulic horsepower} &= \frac{82{,}632 \times 924}{60 \times 33{,}000}\\
&= 38.56.
\end{aligned}$$

From motor rating, motor efficiency is 92 %.

Plant readings show motor power usage = 48.1 kW.

$$\begin{aligned}
\text{Then motor HP input} &= \frac{48.1}{0.746} = 64.5\,\text{HP.}\\
\text{Motor output} &= 64.5 \times 0.92\\
&= 59.3.
\end{aligned}$$

This is brake HP.

$$\text{Then pump efficiency} = \frac{38.56 \times 100\ \%}{59.3} = 65\ \%.$$

Motor is 50 cycle speed. From Fig. 18 for multistage 2,950 rpm. This efficiency figure is about right.

Example calculation No. 2 – checking available NPSH:

Fluid is gas oil from surge drum at 250 °F and 15 psig. Drum is 12 f. above grade (bottom of drum which is horizontal).

Boiling point at 34 psia is 488 °F.

Vapor pressure of gas oil at 250 °F = 0.8 psia (VP curves).

$$\begin{aligned}
\text{Source pressure} &= 29.7\ \text{psia.}\\
\text{SG at conditions} &= 0.815.\\
\text{Head above grade} &= 12\ \text{ft (to bottom of drum).}\\
\text{Pump center line} &= 2\ \text{ft above grade.}\\
\text{Liquid head to pump} &= 10\ \text{ft} \Rightarrow 3.5\ \text{psi.}\\
\text{Friction pressure drop} &= 0.4\ \text{psi (calculated from } 0.2\ \text{psi}/100\ \text{ft).}\\
\text{Less friction} &= 0.4\ \text{psi.}\\
\text{Less vapor press} &= 0.8\ \text{psi.}\\
\text{Available NPSH} &= 33.2 - (0.4 + 0.8) = 32\ \text{psia}\\
&= 91\ \text{ft.}
\end{aligned}$$

Most pumps only require 10 f. or less.

Specifying a Centrifugal Pump

In all engineering companies and in most petroleum refineries, two disciplines are responsible for correctly specifying a pump. These are the mechanical engineer and the process engineer. Most pumps are designed and built in accordance with set and accepted industrial codes, such as the API codes. The mechanical engineer ensures that the mechanical data supplied to the manufacturer for a particular pump meets the requirements of the code and standards to which the pump is to be built. The process engineer develops and specifies precisely the performance required of the pump in meeting the process criteria of the plant. To accomplish this, the mechanical engineer develops a mechanical specification, and the process engineer initiates the pump specification sheet.

Mechanical Specification

This specification is in a narrative form and will contain at least the following topics:

- Scope – introductory paragraph which gives the code to which the pump manufacturer is to conform (such as API 610).
- A list of other standards the pump shall conform to, if these are required.
- Main body of the specification – this covers all additions and any exceptions to the selected code. It provides for the type of drive shaft acceptable if different from code. Items such as impeller size as a percent of maximum allowable by code are given. The need for special bearing arrangements in the case of multistage pumps is detailed in this document.
- Ancillary equipment and piping arrangements – the specification describes in detail the type of cooling medium that shall be used. It provides a guide also to the piping requirements that is required to satisfy the cooling system(s).
- Seal or packing requirements – the mechanical specification details the type of seal or packing that will be installed. It also provides details of the seal arrangement required if this is different from the standard code.
- Pump mounting – some installation guidance is provided by this specification. The method by which the pump is mounted on the base plate is detailed. It also details under what conditions the manufacturer is to provide pedestal cooling facilities.
- Metallurgy – although the process engineer will call out the initial, expected material of construction for the pump (such as carbon steel or cast iron), it is the mechanical engineer who details this. This detail includes the specific grade of the material and in many cases its preoperational treatment.
- Inspection – the mechanical specification will provide details of the inspection that the company will carry out during the manufacture of the pump and before its delivery. This will include dimensional checking during manufacture and some checks on the metallurgy. Prior to shipping, the purchaser may require a running test of the pump and will witness this test. For this purpose, the pump is run in the workshop under specified process conditions.

The mechanical specifications may continue to detail other requirements that the purchaser may wish. Its objective is to ensure that the pump when delivered is mechanically robust, is safe, and is easily maintainable. The mechanical specification must also be aware of the cost implication of the requirements on the pump and to keep them as low as possible.

Process Specification

The data provided by the process engineer must be sufficient to ensure that the pump delivered for the process purpose will meet the duty required of it. These data are furnished to the pump manufacturer in the form of a data sheet similar to the one shown here as Fig. 19. The data sheet collects the essential input from the process engineer, the mechanical engineer, and, later, by the manufacturer to describe fully what is required of the pump and what the manufacturer has supplied. All the data given here will be unique to this pump.

The process input to the pump specification shown on Fig. 19 are those items marked with the "P." Input by other disciplines and the manufacturer are not indicated on the form. The process engineer compiles many of these data from a hydraulic analysis of the piping system (see Appendix 14 and section "Pressure Drop Calculations" of this chapter). A calculation sheet given in Fig. 20 shows the development of this and is described as follows:

Compiling the pump calculation sheet

The pump number, title, and service

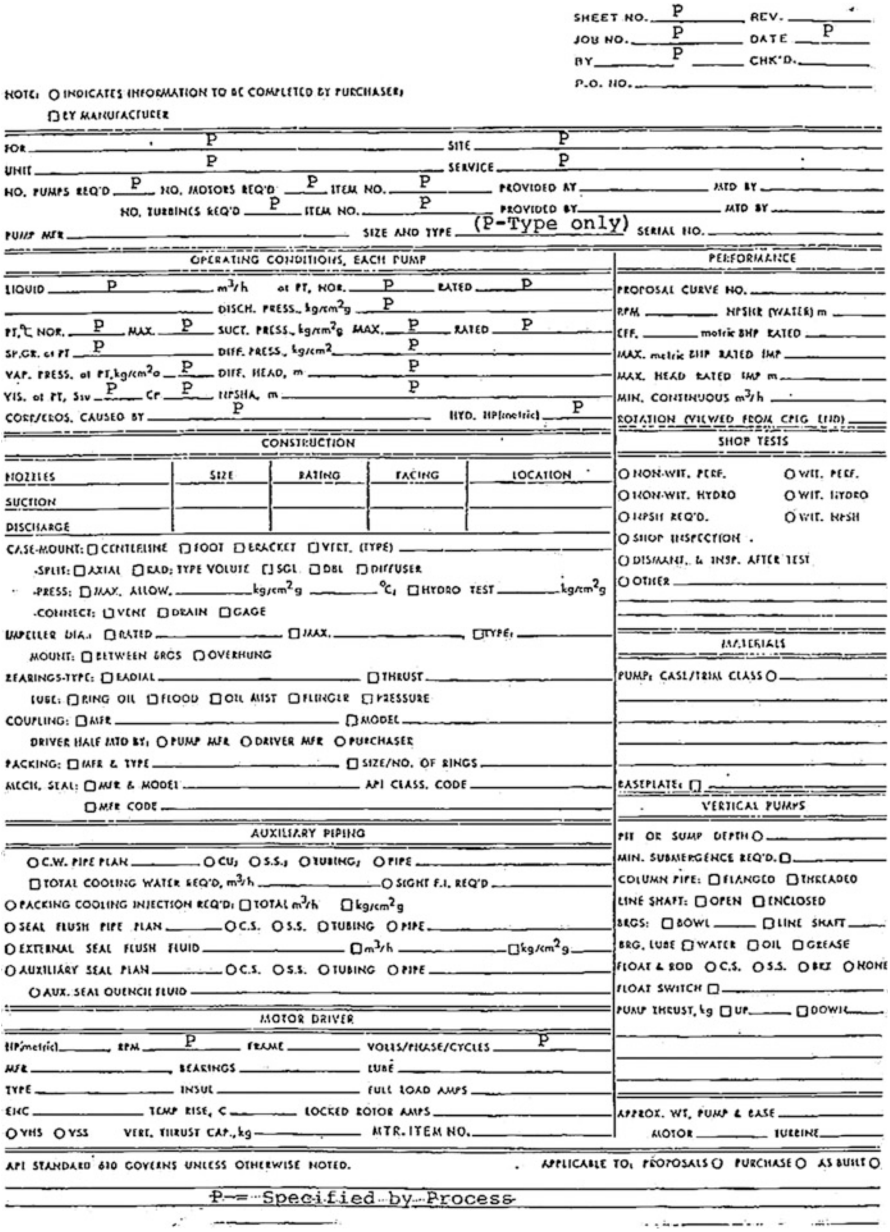
This first section of the calculation sheet is important because it identifies the pump and what it is intended to do. The item number and service description will be unique to this item and will remain as its identification throughout its life. All the data below this section will refer only to this pump and to no other. The item number may contain the suffix "A," "B," "C," etc. This indicates identical pumps in parallel service or as spare or both. This section also shows how many of these pumps are motor driven and how many are turbine (steam) driven. Usually spare pumps in critical service will be turbine driven. The remark column in this section should give any information that will be of benefit to the pump manufacturer or future operators of the pump. For example, if the spare pump is turbine driven, the process engineer may require an automatic start-up of the turbine on a "low flow" of the pumped stream. This should be noted here.

Operating conditions for each pump

The details of the fluid to be pumped and a summary of the calculations given below are entered here. Starting on the left of this section:

Liquid: This is a simple definition of the pumped material. In the example given here, this will simply be "vacuum gas oil."

Pumping temperature (*PT*): This is the temperature of the gas oil at the pump. There are two temperatures called for "normal" and "max." The normal



SHEET NO. P REV.
JOB NO. P DATE P
BY P CHK'D.
P.O. NO.

NOTE: ○ INDICATES INFORMATION TO BE COMPLETED BY PURCHASER;
☐ BY MANUFACTURER

FOR P SITE P
UNIT P SERVICE P
NO. PUMPS REQ'D P NO. MOTORS REQ'D P ITEM NO. P PROVIDED BY MTD BY
NO. TURBINES REQ'D P ITEM NO. P PROVIDED BY MTD BY
PUMP MFR SIZE AND TYPE (P-Type only) SERIAL NO.

OPERATING CONDITIONS, EACH PUMP

LIQUID P m^3/h at PT, NOR. P RATED P
DISCH. PRESS., kg/cm^2g P
PT, °C NOR. P MAX. P SUCT. PRESS., kg/cm^2g MAX. P RATED P
SP.GR. at PT P DIFF. PRESS., kg/cm^2 P
VAP. PRESS. at PT, kg/cm^2a P DIFF. HEAD, m P
VIS. at PT, Ssu P Cp P NPSHA, m P
CORR/EROS. CAUSED BY P HYD. HP(metric) P

CONSTRUCTION

NOZZLES	SIZE	RATING	FACING	LOCATION
SUCTION				
DISCHARGE				

CASE-MOUNT: ☐ CENTERLINE ☐ FOOT ☐ BRACKET ☐ VERT. (TYPE)
-SPLIT: ☐ AXIAL ☐ RAD; TYPE VOLUTE ☐ SGL ☐ DBL ☐ DIFFUSER
-PRESS: ☐ MAX. ALLOW. kg/cm^2g °C; ☐ HYDRO TEST kg/cm^2g
-CONNECT: ☐ VENT ☐ DRAIN ☐ GAGE
IMPELLER DIA.: ☐ RATED ☐ MAX. ☐ TYPE:
MOUNT: ☐ BETWEEN BRGS ☐ OVERHUNG
BEARINGS-TYPE: ☐ RADIAL ☐ THRUST
LUBE: ☐ RING OIL ☐ FLOOD ☐ OIL MIST ☐ FLINGER ☐ PRESSURE
COUPLING: ☐ MFR ☐ MODEL
DRIVER HALF MTD BY: ○ PUMP MFR ○ DRIVER MFR ○ PURCHASER
PACKING: ☐ MFR & TYPE ☐ SIZE/NO. OF RINGS
MECH. SEAL: ☐ MFR & MODEL API CLASS. CODE
☐ MFR CODE

AUXILIARY PIPING

○ C.W. PIPE PLAN ○ CU; ○ S.S.; ○ TUBING; ○ PIPE
☐ TOTAL COOLING WATER REQ'D, m^3/h ○ SIGHT F.I. REQ'D
○ PACKING COOLING INJECTION REQ'D: ☐ TOTAL m^3/h ☐ kg/cm^2g
○ SEAL FLUSH PIPE PLAN ○ C.S. ○ S.S. ○ TUBING ○ PIPE
○ EXTERNAL SEAL FLUSH FLUID ☐ m^3/h ☐ kg/cm^2g
○ AUXILIARY SEAL PLAN ○ C.S. ○ S.S. ○ TUBING ○ PIPE
○ AUX. SEAL QUENCH FLUID

MOTOR DRIVER

HP(metric) RPM P FRAME VOLTS/PHASE/CYCLES P
MFR BEARINGS LUBE
TYPE INSUL FULL LOAD AMPS
ENC TEMP RISE, C LOCKED ROTOR AMPS
○ VHS ○ VSS VERT. THRUST CAP., kg MTR. ITEM NO.

PERFORMANCE

PROPOSAL CURVE NO.
RPM NPSHR (WATER) m
EFF. metric BHP RATED
MAX. metric BHP RATED IMP
MAX. HEAD RATED IMP m
MIN. CONTINUOUS m^3/h
ROTATION (VIEWED FROM CPLG END)

SHOP TESTS

○ NON-WIT. PERF. ○ WIT. PERF.
○ NON-WIT. HYDRO ○ WIT. HYDRO
○ NPSH REQ'D. ○ WIT. NPSH
○ SHOP INSPECTION
○ DISMANT. & INSP. AFTER TEST
○ OTHER

MATERIALS

PUMP: CASE/TRIM CLASS ○
BASEPLATE: ☐

VERTICAL PUMPS

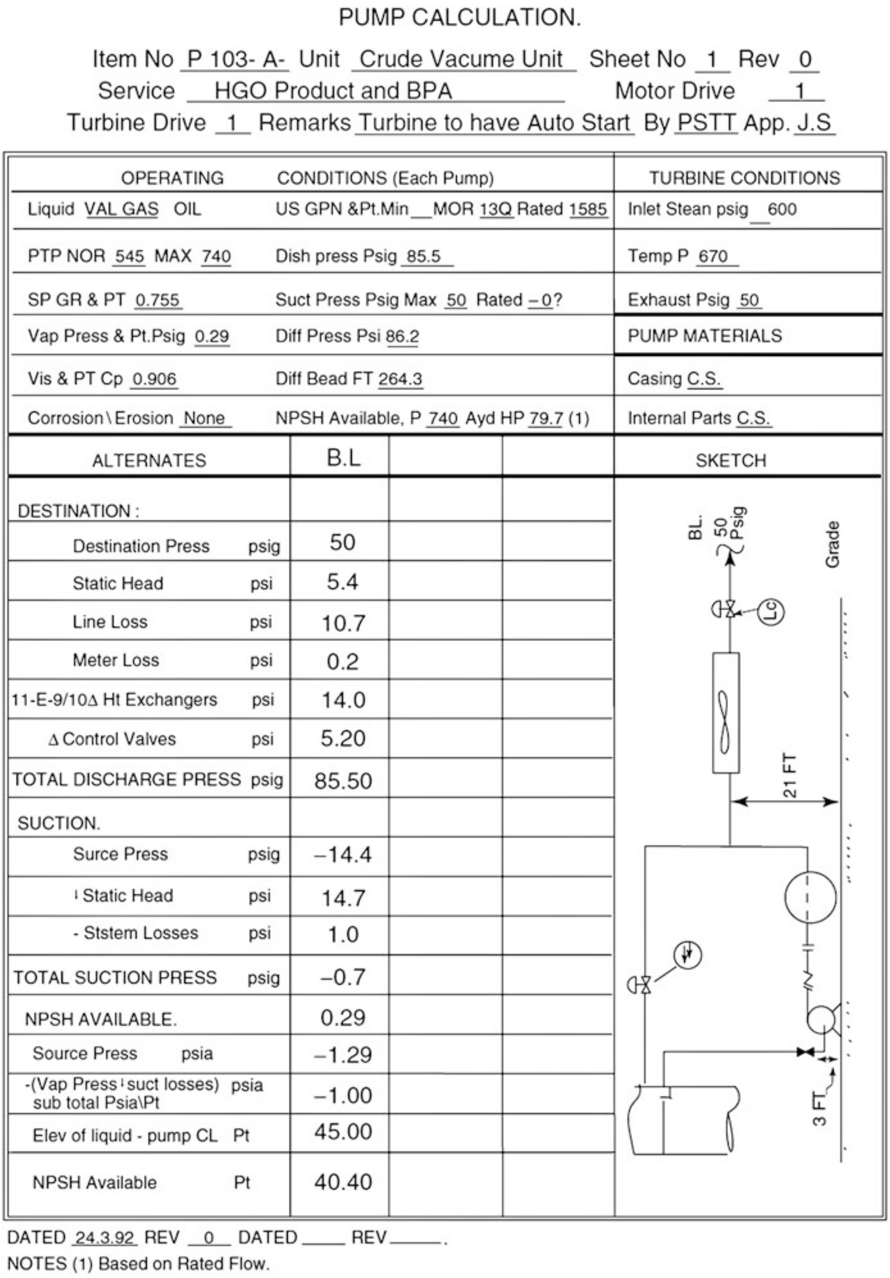
PIT OR SUMP DEPTH ○
MIN. SUBMERGENCE REQ'D. ☐
COLUMN PIPE: ☐ FLANGED ☐ THREADED
LINE SHAFT: ☐ OPEN ☐ ENCLOSED
BRGS: ☐ BOWL ☐ LINE SHAFT
BRG. LUBE ☐ WATER ☐ OIL ☐ GREASE
FLOAT & ROD ○ C.S. ○ S.S. ○ BRZ ○ NONE
FLOAT SWITCH ☐
PUMP THRUST, kg ☐ UP ☐ DOWN

APPROX. WT. PUMP & BASE
MOTOR TURBINE

API STANDARD 610 GOVERNS UNLESS OTHERWISE NOTED. APPLICABLE TO: PROPOSALS ○ PURCHASE ○ AS BUILT ○

P = Specified by Process

Fig. 19 A centrifugal pump specification sheet



PUMP CALCULATION.

Item No P 103- A- Unit Crude Vacume Unit Sheet No 1 Rev 0
Service HGO Product and BPA Motor Drive 1
Turbine Drive 1 Remarks Turbine to have Auto Start By PSTT App. J.S

OPERATING	CONDITIONS (Each Pump)	TURBINE CONDITIONS
Liquid VAL GAS OIL	US GPN &Pt.Min __ MOR 13Q Rated 1585	Inlet Stean psig 600
PTP NOR 545 MAX 740	Dish press Psig 85.5	Temp P 670
SP GR & PT 0.755	Suct Press Psig Max 50 Rated –0?	Exhaust Psig 50
Vap Press & Pt.Psig 0.29	Diff Press Psi 86.2	PUMP MATERIALS
Vis & PT Cp 0.906	Diff Bead FT 264.3	Casing C.S.
Corrosion\Erosion None	NPSH Available, P 740 Ayd HP 79.7 (1)	Internal Parts C.S.

ALTERNATES		B.L		
DESTINATION :				
Destination Press	psig	50		
Static Head	psi	5.4		
Line Loss	psi	10.7		
Meter Loss	psi	0.2		
11-E-9/10Δ Ht Exchangers	psi	14.0		
Δ Control Valves	psi	5.20		
TOTAL DISCHARGE PRESS	psig	85.50		
SUCTION.				
Surce Press	psig	–14.4		
ı Static Head	psi	14.7		
- Ststem Losses	psi	1.0		
TOTAL SUCTION PRESS	psig	–0.7		
NPSH AVAILABLE.		0.29		
Source Press	psia	–1.29		
-(Vap Press ı suct losses) sub total Psia\Pt	psia	–1.00		
Elev of liquid - pump CL	Pt	45.00		
NPSH Available	Pt	40.40		

SKETCH

DATED 24.3.92 REV 0 DATED ____ REV _____.
NOTES (1) Based on Rated Flow.

Fig. 20 A centrifugal pump calculation sheet temperature is that shown on the process flow diagram, while the max temperature is that used for the pump design conditions. It should be the same as the design temperature of the vessel the fluid is pumped from.

Specific gravity at *PT*: This is self-explanatory. Note the item also calls for the SG at 60 °F.

Vapor pressure at *PT*: This is read from the vapor pressure curves given in the Appendix 3 of this chapter. First locate the vapor pressure of the stream at atmospheric pressure (this is the material's normal boiling point). Follow the temperature line down or up to the PT and read off the pressure at that point.

Viscosity at *PT*: This too is self-explanatory. Note this calculation sheet requires the viscosity to be in *centipoise*. This is centistokes × SG.

US gpm at *PT*: This is the pump capacity and three rates are asked for. These are:

- *Minimum rate*: The anticipated lowest rate the pump will operate at for any continuous basis. This rate sets the control valve range.
- *Normal rate*: This is the rate given in the material balance and the basis for the hydraulic analysis.
- *Maximum rate*: This is normally set based on the type of service that the pump will undertake. For example, pumps used only as rundown to storage will have a max rate about 10 % above normal. Those used for reflux to towers will have between 15 % and 20 % above normal.

Discharge pressure, *psig*: This figure is calculated in the column below. It will also have been determined by the hydraulic analysis of the system (Appendix 14 and section "Pressure Drop Calculations" of this chapter).

Suction pressure, *psig*: Two pressures are asked for in this item. Rated pressure is that calculated in the column below and in the hydraulic analysis given in item 1. It is based on the "norm" rate. The "max" suction pressure is based on a source pressure at the *design* pressure rating of the vessel the pump is taking suction from.

Differential pressure, *psi*: This is the discharge pressure minus the rated suction pressure.

Differential head feet: The head is determined from the differential pressure by the equation:

$$\frac{\text{Diff press (psi)} \times 144}{62.2 \times \text{SG @ PT}}. \tag{62}$$

NPSH feet: Calculated in the column below. This is the suction head available greater than the fluid vapor pressure (at the PT) at the pump impeller inlet.

Hydraulic horsepower: This is calculated from the weight per unit time (usually minutes or seconds) of fluid being pumped times the differential head in feet divided by 550 f. lb/s or 33,000 f. lb/min. The differential head is always based on the rated suction pressure and the weight of the rated capacity (gpm) for this calculation.

Corrosion/erosion: The process engineer notes any significant characteristic of the fluid regarding its corrosiveness or abrasiveness here.

Turbine conditions

Although this item is not strictly part of a pump definition, it should be included for completeness in the case of turbine drives. The data required to complete this item is self-explanatory.

Pump material

The process engineer indicates here the expected acceptable material for the pump in handling the fluid. For example, carbon steel, or cast iron, etc.; it is not necessary to specify grade of steel, etc.

The calculation columns

The objective of this section of the calculation sheet is to itemize all the data that are used to provide the figures given in the operating conditions described in section "Operating Conditions for Each Pump" above. The first column lists those items while the other three columns are available for entering the corresponding numbers. These three columns are provided to cater to alternate conditions that may need to be studied. A space is left on the right of the form to sketch the pumping system (it is very advisable to do a sketch).

The first column starts with the destination pressure and continues down with the list of the pressure drops in the system to the pump discharge (see Appendix 14). This section of the column ends with the sum of the pressure drops giving the pump discharge pressure. The items that make up the pump suction pressure are listed next. This starts with the source pressure (usually a vessel) and its static head above the pump. All the pressure drops in the suction side are listed and deducted from the sum of the source pressure and static head to give the pump suction pressure.

The last section in the column itemizes the data that gives the *available* NPSH for the pump. The development of the NPSH is self-explanatory.

Centrifugal Pump Seals

A pump seal is any device around the pump shaft designed to prevent the leakage of liquid out of or air into a pump casing. All industrial pumps have shafts protruding through the casings which require sealing devices. Pump sealing devices are usually either a "packed box" with or without a lantern ring or a mechanical seal. Controlled leakage is a system sometimes used, but fugitive emissions regulations are phasing out this option.

A flushing stream may be introduced into the pump seals for one or more of the following reasons:

- To effect a complete seal
- To provide cooling, washing, or lubrication to the seal
- To keep grit from the seal
- To prevent corrosive liquid from reaching the seal

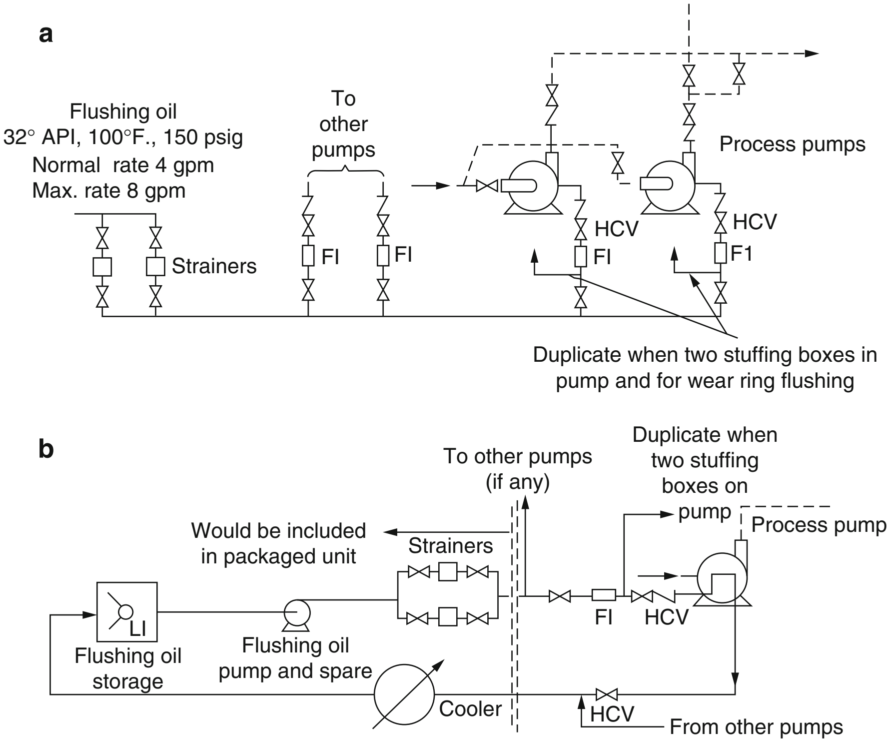


Fig. 21 Typical flushing systems. (**a**) A dead-end system, (**b**) a through – recirculating system

The facilities for accomplishing this are called "flushing system," and there are two types of these in general use.

- A dead-end system
- A through system

In a "dead-end" system, the flushing liquid enters the casing through the stuffing box and combines with the pumped fluid (see Fig. 21a). A "through" system is one in which the flushing liquid is recirculated between a double seal arrangement and does not enter the pump (see Fig. 21b). The liquid source may be external to the pump or, as on most mechanical seals, is a self-flushing system in which the pumped liquid is used as the flushing fluid.

A description of each of the types of sealing devices is presented below and illustrated in Fig. 22.

Packed boxes (*without lantern ring*) Fig. 22a

This is the simplest type of pump seal. Its principal components are a stuffing box, rings of packing, a throat bushing, and a packing gland. A slight leakage

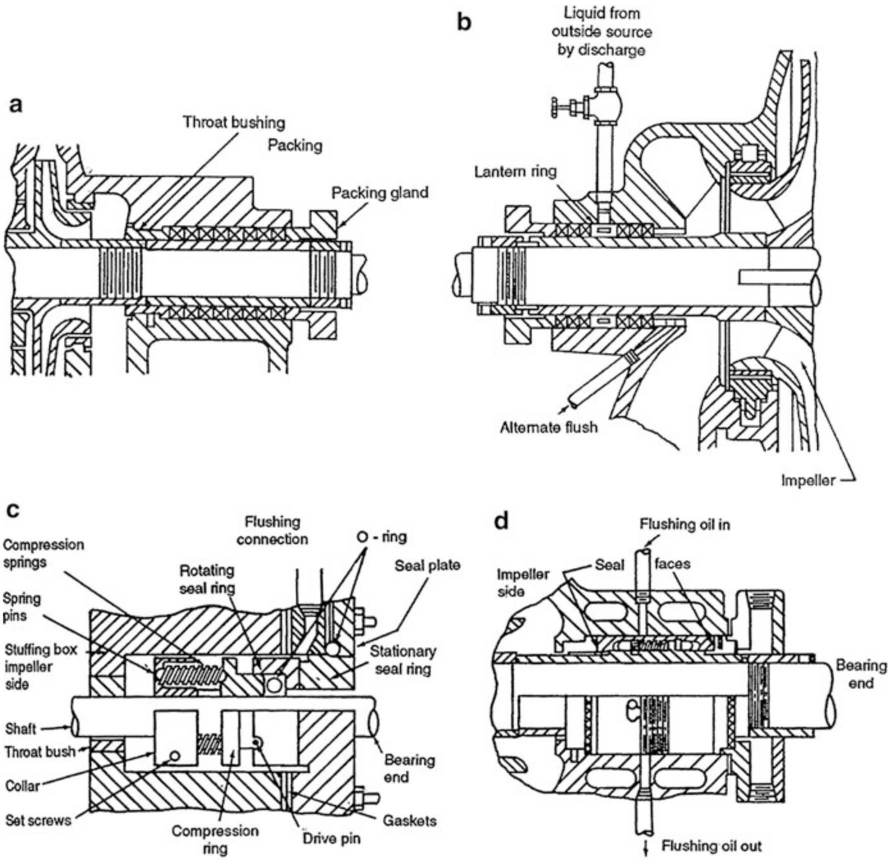


Fig. 22 Pump shaft packing and seals. (**a**) Stuffing box completely filled with packing no lantern ring. (**b**) Externally sealed stuffing box. (**c**) Single mechanical seal. (**d**) Double mechanical seal

through the packing is required at all times to lubricate the packing. A water quench is used at the packing gland if the packing "leakage" is considered flammable or toxic.

Packed box (*with lantern ring*) Fig. 22b

When a packed box pump seal is used in conjunction with a flushing oil system, a lantern ring is usually provided. This metallic ring provides a flow path for the flushing oil to reach the pump shaft. For very erosive or corrosive services, the lantern ring is often located next to the throat bushing and a liquid is injected into the throat bushing to prevent the pumped fluid from reaching the packing area. For a pump operation with vacuum suction conditions, the lantern ring is installed at the middle of the box and liquid is injected to prevent air entering the system. This type also operates with positive leakage with the same comments as the packed box without lantern ring.

Mechanical seals Fig. 22c, d

Typical basic elements of a single seal are shown in Fig. 22c. Sealing is affected between the precision-lapped faces of the rotating seal ring and stationary seal ring. The stationary seal ring is usually carbon and is mounted in the seal plate by an "O" ring. The two "O" ring packing serves the dual purpose of sealing off any liquid tending to leak behind the seal rings and also to provide flexibility in allowing the seal faces to align themselves exactly so as to compensate for any slight "wobble" of the rotating seal face caused by shaft whip.

The rotating seal ring is usually a stainless steel with a Stellite face. The springs furnish the necessary force to set the "O" ring and hold the seal faces closed under low stuffing box pressures. Any pressure in the box exerts additional force on the rotating sealing ring. The seal is frequently "balanced" so that the face pressure is in correct ratio to the liquid pressure to ensure adequate sealing without excessive loading of the faces. Flushing oil enters the stuffing box through a connection in the seal plate.

A double seal consists of two single seals back-to-back. See Fig. 22d. As a double seal is more expensive and requires a complicated seal-oil system, it is used where single seals are not practical. Regulations regarding fugitive volitile organic vapors (VOCs) are also driving most hydrocarbon applications toward double seals.

Figure 23 summarizes the application of the various sealing systems in the refinery operation.

Pump Drivers and Utilities

Most pumps in the process industry are driven either by electric motors, or by steam, usually in the form of steam turbines. The following discussion deals with the calculation of the driver requirements and driver specifications.

Electric Motor Drivers

Electric motors are by far the most common pump driver in industry. They are more versatile and are cheaper than a comparable size of steam turbine. The electric motors used for pump drivers are normally induction-type motors. They range in size from fractional horsepower to several thousand horsepower. Sizing the required motor for a pump driver takes into consideration the pump brake horsepower, the energy losses occurring in the coupling device between the pump and the motor, and a contingency factor of about 10 %. These are expressed by the equation:

$$\text{Minimum driver BHP} = \frac{\text{maximum pump BHP} \times 1.1}{\text{mechanical efficiency of coupling}}. \qquad (63)$$

If the pump is driven through a direct coupling, the efficiency will be 100 %. With gears or fluid coupling, the efficiency will be between 94 % and 97 %.

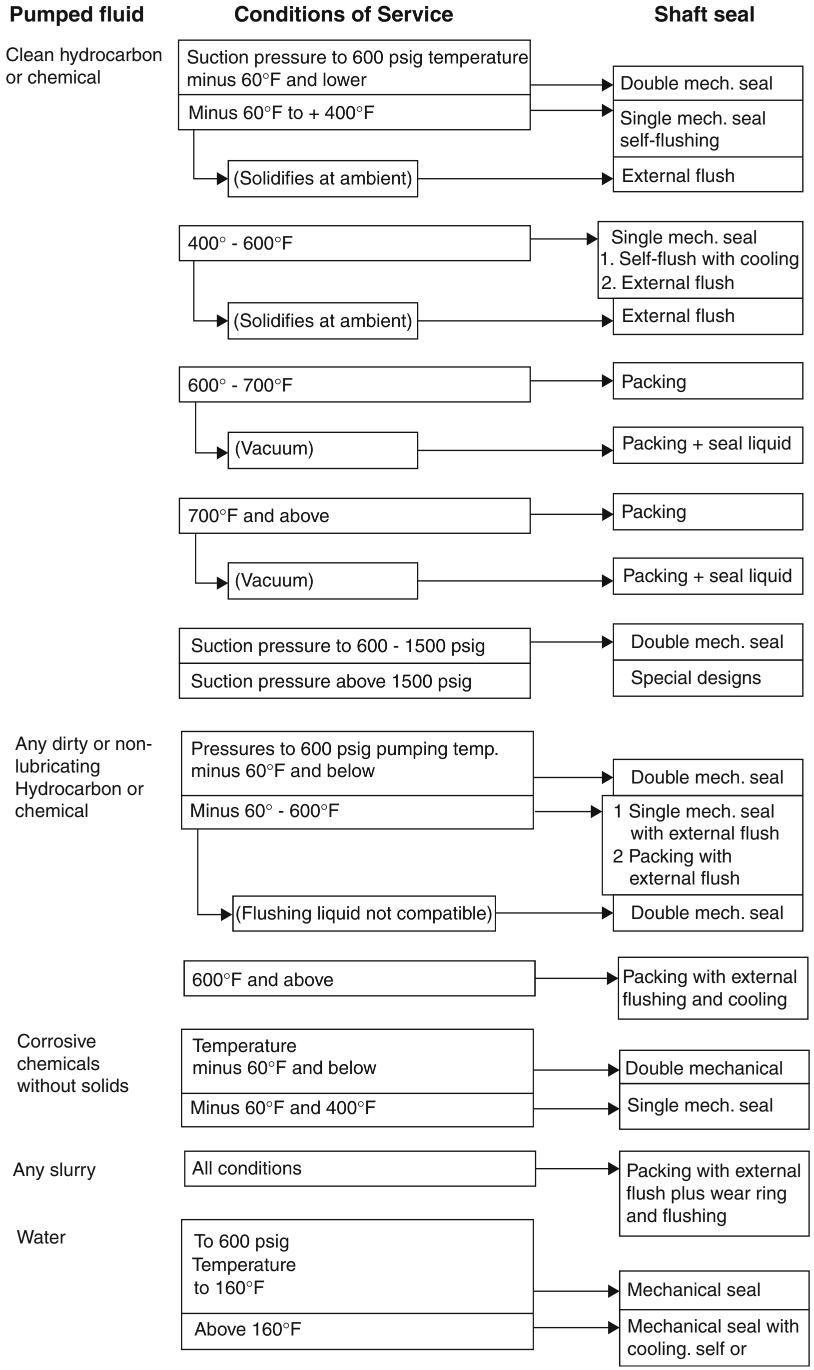


Fig. 23 Application of pump sealing systems

Specifying Motor Driver Requirements

Process engineers are called upon very often to specify pump driver requirements or to check those already existing. In doing this, two items of data need to be obtained or calculated. These are:

- The actual required horsepower of the pump motor to drive the pump at its specified duty
- What is actually installed in terms of horsepower?

These data are tabulated in terms of power load as follows:

Operating load, kW – power input to the motor a normal operating horsepower.
Connected load, kW – power input to the motor at motor-rated horsepower.

If the pump is spared by another motor-driven pump, then the connected load will be the sum of *both motors*.

$$\begin{aligned} \text{Operating load} &= \frac{\text{minimum required driver HP} \times 0.746}{\text{efficiency of the motor at its operating HP}}. \\ \text{Connected load} &= \frac{\text{rated motor HP} \times 0.746 \times \text{number of motors}}{\text{efficiency of the motors at } 100\,\%\text{ full load}}. \end{aligned} \tag{64, 65}$$

Table 14 gives example motor sizes and standard efficiencies at % of full load. (Higher efficiency and variable-speed motors may also be available.)

Example Calculation

Calculate the operating and connected loads for pump 11-P-3 A and B as specified in Fig. 20 of this chapter.

From the pump calculation sheet, the hydraulic horsepower is calculated:

$$\begin{aligned} \text{HHP} &= \frac{\text{lbs/min} \times \text{diff head in ft}}{33{,}000} \\ &= \frac{8{,}665 \times 264.3}{33{,}000} \\ &= 69.4\ \text{HP}. \end{aligned} \tag{66}$$

From Fig. 20 and assuming 60 cycle pump speed pump, efficiency is 79 %.

$$\begin{aligned} \text{Then brake horsepower} &= \frac{\text{hydraulic horsepower}}{0.79} \\ &= 87.8\ \text{HP}. \end{aligned} \tag{67}$$

This will be a direct-driven pump thus coupling efficiency is 100 %.

$$\text{Minimum motor size} = \text{BHP} \times 1.1 = 96.6\ \text{HP}.$$

Table 14 Electric motor size and efficiency

Motor rating BHP	Motor connected load, kW	Motor efficiency at % of full load		
		50	75	100
1	0.98	68	74	76
1.5	1.42	72	76.5	79
2	1.86	73	78	80
3	2.76	77.5	81.5	82
5	4.39	83	82	85
7.5	6.65	81	83.5	84
10	8.78	84	85	85
15	13.0	85	86	86
20	17.05	86.5	87.5	87.5
25	21.0	87.5	88.5	88.5
30	25.1	88	89	89
40	33.5	88	89	89
50	41.7	88	89.5	89.5
75	62.1	89	90	90
100	82.0	84	89	91
125	102.0	85	89.5	91.5
150	123.0	86	89	91
200	161.0	88	91	92.5
250	201.0	90.5	92.5	92.5
300	241.0	90.5	92.5	92.8
350	281.0	90.9	92.6	92.9
400	320.0	91.1	92.8	93.1
450	360.0	91.2	93	93.2

The closest motor size to this requirement is 100 HP (Table 14). This is a little too close so a motor size of 125 HP will be selected.

$$\text{Operating load} = \frac{\text{rated HP} \times 0.746}{\text{efficiency @ \% of full load.}} \tag{68}$$

$$\text{\% of full load} = \frac{87.8}{125} = 70.2\ \%.$$

Efficiency $= 89\ \%$ (from Table 14).

$$\begin{aligned} \text{Operating load} &= \frac{87.8 \times 0.746}{0.89} \\ &= 73.6\ \text{kW.} \end{aligned}$$

$$\begin{aligned} \text{Connected load} &= \frac{125 \times 0.746}{0.915} \\ &= 101.9\ \text{kW say } 102\ \text{kW.} \end{aligned}$$

Note if both regular and spare pumps were motor driven, then the connected load would be $2 \times 102 = 204\ \text{kW}$.

Reacceleration Requirement

To complete the specification for the motor requirement, a degree of process importance of the pump must be established and noted. Voltage drops that can occur in any system may be sufficient to stop the pump. The process engineer must determine how important it is to the process and the safety of the process to be able to restart and reaccelerate the particular pump quickly. The following code of importance has been adopted by some users.

- Reacceleration absolutely necessary – A
- Reacceleration desirable – B
- Reacceleration unnecessary – C

The "A" category involves any pump critical to keeping the process on stream safely and with no possibility of equipment damage. The "B" category applies to those pumps that in operation with the "A" category will maintain the unit "on spec." The "C" category refers to those pumps that can be started manually without any problems.

In the case of the example pump 11-P-3 A and B given here, the service required of the pump is so critical to the operation and orderly shutdown of the process in the case of power failure that the spare pump is turbine driven. Thus, the motor-driven regular pump need only be coded "C" for reacceleration.

Steam Turbine Drivers

Steam turbines are the second most common pump drivers in modern day process industry. Although more expensive than the electric motor, they offer an excellent standby to retain the maximum process "on stream" time. The one big disadvantage with power-driven pumps is the reliability of power availability. Steam turbines therefore offer a good alternative in cases of power failure. Another alternative means of pump drivers is the diesel engine or gas engine, but these require their own fuel storage and are certainly not as reliable as the steam turbine.

Most process plants therefore spare the critical pumps in the process with a turbine-driven unit which may be started automatically on low process flow.

The Principle of the Turbine Driver

Turbines are the most flexible of prime movers in today's industry. Their horsepower output can be varied by the number and size of the steam nozzles used, speeds can be changed readily, and high speeds without gearing are possible. They have a very wide range of horsepower applications. The operation of the steam turbine is analogous to that of a waterwheel where buckets are attached to the wheel which collect the water. The wheel is moved downward by the weight of the water collected and thus causes the rotation of the wheel. In steam turbines, the buckets are replaced by vanes which are impinged by the motive steam to cause the rotating motion. Turbines may consist of one set of vanes keyed to the shaft in the case of a single-stage machine or several sets of vanes in the case of multistage machines. These sets of vanes are called simply "wheels" and the number of stages is referred to as the number of wheels.

In the case of multistage turbines, the steam leaving the first wheel is directed toward a set of stationary vanes attached to the casing. These stationary vanes reverse the steam flow and serve as nozzles directing the steam toward the second wheel attached to the same shaft.

Most turbines used on a regular basis in a process plant are single stage. Multistage machines are more efficient but are also much more expensive. Their use therefore is for drivers requiring horsepower in excess of 300. The power industry is a good example for the use of large multistage turbine drivers. Single or multistage turbines may be operated either condensing or noncondensing. However, pump drivers should not be made *condensing* without a rigorous review to see if other types of drives can be used. The complexity of condensing is hardly worth the small savings in utilities that are made.

Performance of the Steam Turbine

The salient factors in the performance of the steam turbine are:

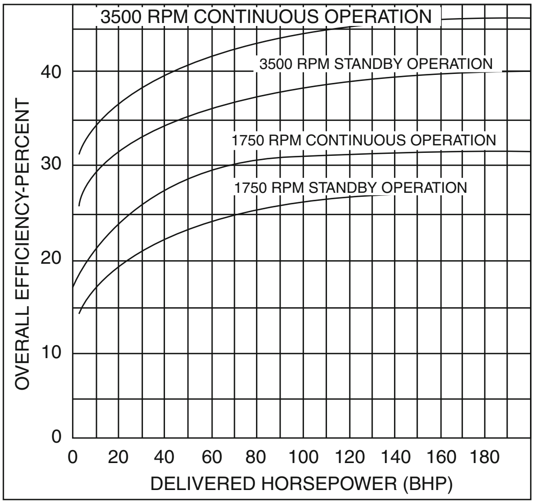
- Horsepower output
- Speed
- Steam inlet and outlet conditions
- Its mechanical construction (e.g., number of wheels, size of the wheel, etc.)

These factors are interrelated and their effect on the performance of the turbine is reflected by a change in overall efficiency. The *overall efficiency may be defined as the ratio of the energy output to the energy of the steam theoretically available at constant entropy as obtained from a Mollier diagram*. This overall efficiency is the product of mechanical and thermal efficiencies. The losses in turbines are partly due to friction losses of the rotating shaft and partly to thermodynamic losses and turbulence. Figure 24 gives the overall efficiencies plotted against delivered horsepower.

The steam required by a turbine for a given horsepower application is called its "water rate." The actual water rate for a turbine is supplied by the manufacturer from test runs carried out on the actual machine in the workshop. Plant operators and other engineers very often need to be able to estimate these water rates for their work. A typical situation arises when determining the best steam balance for a plant. Such estimates may be obtained from Fig. 25. This and the accompanying notes are self-explanatory.

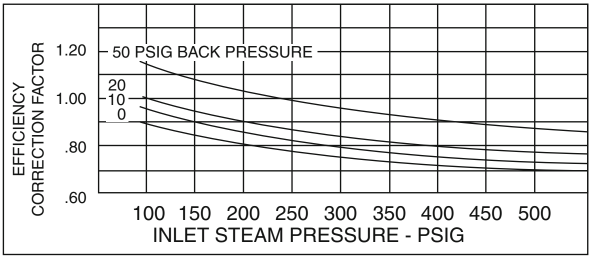
Cooling Water Requirements for Hot Pumps

Many pumps in process service require water cooling to various parts of the pump. This cooling water is applied to bearings, stuffing boxes, glands, and pedestals.



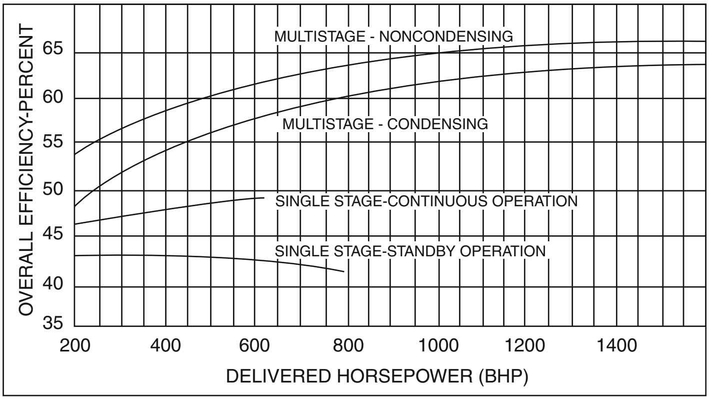
GRAPH 1

EFFICIENCY OF TURBINES AT IIO PSIG SAT STEAM INLET WITH 20 PSIG STEAM EXHAUST



GRAPH 2

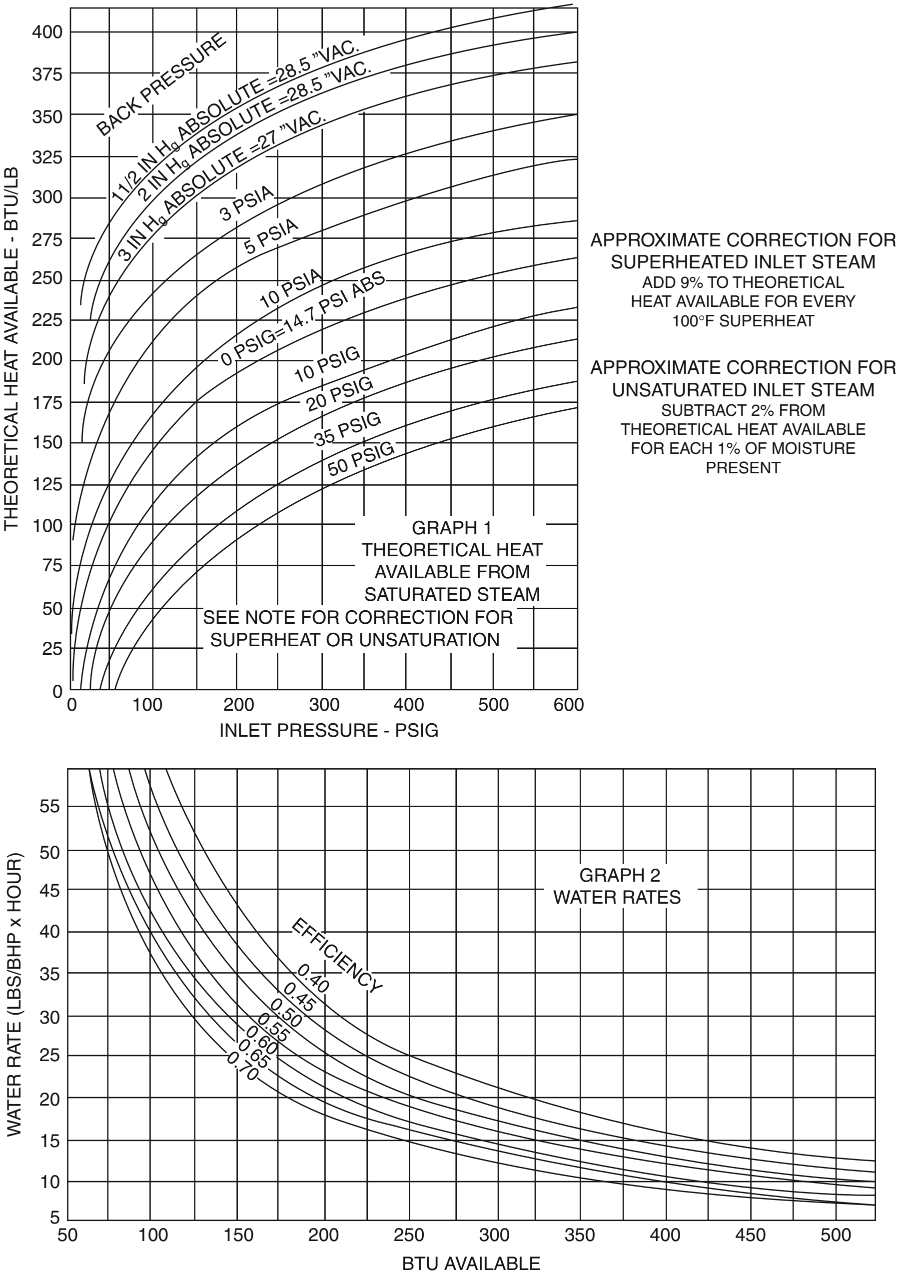
STEAM CONDITION CORRECTION FACTOR FOR GRAPH 1



GRAPH 3

EFFICIENCY OF HIGH HORSEPOWER TURBINES

Fig. 24 Steam turbine efficiencies



APPROXIMATE CORRECTION FOR SUPERHEATED INLET STEAM
ADD 9% TO THEORETICAL HEAT AVAILABLE FOR EVERY 100°F SUPERHEAT

APPROXIMATE CORRECTION FOR UNSATURATED INLET STEAM
SUBTRACT 2% FROM THEORETICAL HEAT AVAILABLE FOR EACH 1% OF MOISTURE PRESENT

Fig. 25 Water rates for condensing and noncondensing turbines

Table 15 Typical cooling water requirements for hot pumps

Temperature, pump or steam	Cooling water rate for pump size	
Pumps	To 1,000 gpm	Above 1,000 gpm
Up to 350°F	0 gpm	0 gpm
350–500°F	2 gpm	4 gpm
Above 500°F	3 gpm	6 gpm
Steam turbines		
Up to 450°F	0 gpm	0 gpm
Above 450°F	3 gpm	3 gpm

The application of the cooling water is determined by the manufacturer in accordance with his standard for the service and conditions that the pump must satisfy. Most of the cooling water may be recovered in a closed cooling water system. However, gland cooling water is never recovered but is routed to the wastewater drain. Table 15 lists some typical cooling water requirements for pumps and steam turbines. A vendor will eventually define the requirements for a specific piece of equipment purchased.

Compressors

Types of Compressors and Selection

Compressors are divided into four general types:

- Centrifugal
- Axial
- Reciprocating
- Rotary

The name given to each type is descriptive of the means used to compress the gas. A comparison of the different types of compressors and typical applications is shown in Table 17. A brief description of each of the types follows:

Centrifugal

This type of compressor consists of an impeller or impellers rotating at high speed within a casing. Flow is continuous and inlet and discharge valves are not required as part of the compression machinery. Block valves are required for isolation during maintenance or emergencies and discharge check valves are normally provided.

Centrifugal compressors are widely used in the petroleum, gas, and the chemical industries primarily due to the large volumes of gas that frequently have to be handled. Long continuous operating periods without an overhaul make centrifugal compressors desirable for use for petroleum refining and natural gas applications. Normally they are considered for all services where the gas rates are continuous and above 400 ACFM (actual cubic feet per minute) for a clean gas and 500 ACFM for a dirty gas. These rates are measured at the discharge conditions of the compressor. Dirty gases are considered to be gases similar to those from a catalytic cracker, which may contain some fine particles of solid or liquid material.

The slowly rising head-capacity performance curves make centrifugal compressors easy to control by either suction throttling or variable-speed operation. Spillback control is also common.

The main disadvantage of this type of compressor is that it is very sensitive to gas density, molecular weight, and polytropic compression exponent. A decrease in density or molecular weight results in an increase in the polytropic head requirement of the compressor to develop the required compression ratio.

Axial flow

These compressors consist of bladed wheels that rotate between bladed stators. Gas flow is parallel to the axis of rotation through the compressor. Axial flow compressors become economically more attractive than centrifugal compressors in applications where the gas rates are above 70,000 ACFM at *suction* conditions. The compressors are extremely small relative to capacity and have a slightly higher efficiency than the centrifugal. Axial flow compressors are widely used as air compressors for jet engines and gas turbines.

Reciprocating

Reciprocating compressors are widely used in the petroleum and chemical industries. They consist of pistons moving in cylinders with inlet and exhaust valves. They are cheaper and more efficient than any other type in the fields in which they are used. Their main advantages are that they are insensitive to gas characteristics and they can handle intermittent loads efficiently. They are made in small capacities and are used in applications where the rates are too small for a centrifugal. Reciprocating compressors are used almost exclusively in services where the discharge pressures are above 5,000 psig.

When compared with centrifugal compressors, the reciprocating compressors require frequent shutdowns for maintenance of valves and other wearing parts. For critical services this requires either a spare compressor or a multiple compressor installation to maintain plant throughput. In addition, they are large and heavy relative to their capacity.

Rotary

Recent developments in the rotary compressor field have opened up areas of application in the process industry with the use of the following types of rotary compressors:

1. *High-pressure screw*

   These compressors have been developed into heavy duty-type machines. They consist of two rotating helices in a casing without actual contact. Rotary compressors are lower in cost and have a higher efficiency than centrifugal compressors. They are not sensitive to gas characteristics since they are positive displacement machines. Parts are standardized production items so that a spare rotor is not generally required to be stocked for emergency replacement.

This compressor is noisy and sensitive to temperature rise along the screws due to the close clearances involved. They are good for fouling services where the fouling material forms a soft deposit. This decreases the clearances and leakage along the screws and casing. They are not recommended for use in fouling services in which the deposits are hard.

Variation in speed and a discharge bypass to suction are the only types of control that can be used.

2. *Low-pressure screw, lobe, and sliding vane*

   These compressors should be used only for low-pressure, light-duty, noncritical applications. They operate on the same principle as the high-pressure screw type but have different mechanical designs. The same advantages and disadvantages apply as those for rotary high-pressure screw compressors. They are even lower in cost than the high-pressure screw compressors but contain parts having limited life, thus requiring more maintenance.

   Only centrifugal and reciprocating compressors will be discussed further in this book.

Calculating Horsepower of Centrifugal Compressors

Centrifugal compressors are used in process service where high-capacity flows are required. A typical example is the recycle compressor for handling a hydrogen-rich stream in some oil refining and petrochemical processes. Tables 16, 17, and 18 give some idea of the centrifugal compressor capacity ranges and efficiencies.

In general the head or differential pressure levels served by centrifugal compressor are considerably lower than that for reciprocal. Figure 26 illustrates this feature.

Process engineers are often required to establish the capability of a centrifugal compressor in a particular service or to assess the machine's capability to handle a different service. In conducting these studies, it is necessary to determine the machine's horsepower under the study conditions. This item provides a procedure where the gas horsepower (and thereafter the brake horsepower) of a compressor can be calculated.

This procedure is as follows:

Step 1. Establish the duty required from the compressor in terms of:

- Capacity in cft/min at inlet conditions
- Design inlet temp
- Design inlet pressure
- The mole wt of the gas to be handled
- Compression ratio (P_2/P_1) P_2 being the discharge pressure and P_1 the inlet pressure

Table 16 Typical operating efficiencies and heads for centrifugal compressors

Centrifugal compressor flow range			
Nominal flow range (inlet acfm)	Average polytropic efficiency	Average adiabatic efficiency	Speed to develop 10,000 f. head/wheel
500–7,500	0.74	0.70	10,500
7,500–20,000	0.77	0.73	8,200
20,000–33,000	0.77	0.73	6,500
33,000–55,000	0.77	0.73	4,900
55,000–80,000	0.77	0.73	4,300
80,000–115,000	0.77	0.73	3,600
115,000–145,000	0.77	0.73	2,800
145,000–200,000	0.77	0.73	2,500

Step 2. Establish the “K” value for the gas. If this is a pure gas (such as oxygen), the “K” value can be read from data books. Otherwise, the “K” value is the ratio C_P/C_V. See Appendix 5 of this chapter. (*Note*: Do not confuse this “K” factor with equilibrium constants.)

Step 3. Calculate volume of the gas in SCF/min. This is the inlet CFM times inlet pressure times 520 divided by 14.7 psia times inlet temperature in °R, thus

$$\mathrm{SCFM} = \frac{1\ \mathrm{CFM} \times \text{inlet press} \times 520}{14.7 \times \text{inlet temp}\ ^\circ\mathrm{R}}. \tag{69}$$

Step 4. Calculate number of moles gas/min by dividing SCF/m by 378. Multiply number of moles by mole wt for lbs/min of gas.

Step 5. Read off the estimated discharge temperature from Fig. 27. Using this and the discharge pressure calculate the volume in cft/min at discharge.

Step 6. Calculate the density of gas at suction and discharge using the weight calculated in step 4 and the CFM for suction and the cft/min calculated in step 5 for discharge. This density will be in lbs/cuft.

Step 7. The average value for Z is taken as Z at suction + Z at discharge divided by 2. Z (compressibility factor) is calculated by the expression

$$Z = \frac{\mathrm{MP}}{T\rho_{\mathrm{v}} \times 10.73} \tag{70}$$

where:

M = mole weight.
P = pressure at psia.
T = °R (°F + 460).
ρ_V = density in lbs/cuft.

Step 8. Calculate the adiabatic head in ft lbs/lb using the expression

$$H_{\mathrm{ad}} = \frac{Z_{\mathrm{ave}} \times R \times T_{\mathrm{i}}}{(K-1)/K}\left[\left(\frac{P_2}{P_1}\right)^{(K-1)/K} - 1\right] \tag{71}$$

Table 17 Comparison of compressors and typical applications

Type and controllable range	Percent availability	Operating speed, volumetric capacity, compression ratio per stage[f]	Compression efficiency	Advantages	Disadvantages	Usual drivers	Common applications
Centrifugal 70–100 %	99.5–100 %[a]	3,000–15,000 RPM[b]	70–78 %	1. Long continuous operating periods	1. Pressure ratio is sensitive to gas density and molecular weight	Steam turbine	Large refrigeration system
		400–500 ACFM minimum at discharge		2. Low maintenance costs	2. Spare rotor required	Gas turbine	Cat cracker air
		150,000 ACFM max suction volume[d]		3. Small size relative to capacity		Electric motor	Reformer and hydroprocessing unit recycle gas
		80–100,000 ft. polytropic head per casing		4. Ease of capacity control		Waste gas expander	
Axial Flow 80–100 %	99.5–100 %	4,000–12,000 RPM[b]	75–82 %	1. Very high throughputs possible	1. Capacity flexibility limited by steep head-capacity curve and short stable operating range, except when variable pitch stators are used	Steam turbine	Cat cracker air (large)
		70,000 min. ACFM		2. Extremely small size	2. Performance and efficiency are sensitive to fouling	Gas turbine	

(*continued*)

Table 17 (continued)

Type and controllable range	Percent availability	Operating speed, volumetric capacity, compression ratio per stage[f]	Compression efficiency	Advantages	Disadvantages	Usual drivers	Common applications
				relative to capacity			
		2–4 compression ratio per casing		3. Higher efficiency than centrifugals	3. Spare rotor and spare stator blading are required	Electric motor	
				4. Good for parallel operation with other axials or centrifugals		Waste gas expander	
Reciprocating; See description for controllable range	98 % clean gas[c]	300–1,000 RPM	75–85 %	1. Handles intermittent loads efficiently	1. Short continuous operating periods require spare or multiple machine installations if service is critical	Synchronous motor	Instrument air
	95 % dirty gas[c]	5 max compression ratio or 330–380 °F max. discharge temperature		2. Lower cost for small capacities	3. Pulsation and vibration require engineered piping arrangement	Coupled or integral electric motor	Refinery air
	95 % clean gas[d]			3. Used for very high discharge pressures (up to 50,000 psig)	4. Availability decreases when non-lubricated machines required to avoid lubricating oil in gas discharge	Coupled or integral engine	Fuel gas

	93 % dirty gas[d]			4. Higher efficiency than centrifugal in lower capacity ranges			Synthesis gas
				5. Insensitive to gas characteristics			Crude gas
							Small hydroprocessing unit recycle gas
							Hydroprocessing unit makeup gas
							Small refrigeration system
Rotary high pressure screw 55–100 %	99–99.5 %	2,500–10,000 RPM	75–80 %	1. Lower cost than centrifugals	1. Noisy, require inlet and discharge silencers	Electric motor	Refinery air
		1,000–20,000 ACFM at suction		2. Higher efficiency than centrifugals	2. Sensitive to temperature rise due to close tolerances	Steam turbine	Fuel gas
		4–7 compression ratio max. per casing, but not exceeding 100 psi differential pressure		3. Not sensitive to gas characteristics	3. Not recommended for use where fouling produces hard deposits	Gas turbine	Cat cracker air (small)

(*continued*)

Table 17 (continued)

Type and controllable range	Percent availability	Operating speed, volumetric capacity, compression ratio per stage[f]	Compression efficiency	Advantages	Disadvantages	Usual drivers	Common applications
				4. Parts are standardized production items, so no spare rotor required	4. Speed or bypass control are only types applicable	Waste gas expander	
Low pressure screw, lobe-, and vane-type rotaries, fixed capacity	Not recommended for continuous service	1,500–3,600 RPM	75–80 %	1. Low first cost	1. Limited life	Electric motor	Low pressure, light duty, non-critical services
		100–12,000 ACFM suction		2. Low maintenance cost	2. Speed or bypass control are only types applicable	Steam turbine	
		2 compression ratio per stage with 50 psi max. discharge pressure		3. Parts are standardized production so no spare rotor is required	3. Very noisy		

[a] Clean service machines have the highest reliability
[b] Large machines run at lower speeds
[c] Between turnarounds of 3 days every 8–12,000 h with electric drive. 95–98 % includes 8 h shutdowns every few months for valve maintenance
[d] Between turnarounds of 2 weeks every 8–12,000 h with engine drive. 93–95 % includes 8 h shutdowns every month for maintenance checks on compressor valves and engine driver
[e] Axial flow compressors should be considered at gas rates above 70,000 ACFM at suction
[f] Stages can be compounded in series for higher rates and pressures

Table 18 Centrifugal compressor categories by head and capacity

	Speed, RPM	Suction, ACFM	Polytropic head, ft lb/lb
Small standard multistage	3,000–3,600	100–1,000	to 8,500
Standard single stage	3,000–3,600	700–60,000	1,000–6,700
Special single stage	3,000–15,000	1,000–60,000	6,700–11,500
Special multistage casing, uncooled	3,000–15,000	1,000–140,000	6,700–100,000
Special multistage, multi-casing, intercooled	3,000–15,000	2,500–140,000	37,000 up

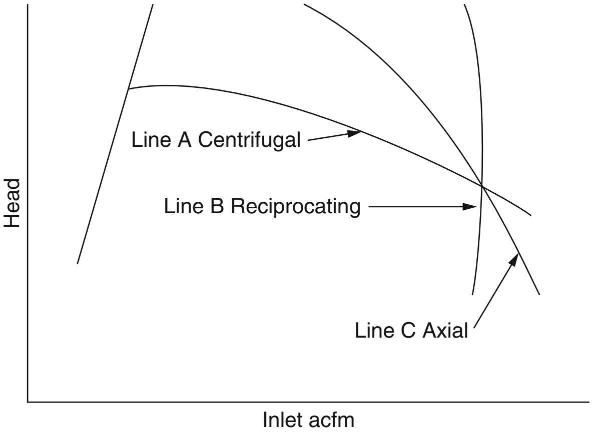


Fig. 26 Head-capacity relationships for difference compressor types

where:

H_{ad} = the adiabatic head in ft lbs/lb.
Z_{ave} = average compressibility factor.
R = gas constant =1,545/mole wt.
K = adiabatic exponent C_P/C_V.
P_2 = discharge pressure psia.
P_1 = suction pressure psia.
T = inlet temperature °R.

Step 9. The gas HP is obtained using the expression

$$\mathrm{HP} = \frac{W \times H_{ad}}{\eta_{ad} \times 33,000} \tag{72}$$

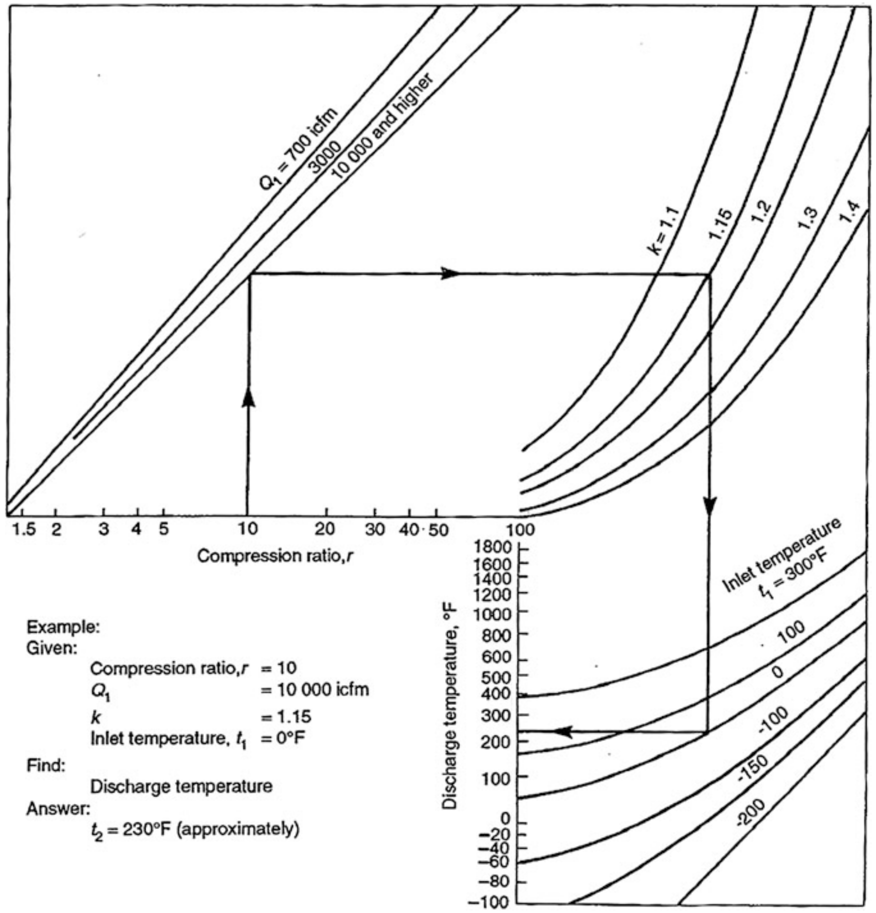
where:

W = weight in lbs/min of gas.
H_{ad} = adiabatic head in ft lbs/lb.
η_{ad} = adiabatic efficiency (0.7–0.75).

Step 10. Check GHP using Fig. 28.

An example calculation now follows:

Example calculation



Example:
Given:
Compression ratio, r = 10
Q_1 = 10 000 icfm
k = 1.15
Inlet temperature, t_1 = 0°F
Find:
Discharge temperature
Answer:
t_2 = 230°F (approximately)

Fig. 27 Estimated discharge temperatures for centrifugal compressors

Determine the Gas HP of a centrifugal compressor assuming isentropic compression:

Compression ratio = 10.0.
Capacity (actual inlet CF/min) = 10,000.
$K_{\text{ave}} = 1.15$.
T_1 °F = 100.
P_1 psia = 100.
Mole wt = 30.
Lbs/min = 5,013.

For isentropic compression

$$H_{\text{ad}} = \frac{Z_{\text{ave}} \times R \times T_{\text{i}}}{(K-1)/K}\left[\left(\frac{P_2}{P_1}\right)^{(K-1)/K} - 1\right] \tag{73}$$

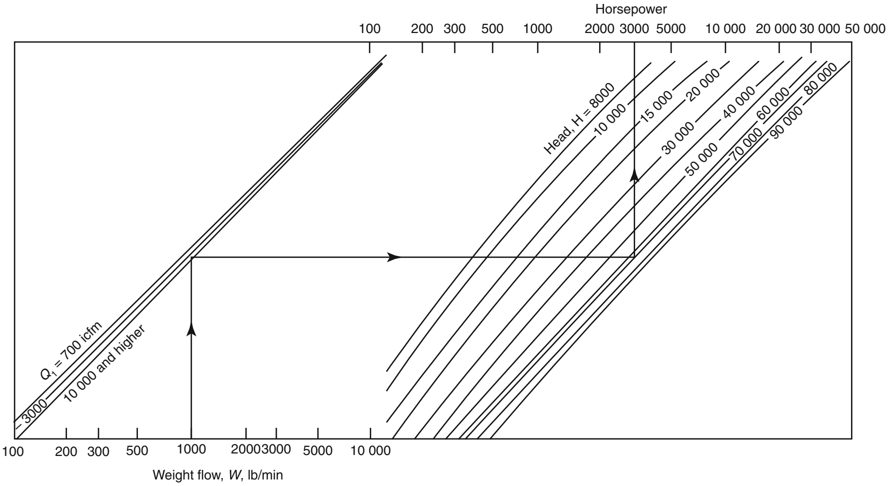


Fig. 28 Determination of centrifugal compressor horsepower

where:

H_{ad} = adiabatic head in ft lbs/lb.
Z = compressibility factor (avg).
R = gas constant =1,545/MW.
K = adiabatic exponent $C_P/C_V = 1.15$.
T = temperature in °R = °F + 460 °F.
P_2 = discharge pressure psia.
P_1 = suction pressure psia.

Z at inlet conditions:

$$\rho_V = 0.5 \text{ lbs/cuft}$$

$$Z = \frac{\text{MP}}{T\rho_V} \times 10.73 = \frac{30 \times 100}{560 \times 0.5} \times 10.73 = 0.998.$$

Estimated discharge temp (Fig. 27) = 400 °F.

$$Z_{\text{dis}} = \frac{30 \times 1,000}{860 \times 3.26} = 0.997.$$

Use 0.998.

$$H_{ad} = \frac{0.998 \times 51.5 \times 560}{\frac{0.15}{1.15}} \left[\left(\frac{1.000}{100} \right)^{0.13} - 1 \right]$$

$$= 220,664\ (1.349 - 1).$$

$$= 77,004 \text{ ft lbs/lb}$$

$$\text{Gas HP} = \frac{W \times H_{ad}}{\eta_{ad} \times 33,000}.$$

Let η_{ad} be 0.75.

$$\frac{5,013 \times 77,004}{0.75 \times 33,000} = 15,598 \text{ GHP}.$$

This compares well with the estimate based on Fig. 28.

Centrifugal Compressor Surge Control, Performance Curves, and Seals

Centrifugal compressors can be counted on for uninterrupted run lengths of between 18 and 36 months after the initial shakedown run. The 18-month run corresponds to a compressor handling dirty gas, such as furnace gas, and the 36-month run corresponds to a clean gas service, such as refrigerant.

Spare compressors are not usually provided. A spare rotor, however, is required to be stocked as insurance against an extended downtime. Since this rotor is part of the capital cost of the equipment, it is not accounted for as spare parts. Only reliable drivers such as an electric motor, steam, or gas turbine can be used where long continuous run lengths are required. In the case of steam and gas turbines, the drivers will probably dictate the maximum possible run length. The high operating speed of a centrifugal compressor also favors the selection of these types of high-speed drivers. The speed of these drivers can be specified to be the same as those of the compressor. For electric motor drives, a speed-increasing gear is normally required. Centrifugal compressors can be broadly classified with regard to head and capacity as shown in Table 18.

As a guide, the maximum head per impeller is about 10,000 ft. Normally, about eight impellers can be used in a casing.

The minimum allowable volume of gas at the compressor discharge is about 400 ACFM for a clean gas and 500 ACFM for a dirty gas. Dirty gases are considered to be similar to the gas from a steam or catalytic cracking unit.

The discharge temperature is limited to about 250 °F for gases that may polymerize and 400 °F for other gases. Normally intercoolers will be used to keep the discharge temperature within these limits. These temperature limitations do not apply to special centrifugal flue gas recirculators which can be obtained to operate at over 800 °F. There is also a temperature rise limitation of about 350 °F per casing. This is the maximum temperature rise that can be tolerated due to thermal expansion considerations.

Use of cast iron as a casing material is limited to 450 °F maximum. Temperatures of –150 °F to –175 °F can be tolerated in conventional designs. Lower temperatures are not common and will require consulting on individual design features.

Surge

A characteristic peculiar to centrifugal and axial compressors is a minimum capacity at which the compressor operation is stable. This minimum capacity is

Table 19 Typical surge points for centrifugal compressors

Wheels/compression stage	% of normal capacity at surge – maximum
1	55
2	65
3 or greater	70

Table 20 Typical maximum increases in pressure ratio from normal to surge for centrifugal compressors

Wheels/compression stage	Minimum % of rise in pressure ratio from normal to surge flow
1	$3\frac{1}{2}$
2	6–7
2 or greater	$7\frac{1}{2}$

referred to as the surge or pumping point. At surge, the compressor does not meet the pressure of the system into which it is discharging. This causes a cycle of flow reversal as the compressor alternately delivers gas and the system returns it.

The surge point of a compressor is nearly independent of its speed. It depends largely on the number of wheels or impellers in series in each stage of compression. Reasonable reductions in capacity to specify for a compressor are shown below (Table 19).

An automatic recirculation bypass is required on most compressors to maintain the minimum flow rates shown. These are required during start-up or when the normal load falls below the surge point. Cooling is required in the recycle circuit if the discharge gas is returned to the compressor suction.

Performance Curves

The rise of performance curves should be specified for a compressor. This is normally done by specifying the pressure ratio rise to surge required in each stage of compression. A continuously rising curve from normal flow rate to surge flow is required for stable control.

The pressure ratio rise to surge is largely a function of the number of impellers per compression stage. Reasonable pressure ratio rises to specify are shown in Table 20.

Frequently, the performance curves for a compressor have to be plotted to determine if all anticipated process operations will fit the compressor and its specific speed control. Three points on the head-capacity curve are always known. These are the normal, surge, and maximum capacity points. The normal capacity is always considered to be on the 100 % speed curve of the compressor. The surge point and the compression ratio rise to surge have been specified. From this the head produced by the compressor at the surge point can be back calculated using the head-pressure ratio relationship. The maximum capacity point is specified to be at least 115 % capacity at 85 % of normal head.

The head-capacity curve retains its characteristic shape with changes in speed. Curves at other speeds can be obtained from the three known points on the 100 % speed curve by using the following relationships:

1. The polytropic head varies directly as the speed squared.
2. The capacity varies directly as speed.
3. The efficiency remains constant.

Figure 29 shows a typical centrifugal compressor performance curve.

Control

Speed

Speed control is the most efficient type of control from an energy consideration. It requires, however, that a variable-speed driver, such as a steam turbine or gas turbine, or a variable-speed electric motor be used. The compressor is controlled by shifting its performance curve to match the system requirements.

Suction Throttling

- *Adjustable inlet guide vanes*. Adjustable inlet guide vanes are the most efficient method of adjusting the capacity of a constant speed compressor to match the system characteristics. They consist of a venetian blind device that is positioned by a rack and pinion linkage. While the guide vanes do some throttling, their main effect is to change the velocity of the gas to that of the impeller vane by changing the direction of flow. This changes the head produced and in effect changes the characteristic of the machine.
- *Suction throttle*. This control consists of a control valve located in the compressor suction which regulates the suction pressure to the compressor. The control valve results in a greater power loss compared to adjustable inlet guide vane control since it is a pure throttling effect. Suction throttle valves are lower in cost than adjustable inlet guide vanes.

Discharge throttling

This control consists of a control valve located in the compressor discharge. Discharge throttle valves are seldom used since they offer relatively little power reduction at reduced capacity. The effect is simply to “push” the compressor back on its curve.

Seals

Table 21 shows the types of seals that are commonly used in centrifugal compressors. The start-up as well as the operating conditions of the compressor should be considered in selecting a seal. Often the system is evacuated when hydrocarbons are handled prior to its start-up. This requires that the seal be good for vacuum conditions.

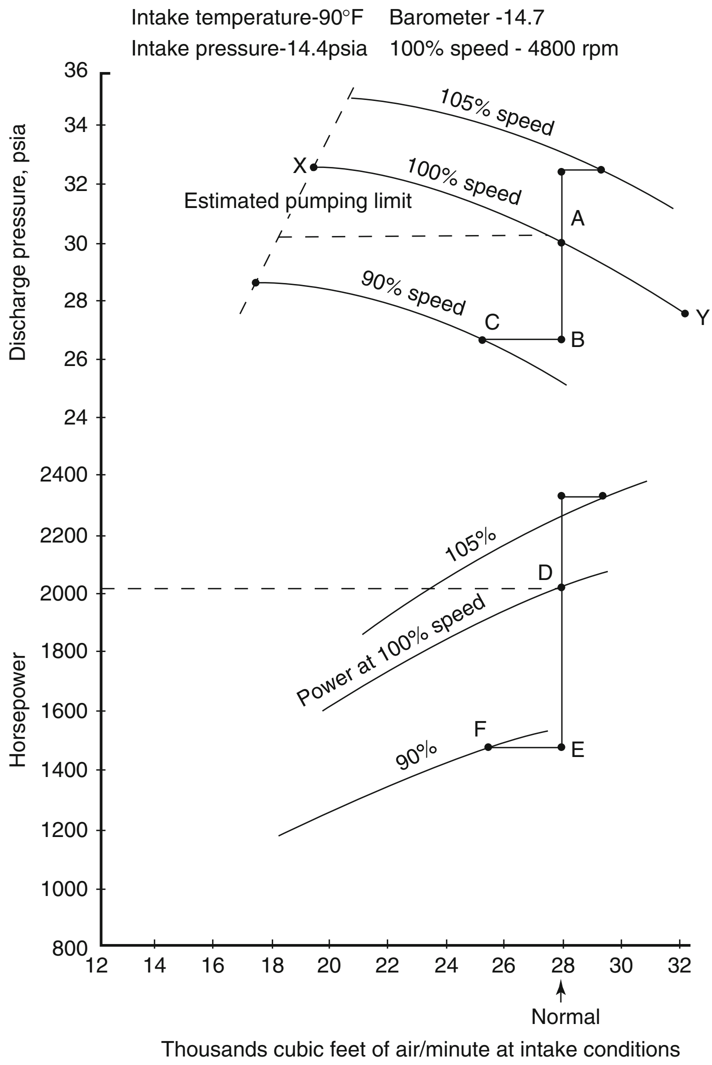


Fig. 29 An example of a centrifugal compressor performance curve

Specifying a Centrifugal Compressor

The process specification must give all the information concerning the gas that is to be handled, its inlet and outlet conditions, the utilities that are available, and the service that is required of the compressor. The process specification sheet for a centrifugal compressor will be similar to that shown in Fig. 34 for a reciprocating compressor. An explanation of this specification now follows covering each of the items in the specification.

Table 21 Centrifugal compressor seals

No	Application	Gas being handled	Inlet pressure, psia	Seal arrangement
1	Air compressor	Atmospheric air	Any	Labyrinth
2	Gas compressor	Noncorrosive	Any	Labyrinth
		Nonhazardous		
		Non-fouling		
		Inexpensive		
3	Gas compressor[a]	Noncorrosive or	10–25	Labyrinth with injection or ejection of fluid being handled
		Corrosive		
		Nonhazardous or		
		Hazardous		
		Non-fouling or fouling		
4	Gas compressor	Noncorrosive	All pressures	Oil seal combined with lube oil system Labyrinth gas seal
		Nonhazardous		
		Non-fouling		
5	Gas compressor	Corrosive	All pressures	Oil seal with seal oil separate from lube oil system
		Nonhazardous or hazardous		Labyrinth gas seal

[a] Where some gas loss or air induction is tolerable

Title Block

This requires the item to be identified by item number and its title. The number of units that the specification refers to is also given here. For a centrifugal compressor, this will normally be just one as very seldom is a spare machine required.

Normal and Rated Columns

More often than not, the conditions and quantities required to be handled will vary during the operation of the machine. The two (or more) columns therefore will be completed showing the average normal data in the first column and the most severe conditions and duty required by the compressor in the second. The severe conditions in column two are for a continuous length of operation not instantaneous peaks (or troughs) that may be encountered.

Gas

The composition and gas stream identification must be included as part of the process specification. Usually the composition of the gas is listed on a separate sheet as shown in the example. Note in many catalytic processes that utilize a recycle gas, the composition of the gas will change as the catalyst in the process ages. Thus, it will be necessary to list the gas composition at the start of the run (SOR) and at the end of the run (EOR).

The compressor may also be required to handle an entirely different gas stream at some time or other. This too must be noted. For example, in many petroleum refining processes, a recycle compressor normally handling a light predominately hydrogen gas is also used for handling air or nitrogen during catalyst regeneration, purging, and start-up.

Volume Flow

This is the quantity of gas to be handled stated at 14.7 psia and 60 F.

Weight Flow

This is the weight of gas to be handled in either lbs/min or lbs/h.

Inlet Conditions

Pressure: This is the pressure of the gas at the inlet flange of the compressor in psia.

Temperature: This is the temperature of the gas at the inlet flange of the compressor.

Mole weight: The mole weight of the gas is calculated from the gas composition given as part of the specification.

C_p/C_v: This is the ratio of specific heats of the gas again obtained from the gas mole wt and Appendix 5 of this chapter.

Compressibility factor (z): Use the value at inlet conditions calculated as shown in step 7 of section "Calculating Horsepower of Centrifugal Compressors" in this handbook chapter.

Inlet volume: This is the actual volume of gas at the conditions of temperature and pressure existing at the compressor inlet. Thus,

$$\text{ACFM} = \frac{\text{SCFM} \times 14.7 \times (\text{inlet temp F} + 460)}{(60\text{ F} + 460) \times \text{inlet press psia}}. \tag{74}$$

Discharge Conditions

Pressure: This is the pressure at the compressor outlet flange and is quoted in either psia or psig.

Temperature: This is estimated using Fig. 27.

C_p/C_v: This will be the same as inlet.

Adiabatic efficiency: This will be as given in Fig. 30.

Approximate Driver Horsepower

This item will include the adiabatic (or gas) horsepower as calculated in the section on calculating the horsepower of centrifugal compressors in this chapter plus the following losses:

Leakage loss – 1 % of adiabatic HP
Seal losses – Allow 35 HP for all HP ranges
Bearing loss – Allow 35 HP for all HP ranges

The remainder of the spec sheet contains all the essential data and requirements that may affect the duty and performance of the compressor. Much of this is self-explanatory; however, there are some items that require comment. These are:

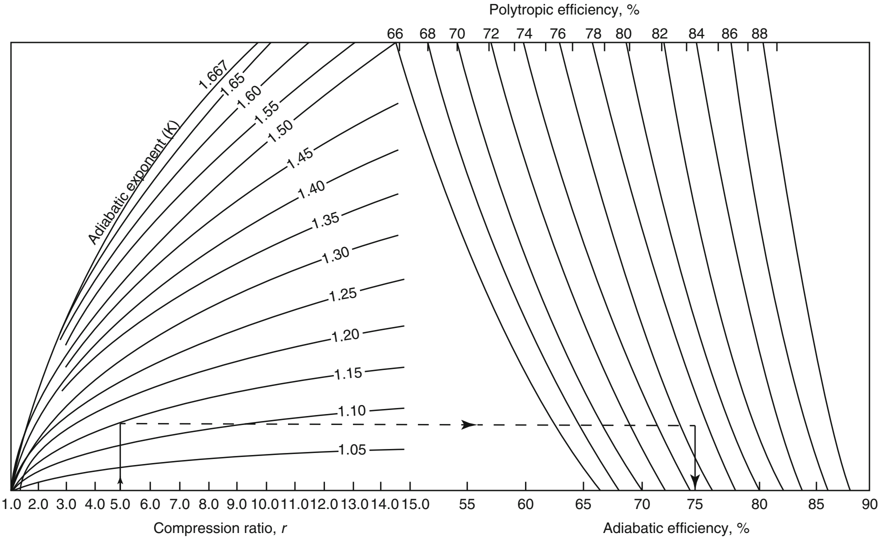


Fig. 30 Adiabatic efficiencies for centrifugal compressors

1. Many compressor installations today are under an open-sided shelter with a small overhead gantry crane assembly for maintenance.
2. Usually the lube and seal oil assemblies have their own pump and control systems. Consequently even if the compressor itself is to be steam driven, there may still be need to give details of utilities for the ancillary equipment.
3. Details of the gas composition is essential for any development of the compressor. This is listed on the last page of the specification together with any notes of importance concerning the machine and its operation.

An example calculation for a specification sheet follows.

Example Calculation

Prepare a process specification sheet for a compressor to handle the hydrogen recycle stream in an o-xylene isomerization plant. Details are as follows:

Fresh feed rate	5,000 bpsd of m-xylene
Recycle gas rate	7,000 Scf of hydrogen per Bbl of fresh feed
Gas composition mole %	

	Start of run (SOR)	End of run (EOR)
H_2	85.00	68.78
C_1	4.4	9.17
C_2	4.2	8.86
C_3	3.6	7.36
iC_4	0.78	1.62
nC_4	0.99	2.05
C_5s	1.03	2.16

Suction pressure	150 psig
Reactor pressure	500 psig
Suction temperature	100 °F

Step 1. Calculate the mole weight of the gas

	SOR			EOR	
	Mole %	MW	wt factor	Mole %	wt factor
H_2	85.0	2	170	68.78	138
C_1	4.4	16	70	9.17	147
C_2	4.2	30	126	8.86	266
C_3	3.6	44	158	7.36	324
iC_4	0.78	58	45	1.62	94
nC_4	0.99	58	57	2.05	119
C_5s	1.03	72	74	2.16	156
Total	100.00	700	100.00	1,244	
MW	7.0			12.44	

Step 2. Calculate volume flow of gas in SCF/min.

$$\begin{aligned}
\text{Total volume of } H_2 \text{ required} &= 5{,}000\ \text{BPSD} \times 7{,}000\ \text{SCF} \\
&= 35.00\ \text{MMScf/day} \\
&= 24{,}306\ \text{Scf/min.} \\
\text{For SOR volume gas flow} &= \frac{24{,}306}{0.85} \\
&= 28{,}595\,\text{Scf/min.} \\
\text{For EOR volume gas flow} &= \frac{24{,}306}{0.6878} \\
&= 35{,}339\ \text{Scf/min.}
\end{aligned}$$

Step 3. Calculate weight flow in lbs/min.

$$\text{Moles/min of gas} = \frac{\text{Scf/min}}{378}.$$
$$\text{For SOR moles/min} = 75.6.$$
$$\text{For EOR moles/min} = 93.5.$$
$$\text{lbs/min for SOR} = 75.6 \times 7.0 = 529\ \text{lbs/min}.$$
$$\text{lbs/min for EOR} = 93.5\ \times\ 12.44 = 1,163\ \text{lbs/min}.$$

Step 4. Calculate ACFM at inlet conditions.

$$\text{Compressor inlet pressure} = 165\ \text{psia}$$
$$\text{temp} = 100^\circ\ \text{F}.$$
$$\text{For SOR, ACFM} = \frac{28,597 \times 14.7 \times 560}{520 \times 165} = 2,744\,\text{cft/min}.$$
$$\text{For EOR, ACFM} = \frac{35,339 \times 14.7 \times 560}{520 \times 165} = 3,391\ \text{cft/min}.$$

Step 5. Estimate the C_p/C_v ratio.

The molal proportions will be used for this purpose. The ratio for each component will be taken from Appendix 5.

SOR				EOR	
	C_p/C_v	Mole %	C_p/C_v fact	Mole %	C_p/C_v fact
H_2	1.40	85.0	119	68.78	96.29
C_1	1.30	4.4	5.7	9.17	11.92
C_2	1.22	4.2	5.12	8.86	10.81
C_3	1.14	3.6	4.10	7.36	8.39
iC_4	1.11	0.78	0.87	1.62	1.80
nC_4	1.11	0.99	1.10	2.05	2.28
C_5s	1.09	1.03	1.12	2.16	2.35
Total		100.00	131.9	100.00	133.84

Then C_p/C_v for the gas is
SOR = 1.319
EOR = 1.338

Step 6. Calculate compressibility factors.

$$Z = \frac{MW \times P_1}{T \times \rho_v \times 10.73}. \tag{75}$$

$$\text{For SOR flows } Z = \frac{7.0 \times 165}{560 \times 0.193 \times 10.73} = 0.996.$$

$$\rho_v = \frac{\text{wt lbs/min}}{\text{ACFM}}.$$

$$\text{For EOR flows } Z = \frac{12.46 \times 165}{560 \times 0.343 \times 10.73} = 0.998.$$

Step 7. Calculate outlet temperature.

Approximate discharge temperature is read from Fig. 27 in this chapter using the following:

$$\text{ACFM for SOR} = 2,744.$$

$$\text{ACFM for EOR} = 3,391.$$

$$\text{Compression ratio} = \frac{515}{165} = 3.12.$$

$$\text{Inlet temp F} = 100.$$

Then:

$$\text{Discharge temp for SOR} = 370\,^{\circ}\text{F}.$$

$$\text{Discharge temp for EOR} = 340\,^{\circ}\text{F}.$$

Step 8. Calculate the approximate driver HP.

$$H_{\text{ad}} = \frac{Z_{\text{ave}} \times R \times T_{\text{i}}}{(K - 1)/K}\left[\left(\frac{P_2}{P_1}\right)^{(K - 1)/K} - 1\right] \tag{76}$$

where:

H_{ad} = adiabatic head in ft lbs/lb.

Z = compressibility factor (avg).

R = gas constant =1,545/MW.

K = adiabatic exponent $C_P/C_V = 1.15$.

T = temperature in °R = °F + 460 °F.

P_2 = discharge pressure psia.

P_1 = suction pressure psi.

Then:

H_{ad} for SOR conditions = 161,063.

H_{ad} for EOR conditions = 91,546.

Step 9. The gas HP is obtained using the expression

$$\text{Gas HP} = \frac{W \times H_{\text{ad}}}{\eta_{\text{ad}} \times 33{,}000} \tag{77}$$

where:

W = mass flow in lbs/min of gas.
H_{ad} = adiabatic head in ft lbs/lb.
η_{ad} = adiabatic efficiency (0.7–0.75).
Let η_{ad} be 0.73.
For SOR gas, HP = 3,536.
For EOR gas, HP = 4,420.

Step 10. The driver HP is as follows:

	SOR	EOR
Gas HP	3,536	4,420
Leakage losses	35	44
Bearing losses	35	35
Seal losses	35	35
Driver HP	3,641	4,534

Calculating Reciprocating Compressor Horsepower

Reciprocating compressors are used extensively in the process industry. They vary in size from small units used for gas recovery (such as those on a crude distillation overhead system) to fairly large complex machines used for recycle gas streams and for transporting natural gas. Engineers are frequently required therefore to assess the horsepower of these machines and their capability to handle various streams. This item describes a method used to determine horsepower and proceeds with the following steps:

Step 1. Obtain the capacity and the properties of the gas to be handled. Fix the ultimate (discharge) pressure level.
Step 2. From the machine data sheet, ascertain the number of stages.
Step 3. Estimate the brake horsepower from the expression

$$\begin{aligned}\text{BHP} = 22 &\times (\text{compr. ratio/stage}) \times \text{no. of stages} \\ &\times \text{capacity}\left(\text{in cuft/day} \times 10^{6}\right) \times \text{F}\end{aligned} \tag{78}$$

where:

$$\begin{aligned}F = {} & 1.0 \text{ for 1 stage} \\ & 1.08 \text{ for 2 stages} \\ & 1.10 \text{ for 3 stages.}\end{aligned}$$

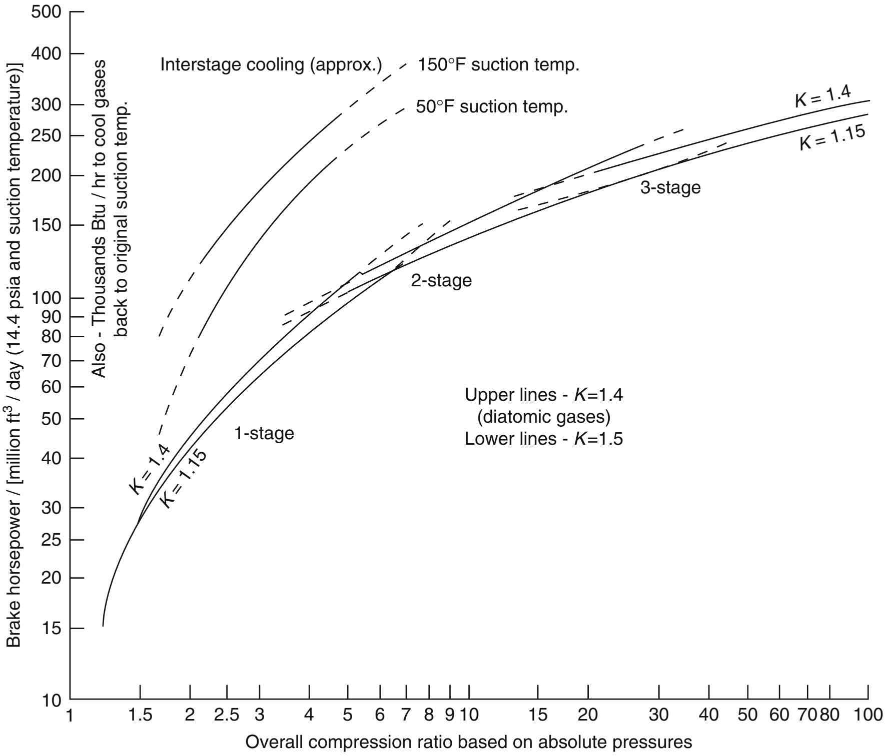


Fig. 31 An estimate of brake horsepower per MMcfd for reciprocating compressors

Ratio/stage = √ ratio for two stages and ∛ ratio for three stages.

Step 4. Check the estimate with Fig. 31.

Step 5. Confirm actual suction conditions and compression ratio required (discharge pressure).

Step 6. Calculate compression ratio/stage.

Step 7. Calculate first-stage discharge pressure. This will be suction pressure times compression ratio per stage from step 6.

Step 8. Allow about 3 % for interstage pressure drop then calculate second-stage discharge pressure. Check that overall compression ratio/stage is close to that calculated for step 6.

Step 9. Calculate the “K” value of the gas. “K” value is C_p/C_v of the gas. If the gas is a mixture of components, “K” value may be calculated as the sum of each component mole fraction multiplied by each of their “K” values given in Appendix 5. Alternatively for a good approximation, data in Fig. 32 may be used.

Step 10. Calculate discharge temperature from first stage using Fig. 33. Assume some intercooling (or calculate intercooling from plant data) and fix second-stage discharge temperature also using Fig. 33.

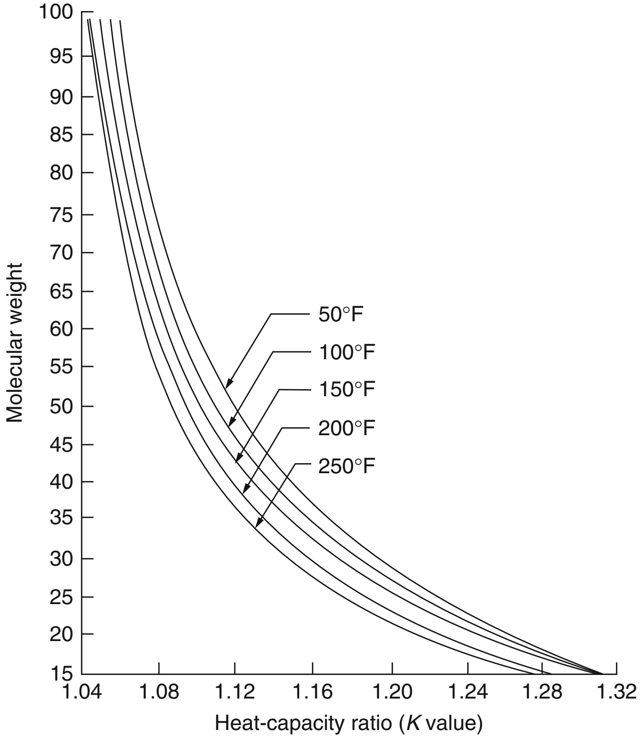


Fig. 32 Approximation of "K" from mole weights

Step 11. Calculate the compressibility factor Z at suction and discharge from the expression

$$\rho_v = \frac{MP}{T \times Z \times 10.73} \tag{79}$$

where:

ρ_v = gas density in lbs/cuft at condition.
T = °Rankine (°F + 460 °F).
Z = compressibility factor.
M = mole weight.
P = pressure in psia.

Use average value at suction and discharge for each stage.

Step 12. Read off BHP/MMcfd at the compression ratio/stage (from step 7) and "K" from step 9 for each stage.

Step 13. Calculate BHP per stage from the expression

$$\text{BHP} = (\text{BHP/MMcfd}) \times \frac{\text{P}_\text{L}}{14.4} \times \frac{T_\text{S}}{T_\text{L}} \times Z_{\text{ave}} \times \text{MMscf/D} \tag{80}$$

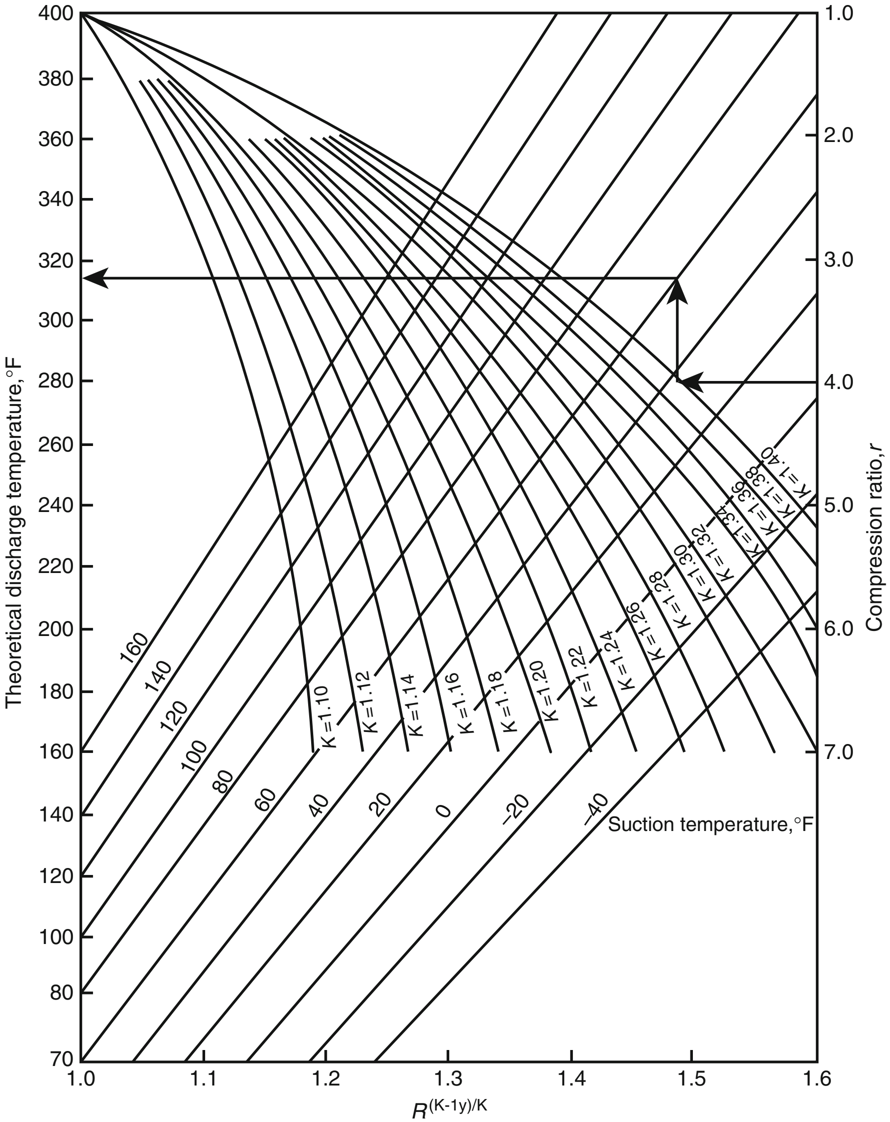


Fig. 33 Determination of discharge temperature for reciprocating compressors

where:

BHP/MMcfd = from Fig. 31.

P_L = pressure base used in psia.

T_S = intake temperature °R.

T_L = temperature base used in °R (usually 520 °R).

Step 14. Brake horsepower for the machine is the sum of the BHP calculated for each stage in step 13 above.

Reciprocating Compressor Controls and Intercooling

A reciprocating compressor is a constant displacement-type compressor. It compresses the same volume of gas to the same pressure level without regard to whether the gas is hydrogen or butane. This characteristic makes them desirable for use in services where the gas will have a widely varying composition. In some cases when an extremely low-density gas will be compressed, a reciprocating compressor may be more economical than a centrifugal compressor, even though the flow rate may be very high, due to the large number of stages required for the centrifugal.

Reciprocating compressors are widely used in process services where the flow rates are too small for centrifugal compressors. These units can be obtained with integral or coupled electric motor in sizes from a few HP to 12,000 HP and separate or integral gas drivers varying in sizes from 100 to 5,500 HP.

A range of air-cooled light-duty compressors is available for intermittent service. They range in size from 1/4 to about 100 HP at pressures up to 300 psig and are usually single acting. A primary process use of such equipment is for starting air compressors on gas engine-driven machines. Reciprocating compressors can be designed to handle intermittent loads efficiently. This is done by using cylinder unloaders such as clearance pockets or suction valve lifters. Power losses are low at part load operation with these devices.

Reciprocating parts and pulsating flow present several engineering problems. The foundation and piping system must be constructed to withstand the vibrations produced by the compressor. The pulsating flow produced by the compressor must be dampened by the use of properly engineered suction and discharge bottles. These problems do not arise with the use of other types of compressors.

Reciprocating Compressor Control

Control of the compressor to prevent driver overload can be accomplished with clearance pockets, suction valve lifters, a throttling valve in the suction line, or a control valve in a bypass around the compressor. A hand-operated bypass without cooler is usually furnished inside the block valves for start-up purposes.

1. *Clearance pockets*

   Of the above types of regulation, control by opening fixed clearance pockets gives the smoothest and most efficient control within its range of application. It has the following advantages:

   - Minimizes the intake pulsation as the gas flow is not reversed in the intake lines to the cylinder.
   - Results in lower bearing loads as all inertia loads are cushioned.
   - Results in very efficient part load operation. When the gas compressed into the pockets is expanded, it follows the adiabatic line of compression and results in little power loss.

   Clearance control has the following disadvantages which sometimes completely eliminates it from consideration:

- When low ratios of compression are combined with high suction pressure, clearance pockets of sufficient size to unload the compressor cannot physically be installed in the machine.
- Clearance control is designed for one set of pressure conditions and any variation in either suction or discharge pressure affects the amount of unloading accomplished by a given pocket.
- Condensable corrosive gases sometimes cause corrosion and liquid slugging problems.

2. *Suction valve lifters*
   Suction valve lifters are the other type of internal unloading devices for compressor cylinders and have characteristics that make them applicable when clearance control is not. Suction valve lifters completely unload their end of the cylinder whenever they are opened, regardless of the pressure. They do result in increased bearing loads due to unbalanced inertial forces. Suction line pulsation may increase because the single acting cylinder may excite a different frequency in the gas.
3. *Suction throttle valve*
   A throttle valve in the suction line should be considered only for small reciprocating compressors. For large-size machines, the suction valve cannot give tight enough shutoff to permit unloading the compressor for starting.
4. *Bypass control*
   External bypass control around the compressor is applicable to all sizes of compressors. It results in a loss of power since the full compressor capacity must be compressed to and delivered at the full discharge pressure before being bled back to suction pressure. Care must be taken with this type of control to ensure that the bypassed gas is cooled sufficiently to prevent increasing the discharge temperature. This type of control is preferred for installations up to several hundred horsepower because of its smoothness and lack of complexity. Individual machines can be shut down for large process variations.
5. *Variable-speed reciprocating compressors*
   With a variable-speed driver, cylinder control can usually be eliminated and speed control used to obtain desired process conditions. However, start-up unloading must be furnished, usually consisting of a hand-operated bypass within the machine, or cylinder block valves. On turbine-driven reciprocating compressors, economics usually dictate that the compressor be run at constant speed and that cylinder controls or system bypasses be used to obtain the required control.

Reciprocating Compressor Intercooling

Intercooling for multistage compressors is advisable whenever there is a large adiabatic temperature rise within the cylinder and the cylinder discharge temperature would exceed 350 °F. When intercooling is employed, the inlet temperature to the higher stage should be as close to the cooling water temperatures as practical. On standard commercial air intercoolers, approach temperatures of 15–20 °F are commonly used. Cooling to first-stage inlet temperature is usually economical on process gas compressors.

Intercooling is employed for two basic reasons:

1. For mechanical reasons whereby discharge temperature must be limited to 350 °F for lubrication purposes.
2. An economic reason as intercooling will save from 3 % to 5 % of the required BHP.

In general, on process compressors handling low "*n*" value gases, intercooling is not employed unless the temperature limitation is exceeded. On high "*n*" value diatomic gas mixtures, such as air, intercooling is the rule above about a 4 compression ratio and ambient temperature at suction.

In general, cooling water for electric-driven compressors can be any water available, including saltwater. (If the compressor is tied into a plant having gas engine-driven compressors, the electric-driven machine should be tied into the closed system.) The cooling water should be available at a minimum pressure of 25 psig.

For estimating purposes, cooling water temperature rise across the cylinders can be taken as 15 °F and that across the inter- and aftercoolers can be taken as 15 °F. For estimating purposes, cooling water requirements are as follows:

Jacket water cooling	500 Btu/BHP/h
Inter cooler	1,000 Btu/BHP/h
After cooler	1,000 Btu/BHP/h

Use motor rating for the horsepower required.

If the discharge temperature of the gas does not exceed 180 °F, it is common practice to eliminate cooling water on the cylinder and operate with cooling passages which are filled with oil. Any jacketed cylinder must be filled with some fluid to ensure even temperature distribution.

Specifying a Reciprocating Compressor

As in the case of the centrifugal compressor, all data necessary to give a precise requirement for the duty and performance required of a reciprocating compressor must be given in the specification sheet. Many of these data are the same as those given in a specification for a centrifugal compressor (discussed earlier in this chapter). For completeness, all the items in a reciprocating compressor are included below. Fig. 34 illustrates a completed reciprocating compressor specification sheet.

Title block

This requires the item to be identified by item number and its title. The number of units that the specification refers to is also given here. For a centrifugal compressor, this will normally be just one as very seldom is a spare machine required. This may not be so in the case of a reciprocating compressor.

Normal and rated columns

More often than not, the conditions and quantities required to be handled will vary during the operation of the machine. The two columns therefore will be completed showing the average normal data in the first column and the most severe conditions and duty required by the compressor in the second. The severe conditions in column two are for a continuous length of operation not instantaneous peaks (or troughs) that may be encountered. Other "off-design" cases may also be shown.

Gas

a

ITEM No. C101 A&B TITLE Hydrotreater Recycle Gas Compressor

Number of units required 3 (2 + 1 spare)

	Normal				Rated			
GAS (see attached composition)	75% H_2				65.8% H_2			
VOL. flow scf/min	4337				4937			
WEIGHT lb/min	74.1				136.3			
INLET CONDITIONS (each stage)	Stage 1	Stage 2	Stage 3	Stage 4	Stage 1	Stage 2	Stage 3	Stage 4
Pressure psia	65	198*			65	198*		
Temperature °F	80	100*			80	100*		
Mol weight	6.44				10.44			
C_P/C_V	1.362				1.347			
Compressibility factor	0.994	0.996			0.996	0.997		
Inlet vol acf/min	1019	347			1159	394		
DISCHARGE CONDITIONS (each stage)								
Pressure psia	198	615			198	615		
Temperature °F	270	299			262	292		
C_P/C_V	1.362				1.347			
Compressibility factor	0.991	0.992			0.995	0.995		
APPROX. DRIVER HORSEPOWER	1055				1190			

COMPRESSOR SERVICE REQUIRED: *After intercooling

Length of uninterrupted service: 8000 hours

Type of compressor: Lubricated Yes
Non Lubricated

Discharge RV setting (each stage) 250 and 750 psig

Fig. 34 (continued)

b

ITEM No. C 101 A&B TITLE Hydrotreater Recycle Gas Compressor

General Data and Requirements

Enclosure:
Open to weather
Under shelter Yes
In building

Corrosiveness and remarks concerning gas
None

Type of driver: Motor: 2 normal operating
Stream turbine:
Condensing
Non-condensing Spare machine

Utilities:
Power:
Voltage
Cycle
Phase
Steam:
Inlet: Pressure (psig) 600
Temperature (°F) 710
Condensing exhaust
Pressure (psia) N/A
Temperature (°F) N/A
Non-condensing exhaust
Pressure (psig) 50
Temperature (°F) (by vendor)

Cooling water: Pressure 60 psig: Temperature 40 °F
Allowable temperature rise 30 °F

Materials of construction:
Cylinder CS Type By vendor
Piston Ni.Cr Type By vendor

Type of shaft seal: Labyrinth

Fig. 34 (continued)

c

ITEM No. C 101 A&B TITLE Hydrotreater Recycle Gas Compressor

General Data and Requirements (cont.)

Gas Composition

Mol %	Start of run	End of run
H_2	74.9	65.80
C_1	14.17	19.31
C_2	5.85	7.97
C_3	2.43	3.31
iC_4	1.13	1.54
nC_4	1.00	1.36
c_5s	0.52	0.71
Total	100.00	100.00

Remarks and notes:

1. Vendor to provide:

Intercoolers: Yes

Aftercooler: Yes

Dampeners: Yes

Flushing and sealing oil systems: Yes

2. If motor driven Re acceleration required class A

3. Suction line: Size 6” RTG 300# RF

Discharge line: Size 4” RTG 600# RF

Fig. 34 (**a**–**c**) An example of a process specification for a reciprocating compressor

The composition and gas stream identification must be included as part of the process specification. Usually the composition of the gas is listed on a separate sheet as shown in the example. Note in many catalytic processes that utilize a recycle gas, the composition of the gas will change as the catalyst in the process ages. Thus, it will be necessary to list the gas composition at the SOR and at the EOR.

The compressor may also be required to handle an entirely different gas stream at some time or other. This too must be noted. For example, in many petroleum refining processes, a recycle or makeup compressor normally handling a light predominantly hydrogen gas is also used for handling air or nitrogen during catalyst regeneration, purging, and start-up.

Volume flow

This is the quantity of gas to be handled stated at 14.7 psia and 60 F.

Weight flow

This is the weight of gas to be handled in either lbs/min or lbs/h.

Inlet conditions

In the case of multistage compressors, the conditions for each stage must be shown. Where interstage cooling is used, the effect must be reflected in the conditions specified.

Pressure: This is the pressure of the gas at the inlet of the compressor stage in psia. Note if intercooling is used, this pressure must include the intercooler pressure drop.

Temperature: This is the temperature of the gas at the inlet of the compressor stage – after the intercooler if applicable.

Mole weight: The mole weight of the gas is calculated from the gas composition given as part of the specification.

C_p/C_v: This is the ratio of specific heats of the gas again obtained from the gas mole wt and Appendix 5.

Compressibility factor (z): Use the value at inlet conditions calculated as shown in step 7 of item on horsepower calculation for reciprocating compressors.

Inlet volume: This is the actual volume of gas at the conditions of temperature and pressure existing at the compressor stage inlet. Thus

$$\text{ACFM} = \frac{\text{SCFM} \times 14.7 \times (\text{inlet temp F} + 460)}{(60\ {}^{\circ}\text{F} + 460) \times \text{inlet press psia}}\,. \tag{81}$$

Discharge conditions

Pressure: This is the pressure at each stage outlet and is quoted in either psia or psig.

Temperature: This is estimated for each stage using Fig. 33.

C_p/C_v: This will be the same as in the inlet.

Approximate driver horsepower

The brake horsepower for the reciprocating compressor is calculated using the method described earlier. This is *brake horsepower* and includes an allowance for mechanical inefficiencies. The approximate minimum driver horsepower is 1.1 × brake horsepower, but the approximate driver HP will be calculated using the inefficiencies for leakage, seals, etc. as for centrifugal compressors.

The reminder of the spec sheet contains all the essential data and requirements that may affect the duty and performance of the compressor. Much of this is self-explanatory; however, there are some items that require comment. These are:

1. Many compressor installations are under an open-sided shelter with a small overhead gantry crane assembly for maintenance.
2. Usually the lube and seal oil assemblies have their own pump and control systems. Consequently even if the compressor itself is to be steam driven, there may still be need to give details of utilities for the ancillary equipment.

3. Details of the gas composition are essential for any development of the compressor. This is listed on the last page of the specification together with any notes of importance concerning the machine and its operation.
4. For environmental purposes, many reciprocating compressors today include sealed and purged distance pieces and crankcases. These are vented to flare or another vapor control system with a purge gas like nitrogen sweeping the volume. The purge requirements must be specified.

An example calculation for a specification sheet follows:

Example calculation

A hydrotreater makeup compressor is required to handle a gas stream such as to provide the unit with 260 SCF per barrel of feed of pure hydrogen. The composition of the gas varies as follows:

Mole %	Start of run	End of run
H_2	74.9	65.80
C_1	14.17	19.31
C_2	5.85	7.97
C_3	2.43	3.31
iC_4	1.13	1.54
nC_4	1.00	1.36
C_5s	0.52	0.71
Total	100.00	100.00

The fresh feed throughput is fixed at 30,000 BPSD (barrels per stream day). It is proposed to use 3 × 60 % machines of which one will be standby and turbine driven. The inlet pressure of the gas is 50 psig at a temperature of 80 °F. The gas is to be delivered at a pressure of 600 psig and 100 °F. Prepare a process specification for reciprocating compressors to meet these requirements.

Step 1. Calculate volume flows.

$$\begin{aligned}\text{SOR conditions total flow required} &= \frac{260}{0.749}\\ &= 347\ \text{Scf of gas per Bbl of feed}\\ &= \frac{347\times 30,000}{24\times 60} = 7,229\ \text{Scf/min.}\\ \text{EOR conditions total flow required} &= \frac{260}{0.658}\\ &= 395\ \text{Scf/Bbl}\\ &= \frac{395\times\ 30,000}{24\ \times 60} =\ 8,229\ \text{Scf/min.}\end{aligned}$$

Volume flow per machine (60 % machines):

SOR = 7, 229 × 0.6 = 4,337

EOR = 8,229 × 0.6 = 4,937

Step 2. Calculate mole wt of gas.

	SOR			EOR	
	MW	Mole %	wt factor	Mole %	wt factor
H_2	2	74.9	149.8	65.8	131.6
C_1	16	14.17	226.7	19.31	309.0
C_2	30	5.85	175.5	7.97	239.1
C_3	44	2.43	106.9	3.31	145.6
iC_4	58	1.13	65.5	1.54	89.3
nC_4	58	1.00	58.0	1.36	78.9
C_5s	72	0.52	37.4	0.71	51.1
Total		100.0	644.3[a]	100.00	1,044.6[b]

[a] SOR gas mole wt = 6.44 (644.3/100)

[b] EOR gas mole wt = 10.44 (1,044.6/100)

Step 3. Weight of gas lbs/min per machine

One mole of any gas occupies about 378 cft at 60 °F and 14.7 psia. Then,

For SOR conditions, $\text{moles/min of gas per machine} = \frac{4,337}{378} = 11.5$

and

$$\begin{aligned}\text{Lbs/min} &= 11.5 \times 6.44 \\ &= 74.06\ \text{lbs/min}.\end{aligned}$$

For EOR conditions, $\text{moles/min of gas per machine} = \frac{4,937}{378} = 13.06$

and

$$\begin{aligned}\text{Lbs/min} &= 13.06 \times 10.44 \\ &= 136.30\ \text{lbs/min}.\end{aligned}$$

Step 4. Inlet conditions.

$$\text{Inlet pressure} = 50\ \text{psig} = 65\ \text{psia}.$$

$$\text{Required outlet pressure} = 600\ \text{psig} = 615\ \text{psia}.$$

$$\text{Overall compression ratio} = \frac{615}{65} = 9.46$$

This will be a two-stage compressor.

Note: At this level of compression in reciprocating compressors, the compression ratio should not exceed 4:1 for any stage.

$$\text{Compression ratio per stage} = \sqrt{9.46} = 3.07.$$

$$\text{Discharge pressure stage 1} = 65 \times 3.07 = 199.6\ \text{psia}$$

Allowing 2 psi for the pressure drop across the intercooler, the suction pressure of stage 2 is 197.6; call it 198 psia.

Check the compression ratio of stage 2:

$$\text{Required discharge pressure} = 615\ \text{psia}$$

$$\text{Compression ratio} = \frac{615}{198} = 3.1$$

which is close to the originally predicted of 3.07.

Step 5. Calculate ratio C_p/C_v.

	SOR			EOR	
	C_p/C_v	Mole %	Factor	Mole %	Factor
H_2	1.4	74.9	1.049	65.8	0.921
C_1	1.3	14.17	0.184	19.31	0.251
C_2	1.22	5.85	0.071	7.97	0.097
C_3	1.14	2.43	0.028	3.31	0.038
iC_4	1.11	1.13	0.013	1.54	0.017
nC_4	1.11	1.00	0.011	1.36	0.015
C_5s	1.09	0.52	0.006	0.71	0.008
Total		100.0	1.362	100.00	1.347

C_p/C_v SOR gas = 1.362
C_p/C_v EOR gas = 1.347

Step 6. Calculate inlet ACFM per stage

SOR.

Inlet volume for first stage:

$$\begin{aligned}\text{ACFM} &= \frac{\text{Scf/min} \times 14.7 \times \text{inlet temp } ^\circ\text{R}}{(60\ +\ 460) \times \text{inlet press psia}} \\ &= \frac{4,337 \times 14.7 \times 540}{520 \times 65} \\ &= 1,019\ \text{cft/min.}\end{aligned} \tag{82}$$

Inlet volume for second stage: (intercooled to 100 °F)

$$\begin{aligned}\text{ACFM} &= \frac{4,337 \times 14.7 \times 560}{520 \times 198} \\ &= 347\ \text{cft/min.}\end{aligned}$$

EOR.

Inlet volume for first stage:

$$\begin{aligned}\text{ACFM} &= \frac{4,937 \times 14.7 \times 540}{520 \times 65} \\ &= 1,159\ \text{cft/min.}\end{aligned} \tag{83}$$

Inlet volume for second stage:

$$\text{ACFM} = \frac{4,937 \times 14.7 \times 560}{520 \times 198}$$
$$= 488.5 \text{ cft/min.}$$

Step 7. Calculate inlet compressibility factor (Z).

$$\text{Z} = \frac{\text{MW} \times P_i}{T_i \times \rho \times 10.73} \tag{84}$$

where:

$$\rho = \frac{\text{wt/min}}{\text{ACFM}}. \tag{85}$$

SOR conditions:

$$\begin{aligned} \text{1st} - \text{stage } Z &= \frac{6.44 \times 65}{540 \times 0.0727 \times 10.73} \\ &= 0.994. \\ \text{2nd} - \text{stage } Z &= \frac{6.44 \times 198}{560 \times 0.213 \times 10.73} \\ &= 0.991. \end{aligned}$$

EOR conditions:

$$\begin{aligned} \text{1st} - \text{stage } Z &= \frac{10.44 \times 65}{540 \times 0.1176 \times 10.73} \\ &= 0.996. \\ \text{2nd} - \text{stage } Z &= \frac{10.44 \times 198}{560 \times 0.345 \times 10.73} \\ &= 0.997. \end{aligned}$$

Step 8. Determine discharge temperature.

From Fig. 33
For SOR conditions:
1st-stage comp ratio = 3.07.
$C_p/C_v = 1.362$.
Suction temp = 80 °F.
Discharge temp reads as 270 °F.
2nd-stage comp ratio = 3.1.
$C_p/C_v = 1.362$.
Suction temp = 100 °F.
Discharge temp reads as 299 °F.

For EOR conditions:
1st-stage comp ratio = 3.07.
$C_p/C_v = 1.347$.
Suction temp = 80 °F.
Discharge temp reads as 262 °F.
2nd-stage comp ratio = 3.1.
$C_p/C_v = 1.347$.
Suction temp = 100 °F.
Discharge temp reads as 292 °F.

Step 9. Compressibility factors for discharge conditions.

SOR conditions:
First-stage ACFM on discharge (before intercooler)

$$= \frac{4,337 \times 14.7 \times 730}{520 \times 200 \text{ (neglect IC pressure drop)}}$$
$$= 447.5 \text{ cft/min.}$$
$$\rho = \frac{74.1}{447.5} = 0.166 \text{ lb/cft.}$$
$$Z = \frac{6.44 \times 200}{730 \times 0.166 \times 10.73}$$
$$= 0.991.$$

Second-stage ACFM on discharge

$$= \frac{4,337 \times 14.7 \times 759}{520 \times 615}$$
$$= 151.3 \text{ cft/min.}$$
$$\rho = \frac{74.1}{151.3} = 0.490 \text{ lb/cft.}$$
$$Z = \frac{6.44 \times 615}{759 \times 0.49 \times 10.73}$$
$$= 0.992.$$

EOR conditions:
These are calculated in the same way as those above and give the following results:
1st-stage Z = 0.995.
2nd-stage Z = 0.995.

Step 10. Approximate driver horsepower.

Use the expression:

BHP = 22 × (comp ratio/stage) × No. of stages × capacity × factor F.
Comp ratio/stage = 3.07.
No. of stages = 2
Capacity per machine in MMcft/day at suction temperature(= 10.81 MMscf/d × 0.6).
Factor for 2 − stage machine = 1.08.

For SOR conditions:

$$\begin{aligned}\text{BHP} &= 22 \times 3.07 \times 2 \times (0.6 \times 10.81) \times 1.08\\ &= 946.\end{aligned}$$

For EOR conditions:

$$\begin{aligned}\text{BHP} &= 22 \times 3.07 \times 2 \times 7.38 \times 1.08\\ &= 1{,}077.\end{aligned}$$

Use the efficiency factors as given in Fig. 30 for centrifugal compressors. In this case, there will be a gear assembly between compressor and driver. Use the efficiency of this as 97 %. Thus:

	SOR	EOR
BHP	946	1,077
Gear losses	29	33
(3 % of BHP)		
Leakage	10	10
Seal	35	35
Bearings	35	35
Driver HP	1,055	1,190

Compressor Drivers, Utilities, and Ancillary Equipment

This item covers details on various compressor drivers, the utilities associated with operating the compressors, and their ancillary equipment.

Compressor Drivers

Table 22 gives a listing of the more common types of compressor drivers. It provides some of the data that would influence the choice of the driver. The most common drivers by far in a process plant are the electric motor and the steam turbine. For very large machines as encountered in handling natural gas, the gas turbine or gas engine becomes the more prominent prime mover.

Sizing Drivers

As a basic rule, drivers are sized for the most severe duty required of the compressor plus a factor as an operating contingency. In general the most severe duty is that design case which has the highest suction temperature, the maximum ratio of specific heats, the lowest suction pressure, and the highest required discharge pressure and the gas molecular weight which gives the highest HP. The driver-rated horsepower will then be greater than

Table 22 Comparison of compressor drivers

Driver	HP range	Available speed, RPM	Efficiency %	Common applications
Synchronous motor	100–20,000	250–3,600	90–97	Reciprocating compressors
Induction motor	1–15,000	3,600	86–94	All types of compressors
Wound rotor induction motor	–	–	–	Normally not used
Steam engine	10–4,000	400–140	60–80	All types of rotary equip
Steam turbine	10–2,000	2,000–15,000	50–76	Centrif, axial, and recip
Combustion gas turbine	3,000–35,000	10,000–3,600	19–24[a]	All types of compressors (except recip)
Gas and oil engines	100–5,000	1,000–300	35–45	Reciprocating compressors

[a] The efficiency given here does not include for waste heat recovery. With WHR the efficiency can be increased to between 28 % and 35 %

$$\text{Driver brake HP} = \frac{\text{max compressor BHP at the most severe duty}}{\text{mechanical efficiency of the power transmission}}. \tag{86}$$

The mechanical efficiency in this case includes energy losses for bearings, seals, lube oil, etc., in the case of centrifugal compressors and gears in the case of reciprocating compressors.

Electric Motor Drivers

Squirrel cage motors are preferred for this type of duty. These may be drip-proof open type where the location is not a fire or explosion hazard. Where it is required that the units must be explosion or fire proof, these motors must be totally enclosed type. In sizing the motor, efficiencies for squirrel cage motors up to 450 HP given in Table 14 for pumps may be used. Table 23 is used for motors above 500 HP.

The driver-rated brake horsepower is the compressor horsepower times a load factor divided by a service factor. Normally the load factor is 10 % and a service factor for an enclosed squirrel cage motor is between 1.0 and 1.15 for an open type.

Example Calculation

Calculate the operating load and the connected load for the driver of a 4,000 HP centrifugal compressor (includes leakage, seal, and bearing losses). A gear is used and this has a 97 % efficiency. The load factor is 10 % and the motor is open-type squirrel cage with a service factor of 1.15. There will be a normal operating unit and a spare, both motor driven.

Table 23 Motor efficiencies

Motor-rated HP	Motor efficiencies, % full load 50	75	100
500	91.4	93.1	93.4
1,000	92.1	93.8	94.1
1,500	92.4	94.1	94.4
2,000	92.7	94.4	94.7
2,500	92.9	94.6	94.9
3,000	93.0	94.7	95.0
3,500	93.0	94.7	95.0
4,000	93.1	94.8	95.1
4,500	93.1	94.8	95.1
5,000	93.2	94.9	95.2

$$\begin{aligned}\text{Minimum required driver HP} &= \frac{4,000 \times 1.1}{0.97}\\ &= 4,536.\end{aligned}$$

$$\text{Driver nameplate rating} = \frac{4,536}{1.15} = 3,944.$$

Call it 4,000 HP.

Connected load for the motor is

$$\begin{aligned}\text{Motor nameplate rating} \times 1.15 &= 4,000 \times 1.15\\ &= 4,600\text{ HP (rated HP)}\\ &= \frac{4,600 \times .746}{0.951\text{ (at 100\% load)}}\\ &= 3,608\text{ kW.}\end{aligned}$$

$$\begin{aligned}\text{There are two units then total connected load} &= 3,608 \times 2\\ &= 7,216\text{kW.}\end{aligned}$$

Operating load for the motor is

$$\begin{aligned}\frac{4,000}{0.97} &= 4,124\text{ HP.}\\ \%\text{ load} &= \frac{4,124}{4,600} = 90\%\text{ (use 75\% eff).}\\ \text{Operating load} &= \frac{4,124 \times 0.746}{0.948}\\ &= 3,245\text{ kW.}\end{aligned}$$

Steam Turbine Drivers

Next to the motor drivers steam turbines are the most common form of drivers for rotary equipment in general and compressors in particular. The two most

Table 24 Steam turbine efficiencies

	Adiabatic efficiencies %	
	Inlet pressures (psig)	
Driver BHP	900	100
500	48	59
800	53	64
1,000	56	67
1,200	58	68
1,500	60	71
2,000	63	73
2,500	65	74
3,000 and up	67	76

common types of these are turbines that exhaust to a lower pressure, but the exhaust steam is not condensed and those in which the exhaust steam is condensed. Normally the latter is only used in the case of large driver horsepower 5,000 and above. It is far more expensive than the noncondensing type as the exhaust is normally subatmospheric in pressure and the cost of the condenser must be included.

Typical steam turbine approximate efficiencies are listed in Table 24.

These efficiencies are based on the exhaust pressure of the steam being 50 psig for noncondensing type and 2″ Hg Abs for the condensing type.

Determining the rated horsepower of the steam turbine driver follows closely to the method for motor horsepower. First determine the minimum horsepower required of the turbine. Thus:

Step 1. Determine the *minimum* driver horsepower by multiplying the compressor BHP by 1.1.

Step 2. Now the turbine will deliver the normal HP at the normal speed. A contingency in the form of additional speed is added to the driver capability. This will be controlled in practice by a steam governor. This contingency is usually 5 % above-normal speed.

Step 3. Horsepower capability varies as the cube of the speed. Thus, the rated horsepower of the turbine will be

Rated HP = minimum HP × $(1.05)^3$.

Step 4. The amount of steam that will be used is calculated by the change in enthalpy of the inlet steam to the outlet steam at constant entropy. The change in enthalpy for the two conditions is read from the steam Mollier diagram.

Step 5. The theoretical steam rate is:

$$\frac{2,544}{\text{Inlet enthalpy} - \text{outlet enthalpy(in Btu/lb)}} \tag{87}$$

This figure divided by the turbine efficiency gives the steam rate in lbs/BHP/h.

Example Calculation

Calculate the turbine horsepower requirements and the theoretical steam rates to drive a 4,000 BHP centrifugal compressor. No gears are included in this case. Steam is available at 650 psig and 760 F. The steam will exhaust into the plant's 125 psig header.

$$\begin{aligned}\text{Minimum driver horsepower} &= 4{,}000 \times 1.1\\ &= 4{,}400\ \text{BHP.}\\ \text{Rated turbine HP at } 105\,\%\ \text{speed} &= 4{,}400 \times (1.05)^3\\ &= 5{,}094\ \text{HP.}\end{aligned}$$

Enthalpy of steam at 650 psig and 760 F = 1,390 (entropy 1.62).

Enthalpy of steam at 125 psig = 1,225 (entropy 1.62).

Difference in enthalpy = 165.

Efficiency of turbine (from Table 24) = 67 %.

$$\begin{aligned}\text{Theoretical steam rate} &= \frac{2{,}544}{165 \times 0.67}\\ &= 23\ \text{lbs/BHP/h.}\end{aligned}$$

Gas Turbine Drivers

These items of equipment are the most expensive, and because they require a high capital investment, their use can only be justified as compressor drivers where the continual load on the compressor is also very high. These drivers therefore are met mostly in the natural gas industry. They are used extensively in recompressing natural gas after treating for dew point control or desulfurizing.

The thermal efficiencies of gas turbines are low (about 16–20 %), but it is common practice to use the exhaust gases, which are usually at a temperature of above 800 °F, in waste heat recovery. This involves exchanging the waste heat of the exhaust gases with boiler feedwater to generate steam or to preheat a process stream, for example, distillation. Table 25 gives some gas turbine sizes and data. It should be noted that considerable development work is continuing in the field of gas turbines and consequently the data given here may be subject to revision or updating.

To obtain the gas turbine rated horsepower for a specific compressor duty follows closely the same calculation route as the steam turbine. Thus:

Step 1. Obtain the *minimum driver horsepower* by multiplying the compressor brake horsepower by 1.05 (BHP includes seals, leakage, etc.).

Step 2. The rated turbine horsepower is the minimum driver HP divided by the gear efficiency.

Step 3. The horsepower of the turbine selected must equal or slightly exceed the horsepower calculated in step 2. This HP must be corrected for site conditions as shown in step 4.

Table 25 Gas turbine sizes and data

		Exhaust		
HP rating at 80 °F, 1,000 ft	Fuel consumption LHV lbs/HP-h	Flow, lb/s	Temp, °F	RPM
430	1.25	10.3	950	19,250
1,000	0.66	11.1	960	19,500
1,080	0.63	13.7	860	22,300
1,615	0.84	23.6	1,000	13,000
2,500	0.76	43.0	795	9,000
3,800	0.75	53.0	900	8,500
5,500	0.76	77.3	945	5,800
7,000	0.80	101.0	938	5,500
8,000	0.65	102.0	935	5,800
9,000	0.70	130.0	850	5,000
10,000	0.59	123.5	805	6,000
12,000	0.65	160.0	720	4,750
13,500	0.62	187.0	800	4,860
15,000	0.61	188.0	835	4,860
24,000	0.61	258.0	850	3,600

Step 4. The HPs given in Table 25 are at an ambient temperature of 80 °F, and at an elevation of 1,000 ft. Correction for any specific site is given by the following expression:

$$\begin{aligned}\text{SITE HP} &= \text{Quoted HP}\ (1.00 + \text{A} \times 10)^{-2}(1.00 - \text{B} \times 10)^{-2}\\ &\times\ (1.00 - \text{C} \times 10)^{-2} \times \frac{\text{Site atmos psia}}{14.7}\end{aligned} \tag{88}$$

where:

A = temp adjustment of % per °F.

B = inlet press loss, % per inches water gauge.

C = discharge press loss, % per inches water gauge.

"A" will be positive for ambient temperatures above 80 °F and negative for ambient temperatures below 80 °F.

Ancillary Equipment

Reciprocating compressor dampening facilities. Dampening facilities are used in conjunction with reciprocating compressors to smooth out the pulsation effect of the compressor action. These facilities are simply in-line bottles sized larger than the gas line which cushion the gas motion. These are essential to minimize expensive piping designs that would be necessary without them. Calculating the size of these bottles is important in the design of the compressor facilities.

The following calculation technique is used to determine the size of new dampers or to evaluate the adequacy of an existing facility. This calculation is described by the following steps:

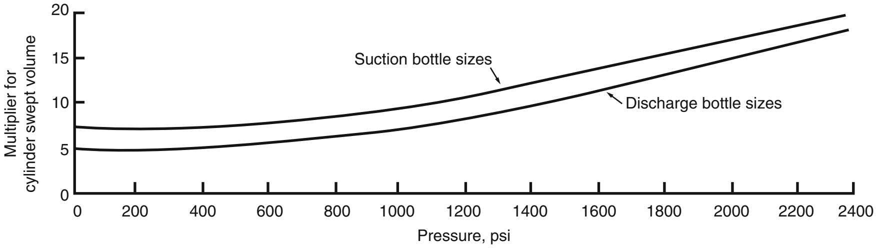


Fig. 35 Dampener bottle sizing

Step 1. From compressor data sheet, obtain cylinder diameter and stroke dimensions.

Step 2. Calculate the swept volume per cylinder using the expression

$$\frac{\pi D^2}{4} \times S \tag{89}$$

where:

D = cylinder diameter.

S = stroke length.

Step 3. Knowing the suction and discharge pressures, the pulsation bottle capacity (both suction and discharge) is obtained from Fig. 35 in terms of a multiple of swept volume.

Step 4. Use the rule of thumb that pulsation bottle diameter equals 1½ times the compressor cylinder diameter. Calculate the suction and discharge bottle length.

Example Calculation

To determine the dimensions of the compressor pulsation bottle of a reciprocating compressor having a 6″ diameter cylinder and a stroke of 15″. The compressor delivers 3.0 MMscf/d gas at a suction pressure of 100 psia and 100 °F and a discharge pressure of 1,200 psia.

The cylinder diameter is 6″ and stroke is 15″.

$$\begin{aligned}
\text{Then swept volume} &= \pi/4 \times 6^2 \times 15 \\
&= 424 \text{ cu.in.} \\
\text{Capacity of machine} &= 3 \text{ MMscf/D.} \\
\text{In a MM CF/D} &= \frac{3 \times 14.7 \times 560}{520 \times 100} \\
&= 0.475 \text{ MM ACFD} \\
&\Rightarrow 330 \text{ ACF/min} \\
&\Rightarrow 570240 \text{ AC in./min.} \\
\text{Machine speed} &= \frac{570240}{424} = 1,345 \text{ RPM.}
\end{aligned}$$

From Fig. 35:

Suction bottle size should be 7 × swept volume (at 100 psia); discharge bottle size should be 7 × swept volume (at 1,200 psia) = 2,968 cu inches or 1.718 cu. ft.

As a rule of thumb, diameter of bottle should be 1½ × cylinder diameter = 0.75 f. (9″) length = 2,968/63.6 = 47 in. or 4 ft.

Heat Exchangers

Types and Selection of Heat Exchangers

Heat exchange is the science that deals with the rate of heat transfer between hot and cold bodies. There are three methods of heat transfer, they are:

- Conduction
- Convection
- Radiation

In a heat exchanger, heat is transferred by conduction and convection with conduction usually being the limiting factor. The equipment used in heat exchanger service is designed specifically for the duty required of it. That is, heat exchange equipment cannot be purchased as a stock item for a service but has to be designed for that service.

The types of heat exchange equipment used in the process industry and their selection for use are as follows:

Shell and tube exchanger

This is the type of exchanger most commonly used in a process plant. It consists of a bundle of tubes encased in a shell. It is inexpensive and is easy to clean and maintain. There are several types of shell and tube exchangers and most of these have removable bundles for easier cleaning. The shell and tube exchanger has a wide variety of services for which it is normally used. These include vapor condensation (condensers), process liquid cooling (coolers), exchange of heat between two process streams (heat exchangers), and reboilers (boiling in fractionator service). Most of this chapter will be dedicated to the uses and design specification of the shell and tube exchanger.

Double-pipe exchanger

A double-pipe exchanger consists of a pipe within a pipe. One of the fluid streams flows through the inner pipe while the other flows through the annular space between the pipes. The exchanger can be dismantled very easily and therefore be easily cleaned. The double-pipe exchanger is used for very small process units or where the fluids are extremely fouling. Either true concurrent or countercurrent flows can be obtained, but because the cost per square foot is relatively high, it can only be justified for special applications. Table 26 gives the heat transfer area for various pipe lengths and diameters.

Table 26 Heat transfer areas for various double-pipe exchanger designs

No of tubes	Shell size, in.	Tube size, in.	Surface area, sqft, for indicated length tubes		
			L=10 ft	L=20 ft	L=30 ft
1	2	1	5.8	11.0	16.3
1	3	1.5	10.9	20.9	30.9
1	4	2	13.7	26.1	38.5

Extended surface or fin tubes

This type of exchanger is similar to the double pipe but the inner pipe is grooved or has longitudinal fins on its outside surface. Its most common use is in the service where one of the fluids has a high resistance to heat transfer and the other fluid has a low resistance to heat transfer. It can rarely be justified if the equivalent surface area of a shell and tube exchanger is greater than 200–300 sqft.

Finned air coolers

These are the more common type of air coolers used in the process industry. Air cooling for process streams gained prominence during the early 1950s. In a great many applications and geographic areas, they had considerable economic advantage over the conventional water cooling. Today it is uncommon to see process plants of any reasonable size without air coolers.

Air coolers consist of a fan and one or more heat transfer sections mounted on a frame. In most cases, these sections consist of finned tubes through which the hot fluid passes. The fan located either above or below the tube section induces or forces air around the tubes of the section.

The selection of air coolers over shell and tube is one of cost. Usually air coolers find favor in condensing fractionator overheads to temperatures of about 90–100 °F and process liquid product streams to storage temperatures. Air coolers are widely used in most areas of the world where ambient air temperatures are most times below 90 °F. At atmospheric temperatures above 100 °F, humidifiers are incorporated into the cooler design and operation. The cost under these circumstances is greatly increased and their use is often not justified.

In very cold climates, the air temperature around the tubes is controlled to avoid the skin temperature of the fluid being cooled falling below a freezing criteria or, in the case of a petroleum product, its pour point. This control is achieved by louvers installed to recirculate the air flow and/or by varying the quantity of air flow by changing the fan pitch. Steam coils may also be used.

Box coolers

These are the simplest form of heat exchanger. However, they are generally less efficient and more costly and require a large area of the plant plot. They consist of a single coil or “worm” submerged in a bath of cold water. The fluid flows through the coil to be cooled by the water surrounding it. The box cooler found use in the older petroleum refineries for cooling heavy residuum to storage temperatures. Modern day practice is to use a tempered water system where the heavy oil is cooled on the shell side of a shell and tube exchanger against water at a controlled temperature flowing in the tube side. The water is recycled through an air cooler to control its temperature to a level which will not cause the skin temperature of the oil in the shell and tube exchanger to fall below its pour point.

Direct-contact condensers

In this exchanger, the process vapor to be condensed comes into direct contact with the cooling medium (usually water). This contact is made in a packed section of a small tower. The most common use for this type of condenser is in vacuum producing equipment. Here the vapor and motive steam for each ejector stage are condensed in a packed direct-contact condenser. This type has a low pressure drop which is essential for the vacuum producing process.

General Design Considerations

Basic Heat Transfer Equations

The following equations define the basic heat transfer relationships.

These equations are used to determine the overall surface area required for the transfer of heat from a hot source to a cold source.

Overall heat transfer equation

The usual heat transfer mechanisms are conduction, natural convection, forced convection, condensation, and vaporization. When heat is transferred by these means, the overall equation is as follows:

$$Q = UA(\Delta t_m) \tag{90}$$

where:

Q = heat transferred in Btu/h.

U = overall heat transfer coefficient, Btu/h/sqft/°F.

A = heat transfer surface area, sqft.

Δt_m = corrected log mean temperature difference, °F.

Overall heat transfer coefficient U

This coefficient is the summation of all the resistances to the flow of heat in the transfer mechanism. These resistances are the resistance to heat transfer contained in the fluids, the resistance caused by fouling, and the resistance to heat transfer of the tube wall. The resistance to the flow of heat from the liquid outside the tube wall is measured by the film coefficient of that fluid. The resistance of the flow of heat from the fluid inside the tube is similarly the film coefficient of the inside fluid. These film coefficients are products of dimensionless numbers which include:

- The Reynolds number
- The Graetz number
- The Grashof number
- The Nusselt number
- The Peclet number
- The Prandtl number
- The Stanton number

The formats of these numbers and their use are found in all standard textbooks on heat transfer. For example, Kern's *Process Heat Transfer* and McAdams *Heat Transmission*.

These resistances are defined therefore by the following expression:

$$\frac{1}{U_o} = \frac{1}{h_o} + \frac{1}{h_i} \times \frac{A_o}{A_i} + \frac{1}{h_w} + (rf)_o + (rf)_i \times \frac{A_o}{A_i} \tag{91}$$

where:

U_o = overall heat transfer coefficient based on outside tube surface, in Btu/h/sqft/°F.
h = the film coefficient in Btu/h/sqft/°F.

rf = fouling factors in $\frac{1}{\mathrm{Btu/h/sqft/°F}}$.

h_w = heat transfer rate through tube wall in Btu/h/sqft/°F.
A = surface area in sqft.

Subscripts "o" and "i" refer to outside surface and inside surface, respectively.

Flow Arrangements

The two more common flow paths are concurrent and countercurrent. In concurrent (or cocurrent) flow, both the hot fluid and the cold fluid flow in the same direction. This is the least desirable flow arrangement and is only used in those chemical processes where there is a danger of the cooling fluid congealing, subliming, or crystallizing at near-ambient temperatures.

Countercurrent flow is the most desirable arrangement. Here the hot fluid enters at one end of the exchanger and the cold fluid enters at the opposite end. The streams flow in opposite directions to one another. This arrangement allows the two stream exit temperatures to approach one another.

Logarithmic Mean Temperature Difference Δt_m

This may also be designated as LMTD or Δt_m. In either countercurrent or concurrent flow arrangement, the log mean temperature difference used in the overall heat transfer equation is determined by the following expression:

$$\Delta t_m = (\Delta t_1 - \Delta t_2)/(\ln(\Delta t_1/\Delta t_2)). \tag{92}$$

The Δt's are the temperature differences at each end of the exchanger and Δt_1 is the larger of the two. In true countercurrent flow, the Δt_m calculated can be used directly in the overall heat transfer equation. However, such a situation is not common and true countercurrent flow rarely exists. Therefore, a correction factor needs to be applied to arrive at the correct Δt_m. These are given in Appendix 6 of this chapter.

Table 27 Typical velocities and pressure drops in various exchanger services

	Tube side		Shell side	
	Velocity, ft/s	Press drop, psi	Velocity, ft/s	Press drop, psi
Nonviscous liquids	6–8	10	1.5–2.5	10
Viscous liquids	6	20	3.0 max	15–20
Clean cooling water	6–8	10–15	–	–
Dirty cooling water	3 min	10+	–	–
Suspended solids, in	2–3 min	10	1.5 min	15 liquids[a]
Gases and vapors	$\frac{100}{\sqrt{\text{Gas density}}}$ max	3–5	–	3
Condensing vapors	–	–	–	3–5

[a]Normally erosion by suspended solids in liquids occurs at velocities of above 6 ft/s

Table 28 Allowable tube velocities for steam in exchanger tubes

Pressure	Velocity ft/s
Below atmospheric	225
Atmos. to 100 psig	175
Above 100 psig	150

Fluid Velocities and Pressure Drops

Film coefficients are a function of fluid velocity, density (vapor), and viscosity (liquids). Within limits increasing the velocity of a fluid reduces its resistance to heat transfer (i.e., it increases its heat transfer coefficient). Increasing the fluid velocity however increases its pressure drop. An economic balance needs to be sought between the cost of heat transfer surface and pumping cost. This exercise should be undertaken to find a pay-out balance of 2–4 years. The exercise has been done many times, and the data in Table 27 are considered to be reasonable balances between velocity and pressure drop for some common cases.

For condensing steam, pressure drop is usually not critical but a minimum steam pressure drop is desirable. Allowable steam velocities in tubes are in Table 28.

Choice of Tube Side Versus Shell Side

There are no hard and fast rules governing which fluid flows on which side in a heat exchanger. Much is left to the discretion of the individual engineer and his experience. There are some guidelines and these are as follows:

Tube side flow

Fouling liquids. Tube cleaning is much easier than cleaning the outside of the tubes. Also fouling can be reduced by higher tube side velocities.

Corrosive fluids. It is cheaper to replace tubes than shells and shell baffles, so as a general rule corrosive fluids are put on the tube side. There are exceptions and a major one is for corrosive fluids that become more corrosive at high velocities. An example of this is naphthenic acids, which are present in some crude oils and their products.

High pressure. Fluids at high pressure are usually put on the tube side as only the tubes, tube sheet, and channel need to be rated for high pressure in the unit design. This reduces the overall cost of the exchanger. Tube failure scenarios need to be considered in shell-side design, however.

Suspended solids. Fluids containing suspended solids should, whenever possible, be put on the tube side. Shell side flows invariably have "dead spaces" where solids come out of suspension and build up, causing fouling. If not feasible to put the fouling service on the tube side, the dead zones can be minimized by special baffle arrangements, such as spiral baffling.

Cold boxes. These are exchangers used in cryogenic processes where condensing of a vapor on one side of the exchanger is accompanied by boiling of a liquid on the other side. The condensing fluid is preferred on the tube side. Better control of the refrigerant flow is accomplished by the level control across the shell side.

Shell side flow

Available pressure drop. Shell side flows generally require lower pressure drop than tube side. Therefore, if a stream is pressure drop limited, it should be routed to the shell side.

Condensers. Condensing vapors should flow on the shell side wherever possible. The larger free area provided by the shell side space permits minimum pressure drop and higher condensate loading through better film heat transfer coefficients.

Large flow rates. In cases where both streams are of a similar nature with similar properties, the stream with the largest flow rate should be sent to the shell side where the difference in flow rates is significant. The shell side provides more flexibility in design by baffle arrangements to give the best heat transfer design criteria.

Boiling service. The boiling liquid, as in the case of reboilers, waste heat recovery units, and the like, should be on the shell side of the exchanger. This allows space for the proper disengaging of the vapor phase and provides a means of controlling the system by level control of the liquid phase.

Types of shell and tube exchangers

Figure 36 gives some of the more common arrangements in shell and tube exchanger design. The arrangements shown here are all one shell pass and one or two tube passes. Equipment with more than two tube passes (up to five) is also fairly common particularly in petroleum refining. Shell arrangements are however left at one if at all possible. Where multi-pass shell side is required, companies prefer to use complete exchangers in series or in parallel or both rather than making two or more shell passes using horizontal baffling in one exchanger.

Estimating Shell and Tube Surface Area and Pressure Drop

There are many excellent computer programs available that calculate exchanger surface area and pressure drops from simple input. The actual calculation when

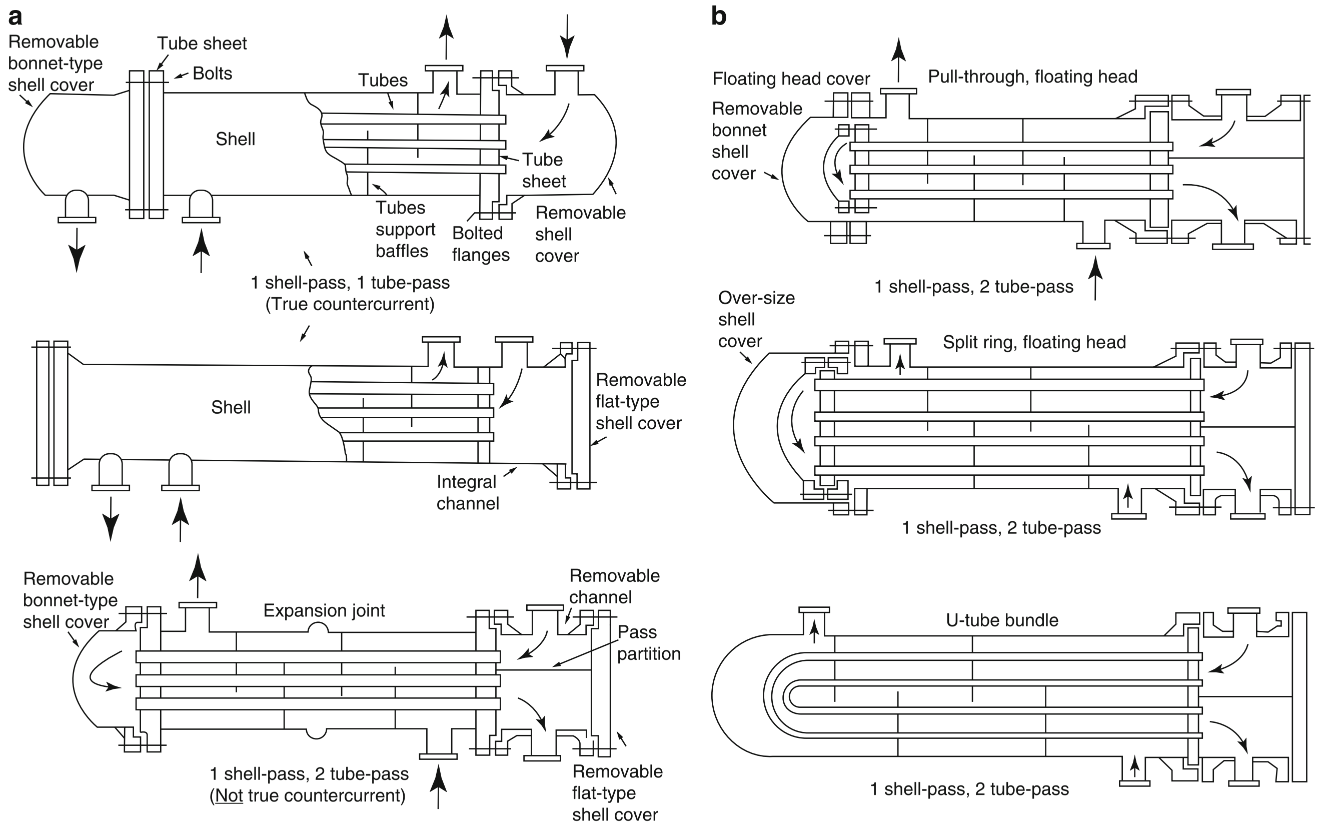


Fig. 36 Some common types of shell and tube exchangers, (**a**) fixed tube sheet, (**b**) removable bundle

done manually is tedious and long. However, to understand a little of the importance of the input required by these computer programs, it is educational to at least view a typical manual calculation. The one given here is for a shell and tube cooler with no change of phase for either tube side or shell side fluids.

The calculation follows these steps:

Step 1. Establish the following data by heat balances or from observed plant readings:

- The inlet and outlet temperatures on the shell side and on the tube side.
- The flow of tube side fluid and that for the shell side. It may be necessary to calculate one or the other from a heat balance over the exchanger.
- Calculate the duty of the exchanger in heat units per unit time (usually hours).
- Establish the stream properties for tube side and shell side fluids. The properties required are: SG, viscosity, specific heats, and thermal conductivity.

Step 2. Calculate the log mean temperature difference (Δt_{m}). Assume a flow pattern (i.e., either cocurrent or countercurrent). Most flows will be a form of countercurrent. Then show the temperature flow as follows:

	Shell In ⟶	Shell Out
	Tube out ⟵	Tube In
Temp difference:	Δt_1	Δt_2

The log mean temperature difference is then calculated using the expression

$$\Delta t_{\mathrm{m}} = \frac{\Delta t_1 - \Delta t_2}{\log_{\mathrm{e}} \dfrac{\Delta t_1}{\Delta t_2}} \tag{93}$$

This temperature needs to be corrected for the flow pattern, and this is done using the correction factors given in Appendix 6 of this chapter. The use of these is given in the Appendix figures.

Step 3. Calculate the approximate surface area.

From Appendix 7 of this chapter, select a suitable overall heat transfer coefficient U in Btu's/h sqft. F. Use the expression to calculate "A", the area.

$$Q = UA\Delta t_m \tag{94}$$

where:

Q = Heat transferred in Btu/h (the exchanger duty).
U = overall heat transfer coefficient.
A = exchanger surface area in sqft.
Δt_m = log mean temperature difference (corrected for flow pattern) in °F.

From the surface area calculated, select the tube size and pitch. Usually 3/4 in. on a triangular pitch for clean service and 1″ on a square pitch for dirty or fouling service. A single standard shell will hold about 4,100 sqft of surface per pass.

Many companies prefer to avoid multi-pass shells and instead prefer sets of shells in series if this becomes necessary. The "norm" therefore is single pass shells each containing up to 4,100 sqft of surface.

Step 4. Calculate the tube side flow and the number of passes. If it cannot be read from plant data, estimate the tube side flow in cuft/h by heat balance. Select the tube gauge and length. The tube data are given in Appendix 8 of this chapter and standard lengths of tubes are 16 and 20 ft. Calculate the number of selected tubes per pass from the expression

$$N_p = \frac{F_t \times 144}{3,600 \times A_t \times V_t} \tag{95}$$

where:

N_p = number of tubes per pass.
F_t = tube side flow in cuft/h.
A_t = cross-sectional area of one tube.
V_t = linear velocity in tube in ft/s.

See earlier item on "Fluid Velocities and Pressure Drop" for recommended fluid velocities. The number of tube passes is arrived at by dividing the total surface area required by the total (external) surface area of the number of tubes per pass calculated above.

Step 5. Calculate tube side film coefficient corrected to outside diameter (h_{io}). The tube side film coefficient may be calculated for water by the expression

$$h_{io} = \frac{300 \times (\mathrm{V_t} \times \text{tube ID ins})^{0.8}}{\text{tube OD ins}} \tag{96}$$

where:

h_{io} = inside film coefficient based on outside tube diameter in Btu/h sqft °F.
V_t = linear velocity of water tube side in ft/s.

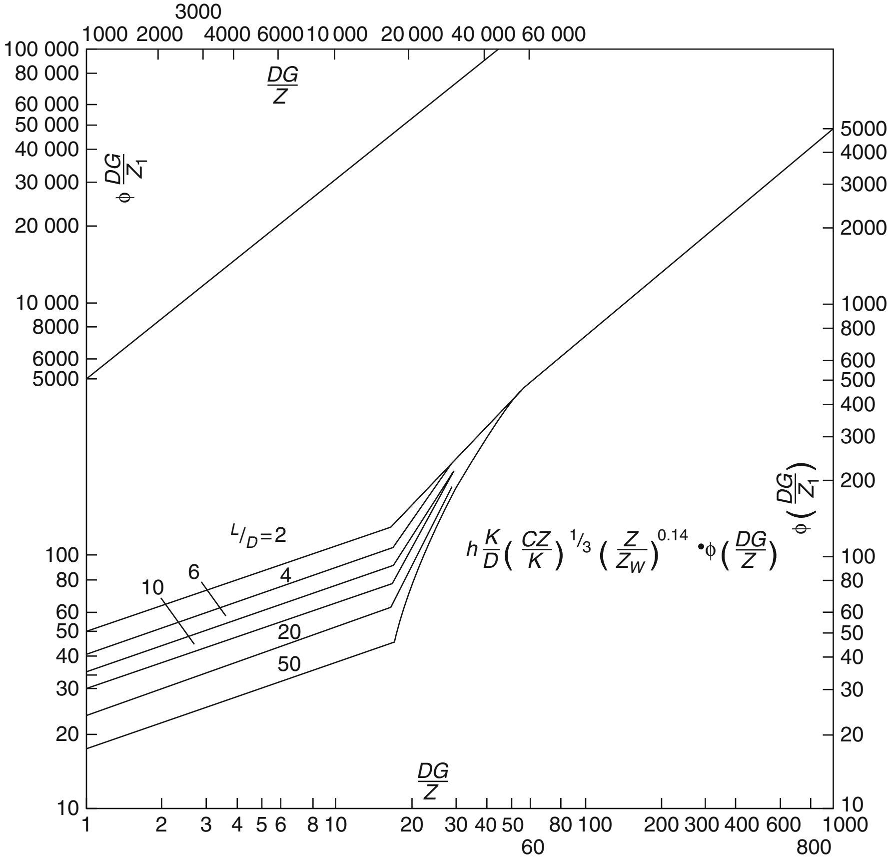
For fluids other than water flowing tube side, use the expression

$$h_{io} = \frac{K}{D_o}(C\mu/K)^{1/3}(\mu/\mu_w) \cdot \phi\left(DG^{0.14}/\mu\right) \tag{97}$$

where:

h_{io} = inside film coefficient based on outside diameter in Btu/h sqft °F.
K = thermal conductivity of the fluid in Btu/h/sqft/(°F per ft). See Maxwell *Data Book on Hydrocarbons* or Perry *Chemical Engineers Handbook.*
D = inside tube diameter in inches.
D_o = outside tube diameter in inches.
C = specific heat in Btu/lb/°F.
G = mass velocity in lbs/s sqft.
μ = absolute viscosity cPs at average fluid temp.
μ_w = absolute viscosity cPs at average tube wall temp.
ϕ (DG/μ) = from Fig. 37.

Step 6. Calculate shell side dimensions. First determine the shell side average film temperature as follows:



h = Film coefficient (Btu/h/ft^2/°F)
K = Thermal conductivity (Btu/ h ft^2/ (°F per ft)
L = Heated tube length (ft)
D = Inside tube diameter (in)
G = Mass velocity (lb/ s / ft^2)
C = Specific heat of fluid at av. fluid temp. (Btu/ lb/ °F)
Z = Absolute viscosity (cPs) at av. temp. of fluid
Z_W = Absolute viscosity (cPs) at av. tube wall temp.

Fig. 37 Heat transfer inside tubes

$$\text{Inlet ave} = \frac{T_1 + T_2}{2} \quad \text{Outlet ave} = \frac{T_3 + T_4}{2} \tag{98}$$

where:

T_1 = shell fluid inlet temperature.
T_2 = tube outlet temperature.
T_3 = shell outlet temperature.
T_4 = tube inlet temperature.

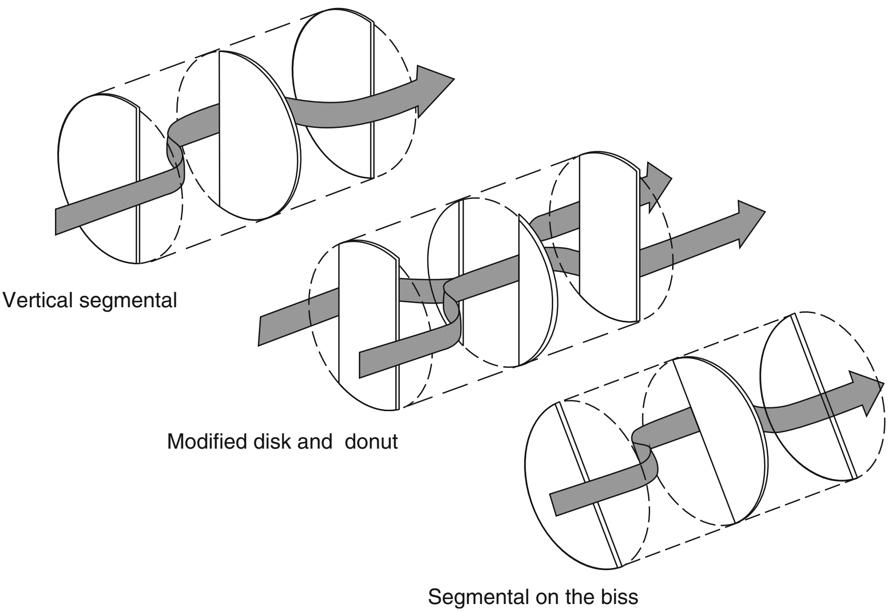


Fig. 38 Types of baffles

Average shell side film temperature:

$$\frac{\text{Inlet ave} + \text{outlet ave}}{2} \tag{99}$$

Use this temperature to determine density and viscosity used in the shell side film coefficient calculations.

The shell diameter. Next calculate the diameter of the tube bundle and the shell diameter. For this use one of the following equations to calculate the number of tubes across the center line of the bundle:

1. For square-pitch tube arrangement:
   $T_{\mathrm{cl}} = 1.19\ (\text{number of tubes})^{0.5}$.
2. For triangular pitch tube arrangement:
   $\mathrm{T}_{\mathrm{cl}} = 1.10\ (\text{number of tubes})^{0.5}$.

Note these equations use the *total* number of tubes, namely, those calculated in step 4 times number of tube passes.

Set number of baffles and their pitch. The types of baffles usually used are shown in Fig. 38. Disc- and donut-type baffles are only used where pressure drop available is very small and there is a pressure drop problem. Baffles on the bias are used in sq-pitch tube arrangement and baffles perpendicular to the tubes are usual for triangular tube arrangements.

Other types of baffling are applied in severely fouling services. These types include "rod-baffle" and spiral baffle patterns.

The minimum baffle pitch should not be less than 16 % of the shell diameter. Pitch in this case is the space between two adjacent baffles. Normally 20 % of shell ID is used for the baffle pitch. The number of baffles is calculated from the expression

$$N_B = \frac{10 \times \text{tube length}}{\text{baffle pitch\%} \times \text{diameter of shell.}} \tag{100}$$

Free area of flow between baffles. The space available for flow on the shell side is calculated as

$$W = D_\mathrm{i} - (d_\mathrm{o} \times T_\mathrm{cl}) \tag{101}$$

where:

W = space available for flow in sq inches.
D_i = shell inside diameter in inches.
d_o = tube outside diameter in inches.
T_cl = number of tubes across centerline.

The free area of flow between baffles is now calculated as follows:

$$A_\mathrm{f} = W \times \left(B_\mathrm{p} - 0.187\right) \tag{102}$$

where:

A_f = free flow area between baffles in sq inches.
B_p = baffle pitch in inches.

Step 7. Calculate the shell side film coefficient h_o. The following expression is used to determine the outside film coefficient:

$$h_\mathrm{o} = \frac{K}{d_\mathrm{o}}(C\mu/K)^{1/3} \cdot \phi(d_\mathrm{o}G_\mathrm{m}/\mu_\mathrm{f}) \cdot \frac{4P_\mathrm{b}}{D} \tag{103}$$

where:

h_o = outside film coefficient in Btu/h sqft °F.
G_m = maximum mass velocity in lbs/s sqft.
d_o = outside tube diameter in inches.
K = thermal conductivity of fluid in Btu/h/sqft/(°F/ft) .
C = specific heat of fluid in Btu/lb/F.
μ_f = viscosity at mean film temperature in cPs.
P_b = baffle pitch in inches.
D = shell internal diameter in inches.

$\phi(d_\mathrm{o}G_\mathrm{m}/\mu_\mathrm{f})$ is a function of the Reynolds number read from Fig. 39. The Reynolds number in this case is

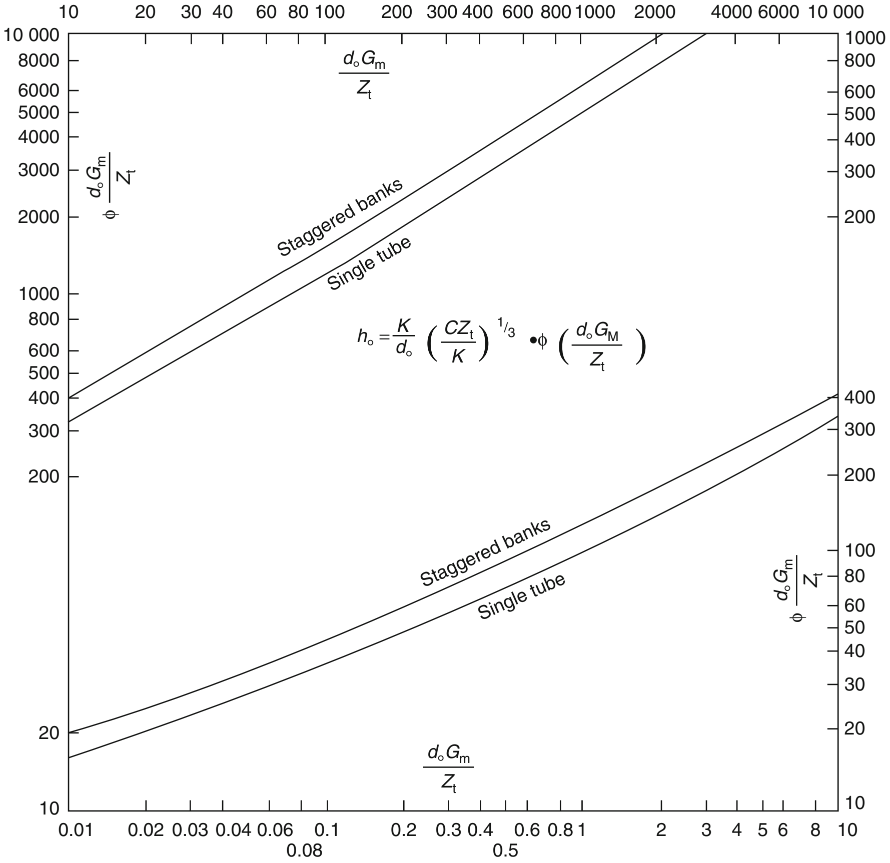


Fig. 39 Heat transfer to fluids outside tubes (See Fig. 37 for definitions.)

$$\mathrm{Re} = \frac{d_o G_m}{\mu_f} \tag{104}$$

where: G_m = lbs/s sqft.

This film coefficient is corrected for the type of baffle and tube arrangement by multiplying it by one of the following factors:

For square pitch vertical to tube rows	0.50
Square pitch on the bias	0.55
Triangular tube pitch	0.70

Step 8. Calculate the overall heat transfer coefficient U_o. The film coefficients calculated in steps 5 and 7 are now used in the expression

Table 29 Thermal conductivities of tube metals

Material	*K*, Btu/h sqft F/ft
Admiralty brass	64
Aluminum brass	58
Aluminum	117
Brass	57
Carbon steel	26
Copper	223
Cupronickel	41
Lead	20
Monel	15
Nickel	36
Red brass	92
Type 316 alloy steel	9
Type 304 alloy steel	9
Zinc	65

$$\frac{1}{U_o} = \frac{1}{h_{io}} + r_{io} + \frac{1}{h_o} + r_o + r_w \tag{105}$$

where:

U_o = overall heat transfer coefficient in Btu/h sqft °F.

r_{io} and r_o = tube side and shell side fouling factors, respectively, in h sqft °F/Btu. For clean tubes, this is 0.001 as a sum of both factors. For fouling services, 0.005 or higher may apply.

r_w = tube wall resistance to heat transfer in h sqft °F/Btu, which is expressed as

$$r_w = \frac{t_w \cdot d_o}{12 \times K \times (d_o - 2t_w)} \tag{106}$$

where:

t_w = tube wall thickness inches.

d_o = outside tube diameter inches.

K = thermal conductivity Btu/h sqft °F/ft. See Table 29.

Compare the calculated value of the overall heat transfer coefficient with the assumed one in step 3.

If there is agreement within ±10 %, then the calculated one will be used for revising the calculation for surface area and the other dimensions. If there is no agreement, repeat the calculation using a new value for the assumed *U* until they agree within tolerance.

Step 9. Calculate tube side pressure drop. Using the adjusted dimensional values from the calculated U_o, calculate the tube side pressure drop using one of the following equations:

For water only:

$$\Delta P_t = 0.02F_t \times N_p \times \left(V^2 + \left(0.158LV^{1.73}/d_i\right)^{1.27}\right). \tag{107}$$

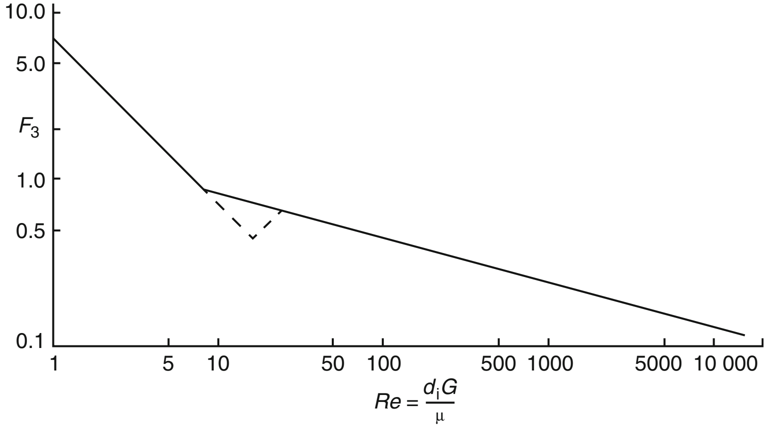


Fig. 40 Pressure drop factor F_3 for flow inside tubes

Table 30 Values of F_t for various tube sizes and materials

Tube OD, inches	Tube metal	F_t
0.75	Steel	1.50
1.00	Steel	1.40
1.50	Steel	1.20
0.75	Ad brass	1.20
1.00	Copper	1.15

For fluids other than water, use

$$\Delta P_t = F_t \times N_p \times (\Delta P_{tf} + \Delta P_{tr}) \tag{108}$$

where:

$$\Delta P_{tf} = F_3 \cdot \frac{L}{d_i} \cdot \left(\rho_m \times V^2/9,270\right) \cdot (\mu_w)^{0\cdot 14}. \tag{109}$$

$$\Delta P_{tf} = 3 \times \left(\rho_m \times V^2/9,270\right). \tag{110}$$

F_3 = factor based on Reynolds number; see Fig. 40
ρ_m = density in lbs/cuft at mean fluid temperature.
μ_w = viscosity of fluid at tube wall temperature in cPs (use mean film temperature).
V = linear velocity in ft/s.
F_t = pressure drop fouling factor (dimensionless) from Table 30.

The pressure drop figure calculated by these equations is for one unit. Where there are more shells in series, multiply the figures by the number of shells.

Step 10. Calculate the shell side pressure drop. Using the revised dimensions calculated in step 8, the total shell side pressure drop is calculated using the following equation:

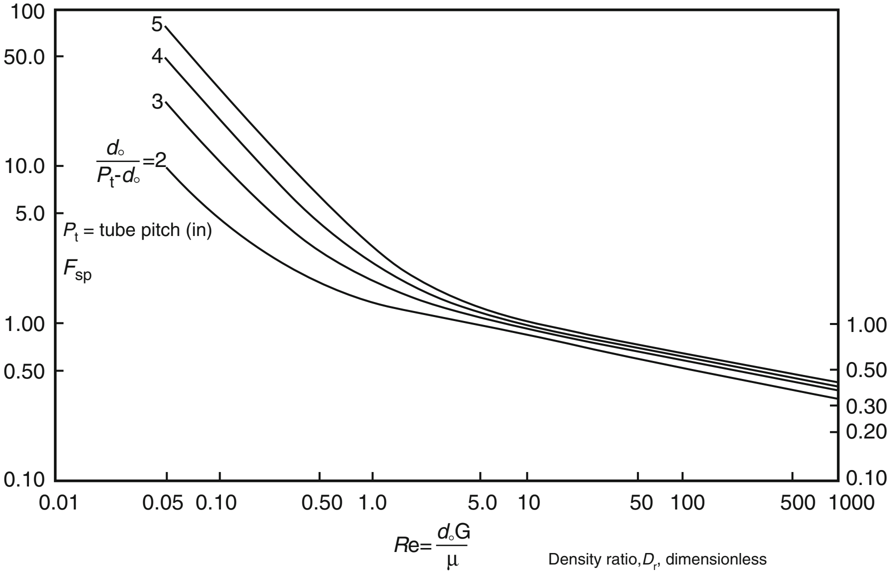


Fig. 41 Pressure drop factor F_{SP} for flows across banks of tubes

$$\Delta P_s = F_s \times (\Delta P_{sr} + \Delta P_{sf}) \tag{111}$$

where:

$\Delta P_{sf} = B_2 F_{sp} N_{tc} N_b \left(m \times V^2/9,270\right)$.

ΔP_{sr} = pressure drop due to turns given by

$$(N_b + 1) \cdot (3.5 - 2P_b/D) \cdot \frac{\left(m \times V^2\right)}{9,270}. \tag{112}$$

B_2 = factor as follows:

Baffle position	Tube layout	B_2
Vertical	Square	0.30
Bias at 45°	Square	0.40
Vertical	Triangular	0.50

F_{sp} = factor based on Reynolds number. See Fig. 41.
N_{tc} = number of tubes on center line.
N_b = number of shell baffles.
P_b = space between baffles, inches.
D = shell ID in inches.

The pressure drop calculated here is for one shell. If there are more shells in series, then multiply these pressure drops by the number of shells.

Air Coolers and Condensers

Air cooling of process streams or condensing of process vapors is more widely used in the process industry than cooling or condensing by exchange with cooling water. Cooling water is normally reserved for smaller "trim" coolers or when lower temperatures are required. The use of individual air coolers for process streams using modern design techniques has economized in plant area required. It has also made obsolete those large cooling towers and ponds associated with product cooling. This item of the chapter describes air coolers in general and outlines a method to estimate surface area, motor horsepower, and plant area required by the air coolers.

As in the case of shell and tube exchangers, there are many excellent computer programs that can be used for the design of air coolers. The method given here for such calculation may be used in the absence of a computer program or for a good estimate of a unit. The method also emphasizes the importance of the data supplied to manufacturers for the correct specification of the units.

General Description of Air Coolers/Condensers

Figure 42 shows the two common types of air coolers used in the process industry. Both units consist of a bank of tubes through which the fluid to be cooled or condensed flows. Air is passed around the tubes either by a fan located below the tubes forcing air through the tube bank or a fan located above the tube bank drawing air through the tube bank. The first arrangement is called "forced draft" and the second "induced draft."

Air in both cases is motivated by a fan or fans driven by an electric motor or a steam turbine or in some cases a gas turbine. The fan and prime driver are normally connected by a "V" belt or by a shaft and gearbox. Electric motor drives are by far the most common prime drivers for air coolers.

The units may be installed on a structure at grade or, as is most often the case, on a structure above an elevated pipe rack. Most air coolers in condensing service are elevated above pipe racks to allow free flow of condensate into a receiving drum.

Thermal Rating

Thermal rating of an air cooler is similar in some respects to that of a shell and tube exchanger described in the previous item. The basic heat transfer equation

$$Q = U \Delta T\, A \tag{113}$$

is used to determine the surface area required. The calculation for U is different in that it requires the calculation for the air-side film coefficient. This film coefficient is usually based on an extended surface area which is formed by adding fins to the bare surface of the tubes. Thermal rating, surface area, fan dimensions and horsepower are calculated by the following steps:

Step 1. Calculate the heat duty and the tube side material characteristics.

Step 2. Calculate the log mean temperature for the exchanger. Using the following equation, determine the temperature rise for the air flowing over the tubes:

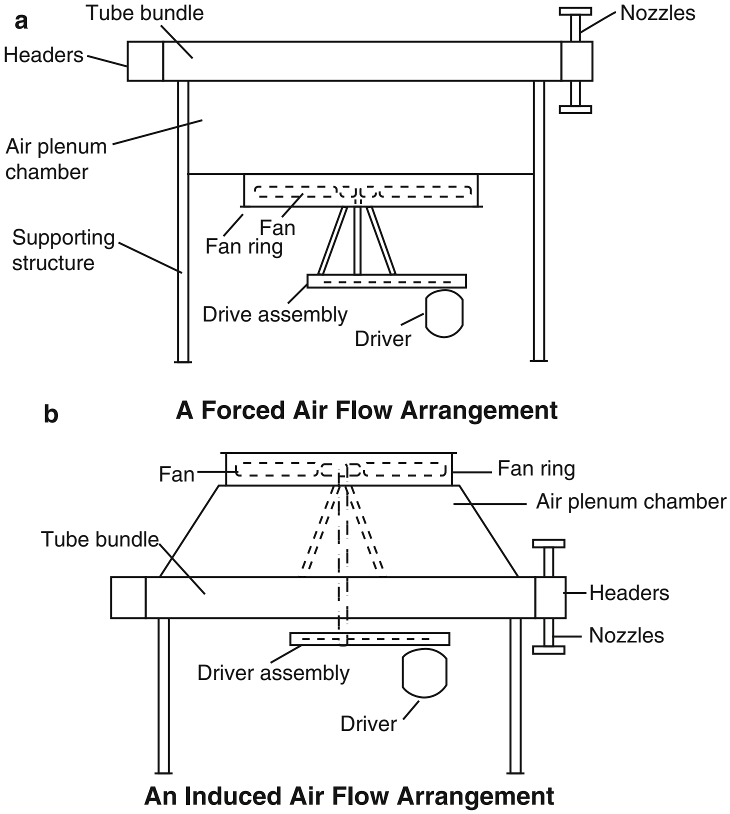


Fig. 42 Air coolers. (**a**) Forced draft. (**b**) Induced draft

$$\Delta t_{\mathrm{m}} = ((U_{\mathrm{e}} + 1)/10)) \cdot ((\Delta t_{\mathrm{m}}/2) - t_1)) \tag{114}$$

where:

Δt_{m} = air temperature rise °F.
U_{e} = overall heat transfer coefficient assumed (From Table 31).
Δt_{m} = mean tube side temperature °F
t_1 = inlet air temperature °F.

Calculate the log mean temperature difference (LMTD) as in step 2 of the previous item on shell and tube exchanger design.

Step 3. Determine an approximate extended surface area using the expression:

$$A_{\mathrm{E}} = \frac{Q}{U_{\mathrm{E}} \cdot \Delta t_{\mathrm{m}}} \tag{115}$$

where:

A_{E} = extended surface area in sqft.
Q = exchanger duty in Btu/h.
U_{E} = overall heat transfer coefficient based on extended surface from Table 31.
Δt_m = log mean temperature difference corrected for number of passes, in °F.

Table 31 Some common overall transfer coefficients for air cooling

	1/2″ by 9		5/8″ by 10	
	Fin ht. by fin/in.		Fin ht. by fin/in.	
Service	U_e	U_o	U_e	U_o
Process water	95	6.5	110	5.2
Hydrocarbon liquids				
Visc at avg temp cps				
0.2	85	5.9	100	4.7
1.0	65	4.5	75	3.5
2.5	45	3.1	55	2.6
6.0	20	1.4	25	1.2
10.0	10	0.7	13	0.6
Hydrocarbon gases				
at pressures psig				
50	30	2.1	35	1.6
100	35	2.4	40	1.9
300	45	3.1	55	2.6
500	55	3.8	65	3.0
1,000	75	5.2	90	4.2
Hydrocarbon condensers				
Cooling range 0 °F	85	5.9	100	4.7
10 °F	80	5.5	95	4.4
60 °F	65	4.5	75	3.5
100 + °F	60	4.1	70	4.2
Refrigerants				
Ammonia	110	7.6	130	6.1
Freon	65	4.5	75	3.5

U_e is transfer coefficient for finned surface
U_o is transfer coefficient for bare tubes

Step 4. Calculate the number of tubes from the expression

$$N_t = \frac{A_E}{A_f \times L} \tag{116}$$

where:

N_t = total number of tubes.
A_E = extended surface area in sqft.
A_f = extended area per ft of fin tube read from Table 32.
L = length of tube (30 f. is standard).

Step 5. Fix the number of passes (usually 3 or 4) and calculate the mass flow of tube side fluid using the expression

$$\mathrm{G} = \frac{\text{lbs/h of tube side fluid} \times N_p \times 144}{N_t \times A_t \times 3,600} \tag{117}$$

Table 32 Fin tube to bare tube relationships based on 1″ O/D tubes

Fin Ht. by fins/in.	1/2″ by 9		5/8″ by 10	
Area/ft fin tube	3.8		5.58	
Ratio of areas, fin/bare tube	14.5		21.4	
Tube pitch in.	2Δ	2¼Δ	2¼Δ	2½Δ
Bundle area sqft/ft[a]				
3 rows	68.4	60.6	89.1	80.4
4 rows	91.2	80.8	118.8	107.2
5 rows	114.0	101.0	148.5	134.0
6 rows	136.8	121.2	178.2	160.8

[a] Bundle area is the external area of the bundle face area in sqft/ft

where:

G = Mass velocity in lbs/s sqft.
N_p = Number of tube passes.
A_t = inside cross-sectional area of tube in sq inches

Step 6. Calculate the Reynolds number for tube side using the expression

$$\mathrm{Re} = \frac{d_i \cdot G}{\mu} \tag{118}$$

where:

R_e = Reynolds number (dimensionless).
d_i = tube ID in inches.
μ = tube side fluid viscosity at average temperature in cPs.

Step 7. Calculate the inside film coefficient from the expression

$$h_{io} = \frac{K}{D}(C\mu/K)^{1/3} \cdot (\mu/\mu_w)^{0.14} \cdot \phi(DG/Z) \tag{119}$$

where:

h_i = inside film coefficient in Btu/h·sqft °F.
K = thermal conductivity of the fluid in Btu/h/sqft/(° F per ft). See Maxwell *Data Book on Hydrocarbons*.
D = inside tube diameter in inches.
C = specific heat in Btu/lb/°F.
G = mass velocity in lbs/s sqft.
μ = absolute viscosity cPs at average fluid temp.
μ_w = absolute viscosity cPs at average tube wall temp.
$\phi\ (DG/\mu)$ = from Fig. 37

Step 8. Calculate the mass velocity of air and the film coefficient on the air side, thus

$$\text{Weight of air} = \frac{Q}{C_{\text{Air}} \times \Delta t_{\text{Air}}} \tag{120}$$

where:

Q = exchanger duty in Btu/h.
C_{Air} = specific heat of air (use 0.24).
Δt_{Air} = temperature rise of the air °F.

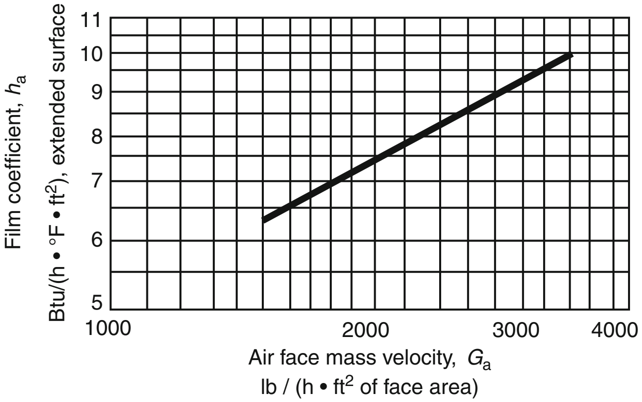


Fig. 43 Air film coefficients

Face area of tubes A_f is calculated as follows:

Set the OD of the tubes (usually 1″), length, fin size (usually 5/8″ at 10 fins to the inch or 1/2″ at 9 fins to the inches), Pitch (see Table 32), and number of tube rows (start with 3 or 4). Then face area is

$$A_f = \frac{\text{Total extended surface area } \mathrm{A_E}}{\text{External area per ft of bundle (from Table 32)}}. \tag{121}$$

Mass velocity of air is calculated from the expression

$$G_a = \frac{\text{lbs per hour of air flow}}{\text{face area } A_f}. \tag{122}$$

The film coefficient for the air side is read from Fig. 43.

Step 9. Calculate the overall heat transfer coefficient as follows:

Area ratio of bare tube outside to fins outside is read from Table 32. Then, the factor to convert all heat flow resistance to outside tube diameter basis is

$$F_t = \frac{A_r \times \text{tube OD}}{A_t} \tag{123}$$

where:

A_r = area ratio.
A_t = inside tube cross-sectional area sq inches.
then:

$$\frac{1}{U_o} = \frac{1 + (r_t \times F_t) + r_w + 1}{h_i h_o} \tag{124}$$

where:

r_t = inside fouling factor.
r_w = tube metal resistance (normally ignored).

If the calculated U is within 10 % of the assumed, there will be no need to recalculate with a new assumed value for the U. The dimensions and data are adjusted however using the calculated value for U.

Step 10. Calculate the required fan area and the fan diameter as follows:

$$\text{Fan area} = \frac{0.4 \times \text{Face Area } A_\text{f}}{\text{Assumed Number of Fans}}. \tag{125}$$

Begin by assuming 2 fans and continue with multiples of 2 until a reasonable fan diameter (about 10–12 ft) is obtained. On very large units, fans can be maximized at 16 ft.

$$\text{Fan diameter} = \surd(\text{Fan area} \times 4/\pi). \tag{126}$$

Step 11. Calculate air-side pressure drop and actual air flow in cuft/min.

$$\text{Average air temperature} = \frac{t_1 + t_2}{2}. \tag{127}$$

From Fig. 44, D_r = relative density factor for air at elevations of site.

From Fig. 45, ΔP_a = pressure drop of air in inches of H_2O.

$$\Delta P_\text{a} \text{ corrected} = \frac{\Delta P_\text{a} \times \text{No of rows}}{D_\text{r}}. \tag{128}$$

Density of air at corrected ΔP_a:

$$\frac{29}{(378 \times 14.7 \times T_2)/(T_1 \times (\text{Corr } \Delta P_\text{a} + 14.7))} \tag{129}$$

where T_1 and T_2 are absolute temperatures.

ACFM of air therefore is

$$\frac{\text{lbs/h of air}}{\text{Density} \times 60}. \tag{130}$$

ΔP of air at the fan is obtained by the expression

$$\Delta P_\text{m} = \left[\frac{\text{ACFM}}{(4,000(\pi d)/4)}\right]^2 \tag{131}$$

in inches of water gauge.

Step 11. Calculate the fan horsepower as follows:

$$\begin{aligned} \text{Hydraulic HP} &= \frac{\text{ACFM} \times \text{density of air} \times \text{diff head in ft}}{33,000} \\ \text{Differential head} &= \frac{\text{total } \Delta P \text{ at fan in in. } H_2O \times 5.193}{\text{Density}} \\ \text{BHP} &= \frac{\text{hydraulic HP}}{\eta_\text{r}} \end{aligned} \tag{132, 133, 134}$$

where η_r is the fan efficiency (usually 70 %).

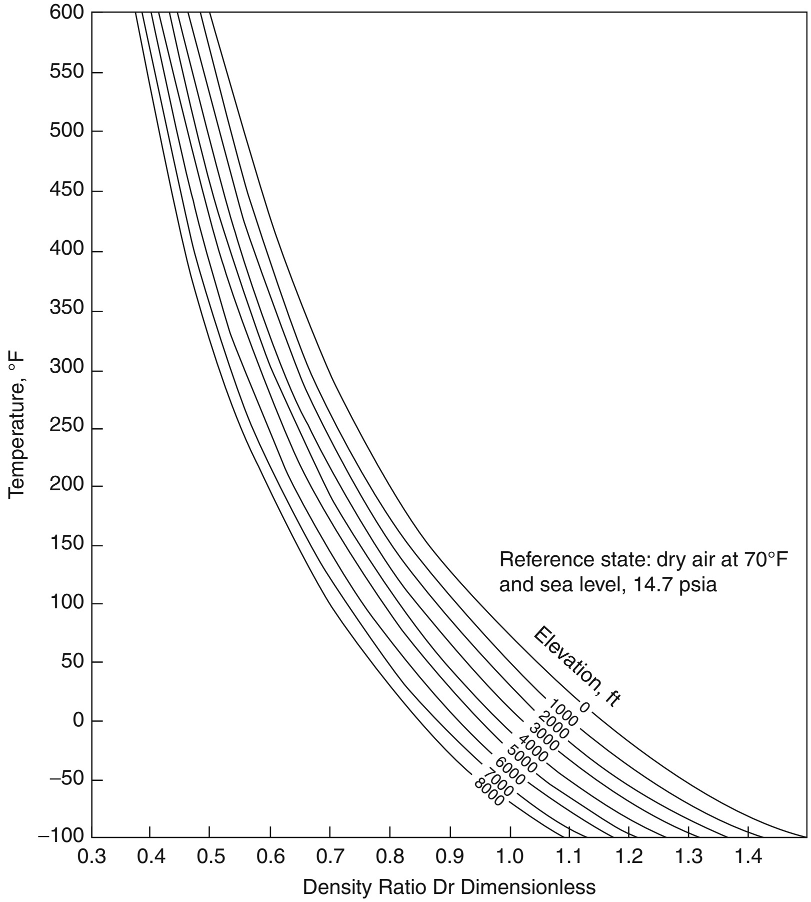


Fig. 44 Relative density of air

Condensers

In petroleum refining and most other chemical process plants, vapors are condensed either on the shell side of a shell and tube exchanger, the tube side of an air cooler, or by direct contact with the coolant in a packed tower. By far the most common of these operations are the first two listed. In the case of the shell and tube condenser, the condensation may be produced by cooling the vapor by heat exchange with a cold process stream or by water. Air cooling has overtaken the shell and tube condenser in the case of water as coolant in popularity as described in the previous item.

In the design or performance analysis of condensers, the procedure for determining thermal rating and surface area is more complex than that for a single-phase

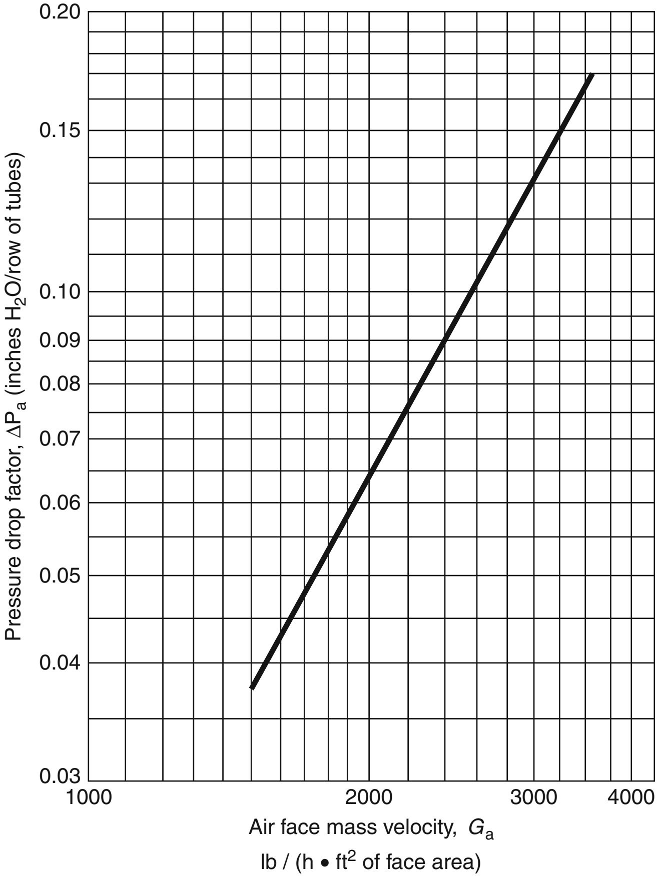


Fig. 45 Pressure drop air side in inches of water

cooling and heating. In condensers there are three mechanisms to be considered for the rating procedure. These are:

- The resistance to heat transfer of the condensing film
- The resistance to heat transfer of the vapor cooling
- The resistance to heat transfer of the condensate film cooling

Each of these mechanisms is treated separately and along preselected sections of the exchanger. The procedure for determining the last two of the mechanisms follows that described earlier for single-phase heat transfer. The following expression is used to calculate the film coefficient for the condensing vapor:

$$h_c = \frac{8.33 \times 10^3}{(M_c/L_c \cdot N_s)^{0.33}} \times k_f \times \left[\frac{SG_c^2}{\mu_f}\right]^{0.33} \tag{135}$$

where:

h_c = condensing film coefficient.
M_c = mass condensed in lbs/h
L_c = tube length for condensation.

$$= \frac{A_{\text{zone}}}{A} \times (L - 0.5). \tag{136}$$

$N_s = 2.08\ N_t^{0.495}$ for triangular pitch.
k_f = thermal conductivity of condensate at film temperature.
SG_c = specific gravity of condensate.
μ_f = viscosity of condensate at film temperature in cPs.

Again there are many excellent computer programs that calculate condenser thermal ratings, and these of course save the tedium of the manual calculation. However, no matter which method of calculation is selected, there is required one major additional piece of data over that required for single-phase heat exchange. That item is the enthalpy curve for the vapor.

Enthalpy curves are given as the heat content per lb or per hour contained in the mixed-phase condensing fluid plotted against temperature. An example of such a curve is given in Fig. 46. These enthalpy curves are developed from the vapor/liquid or flash calculations described in the handbook chapter "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries."

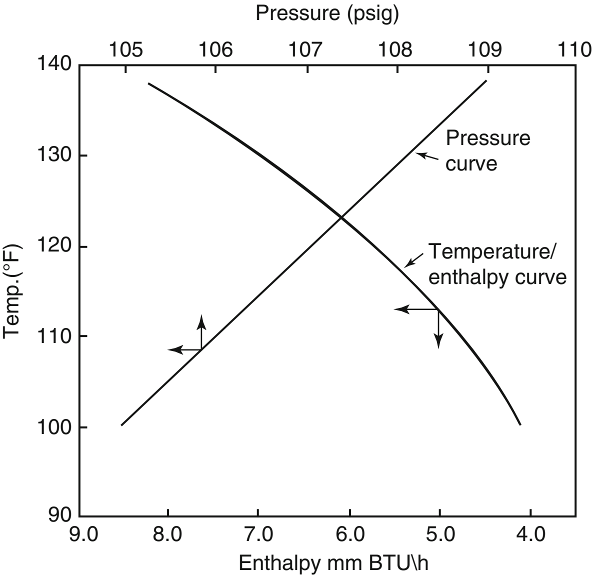
Briefly the calculation for the curve commences with determining the dew point of the vapor and the bubble point of the condensate. Three or more temperatures are selected between the dew and bubble points and the V/L calculation of the fluid at these temperatures carried out. Enthalpy for the vapor phase and the liquid phase are added for each composition of the phases at the selected temperatures. These together with the enthalpy at dew point and bubble point are then plotted.

As in the case of the shell and tube exchanger and the air cooler, a manual calculation for condensers is described here. Again this is done to provide some understanding of the data required to size such a unit and its significance in the calculation procedure. Computer-aided designs should however be used for these calculations whenever possible.

The following calculation steps describe a method for calculating the film coefficient of a vapor condensing on the shell side of an S and T exchanger. The complete rating calculation will not be given here as much of the remaining calculation is simply repetitive.

Step 1. Calculate the dew point of the vapor stream at its source pressure. Estimate the pressure drop across the system. Usually 3–5 psi will account for piping and the exchanger pressure drop. Calculate the bubble point of the condensate at the terminal pressure. Select three or more temperatures between dew point and bubble point and calculate the vapor/liquid quantities at these conditions of temperature and pressure.

Fig. 46 Enthalpy curve for a debutanizer overhead condenser



Step 2. Calculate the enthalpy of the vapor and liquid at these temperatures. Plot the total enthalpies against temperature to construct the enthalpy curve. Establish the properties of the vapor phase and liquid phase for each temperature interval. The properties mostly required are SG, viscosity, mole wt, thermal conductivity, and specific heat.

Step 3. In the case of a water cooler, calculate the duty of the exchanger and the quantity of water in lbs/h. Commence the heat transfer calculation by assuming an overall heat transfer coefficient (use the data given in Appendix 7), calculating the corrected LMTD and the surface area.

Step 4. Using the surface area calculated in step 3, define the exchanger geometry in terms of number of tube passes, number of tubes on the center line, shell diameter, baffle arrangement, and the shell free flow area. Calculate also the water flow in feet per sec.

Step 5. Divide the exchanger into three or four zones by selecting the zone temperatures on the enthalpy curve. Calculate the average weight of vapor and the average weight of condensate in each zone. Using these averages, calculate the average heat transferred for:

Cooling of the vapor Q_v

Cooling of the condensate Q_L

Condensing of the vapor which will be:

Total heat in the zone (from the enthalpy curve) less the sum of Q_v and Q_L

Step 6. Calculate the film coefficient for the tube side fluid. See previous item "Estimating Shell and Tube Surface Area and Pressure Drop."

Step 7. Starting with zone 1 and knowing the outlet temperature of the coolant fluid, the total heat duty of the zone, and the shell side temperatures, calculate the coolant inlet temperature. Using this calculate the LMTD for the zone and, assuming a zone overall heat transfer coefficient U, calculate a surface area for the zone. Using this and the total exchanger area estimated in step 4, establish L_c in feet.

Step 8. Calculate the condensing film coefficient from the equation given earlier. This will be an uncorrected value for h_c. This will be corrected to account for turbulence by the expression

$$h_{c(\mathrm{corr})} = h_c \times (G_v/5) \tag{137}$$

where:

G_v = average vapor mass velocity in lbs/h·sqft.

Step 9. Calculate the value of G_v using the free flow area allocated to the vapor γ_v. The following expressions are used for this:

$$\begin{aligned}
\gamma_v &= 1 - \gamma_L. \\
\frac{1}{\gamma_L} &= 1 + \frac{\text{ave mass vapor}}{\text{ave mass liquid}} \times (\mu_v/\mu_L)^{0.111} \times (\rho_L/\rho_V)^{0.555}. \\
G_v &= \frac{\text{ave mass vapor}}{25 \times \text{free flow area} \quad \times \gamma_v}.
\end{aligned} \tag{138, 139, 140}$$

Step 10. Calculate the film coefficient h_v for the vapor cooling mechanism. This will be the procedure used for a single-phase cooling given in a previous item. This is corrected to account for resistance of the condensate film by the expression

$$\frac{1}{h_{v\,\mathrm{corr}}} = -\frac{1}{h_c} + \frac{1}{1.25h_v}. \tag{141}$$

Step 11. Calculate the film coefficient for the condensate cooling mechanism. Again this is the procedure described in the item for single-phase cooling on the shell side. This is corrected for drip cooling that occurs over a tube bank.

$$\begin{aligned}
\text{Drip cooling } h_{dc} &= 1.5 \times h_c \\
\text{and } h_L \text{ corrected} &= \frac{2 \times h_{dc} \times h_L}{h_{dc} + h_L}.
\end{aligned} \tag{142, 143}$$

Step 12. Calculate the total zone film coefficient h_o using the following expression:

$$h_o = -\frac{Q_{\mathrm{zone}}}{\dfrac{Q_c}{h_c} + \dfrac{Q_v}{h_v} + \dfrac{Q_L}{h_L}} \tag{144}$$

where:

Q_c, Q_v, and Q_L are the enthalpies for condensing, vapor cooling, and condensate cooling, respectively.

Step 13. Calculate the overall heat transfer coefficient neglecting the shell side coefficient from step 12. Thus,

$$\frac{1}{U_x} = r_o + r_w + r_{io} + R_{io} \tag{145}$$

where:

r_o, r_w, and r_{io} are fouling factors for shell fluid, wall, and tube side fluid, respectively. R_{io} is the tube side film coefficient calculated in step 6.

Step 14. Calculate the overall heat transfer coefficient U_{zone} for the zone using the expression

$$U_{zone} = \frac{h_o \times U_x}{h_o + U_x}. \tag{146}$$

Check the calculated U against that assumed for the zone. Repeat the calculation if necessary to make a match.

Step 15. Calculate the zone area using the acceptable calculated U. Repeat steps 7 through 14 for the other zones. The total surface area is the sum of those for each zone.

Reboilers

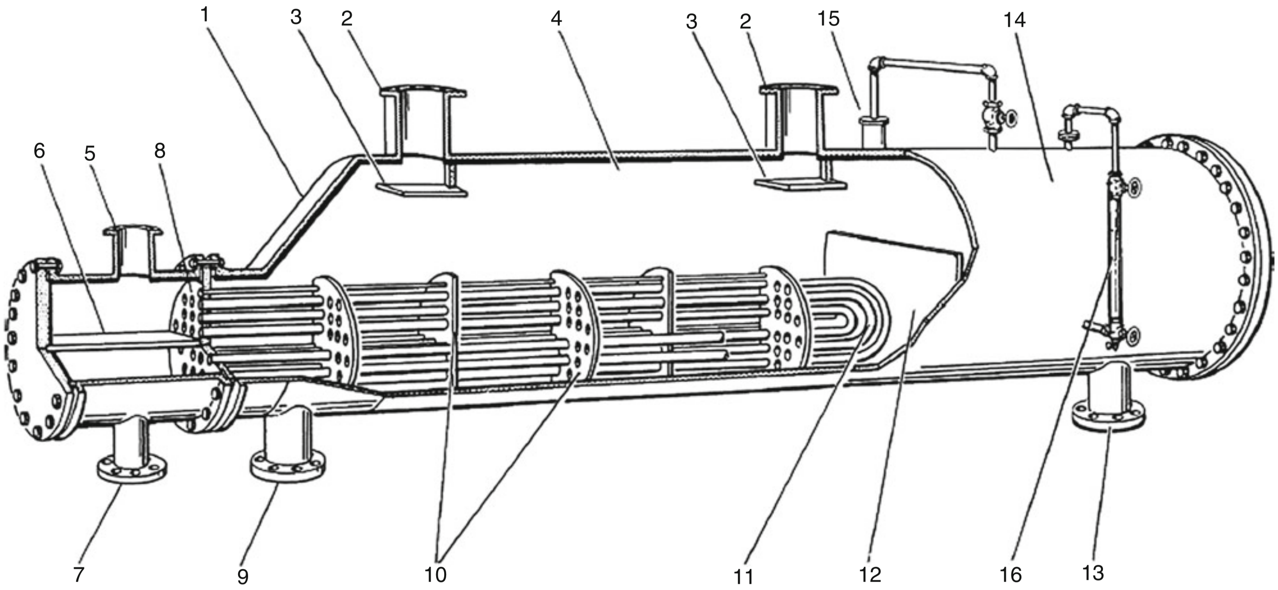
Reboilers are used in fractionation to provide a heat source to the system and to generate a stripping vapor stream to the tower. Reboilers are operated either by the natural circulation of a fluid or by forced circulation of the fluid to be reboiled. This chapter deals only with natural circulation reboilers.

There are three common types of reboilers and these are:

- The kettle-type reboiler
- The once-through thermosiphon reboiler
- The recirculating thermosiphon reboiler

The Kettle Reboiler

This type of reboiler (Fig. 47) is extremely versatile. It can handle a very wide range of vaporization loads (e.g., when used as LPG vaporizer for fuel gas purposes, it vaporizes 100 % of the feed). The equipment consists of a large shell into which is fitted a tube bundle through which the heating medium flows. The liquid to be reboiled enters the bottom of the shell at the end adjacent to the tube inlet/outlet chamber. The liquid is boiled and partially vaporized by flowing across the tube bundle. The diameter of the shell is sized such that there is sufficient space above the tube bundle and the top of the shell to allow some disengaging of the liquid and vapor. A baffle weir is installed at the end of the tube bundle furthest from the inlet. This baffle weir establishes a liquid level over the tube bundle in the shell. The boiling liquid flows over this weir to the shell outlet nozzle, while the vapor generated is allowed to exit from the top of the shell through one or two nozzles.



1. Shell ; 2. Shell outlet nozzles Vapor ; 3. Entrainment Baffles ; 4. Vapor Disengaging Space. 5. Channel Inlet Nozzle ; 6. Channel Partition ; 7. Channel outlet nozzle. ; 8. Tube Sheet; 9. Shell inlet nozzle.; 10. Tube support sheets.; 11. U Tube returns.; 12. Weir. ; 13 Shell outlet nozzle (liquid).; 14. Liquid hold up (Surge) section.; 15. Top of level - instrument housing (external displacer).; 16. Liquid level gauge.

Fig. 47 The components of a kettle reboiler

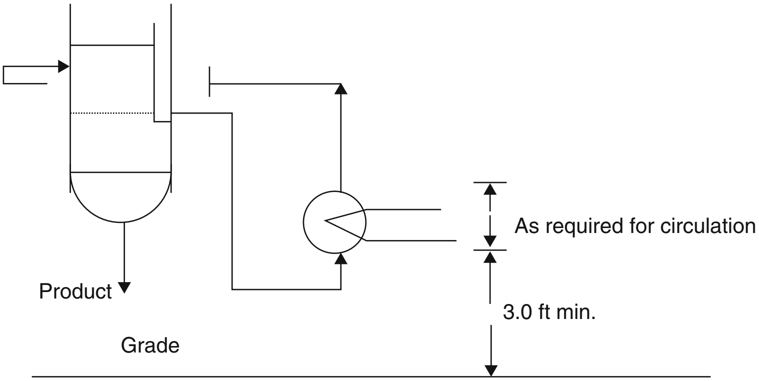


Fig. 48 Once-through thermosiphon reboiler arrangement

The space downstream of the weir is sized for liquid holdup to satisfy the surge requirements for the product. Thus, it is not necessary to provide space in the bottom of the tower for product surge. If the heating medium is non-fouling, it is permissible to use U tubes for the tube bundle. Otherwise, the tube bundle is often of the floating head type. New, smaller hydroblast nozzles and cleaning methods for U-tubes, however, allow use of these even in fouling services. The kettle-type reboiler should always be the first type to be considered if there are no elevation constraints to pumping the bottoms product away.

Once-Through Thermosiphon Reboiler

This type of reboiler and its location relative to the tower are illustrated Fig. 48.

This type of reboiler should be considered when a relatively high amount of surge is required for the bottom product and when it is necessary to provide head for the product pump (NPSH requirement).

This type of reboiler takes the liquid from the bottom tray of the fractionator as feed. This stream enters the shell side of a vertical single tube pass shell and tube exchanger by gravity head to the bottom of the shell. The heating medium flows tube side to partially vaporize the liquid feed. A siphoning effect is caused by the difference in density between the reboiler feed and the vapor/liquid effluent. This allows the reboiler effluent to exit from the top of the shell side and reenter the tower where the vapor disengages from the liquid phase. The liquid is the bottom product of the fractionator and is discharged from the bottom of the tower.

Both the kettle type and the once-through thermosiphon type constitute a theoretical tray as regards fractionation. Unlike the kettle reboiler, the once-through thermosiphon is limited to a vaporization of not more than 60 % of the feed. The low holdup of the feed from a tray results in severe surging through the reboiler at high vaporization rates.

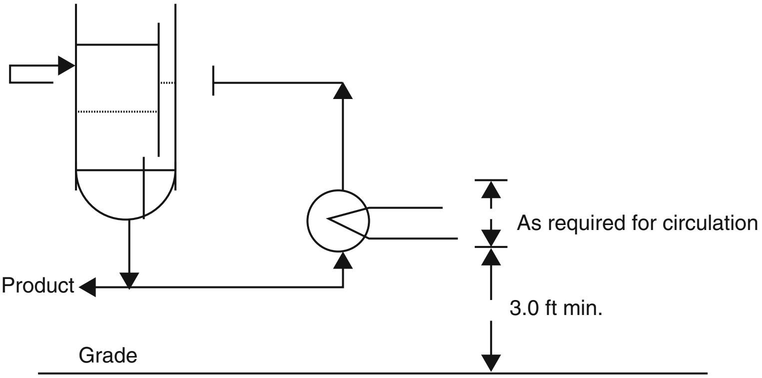


Fig. 49 Recirculating thermosiphon reboiler arrangement

Recirculating Thermosiphon Reboiler

When vaporization rates higher than 60 % of reboiler feed are required and a kettle reboiler is unsuitable, a recirculating thermosiphon-type reboiler should be considered. A sketch showing this type of reboiler is given in Fig. 49.

This reboiler is similar to the once-through thermosiphon in that it operates by flowing a liquid feed through the shell side of the vertical reboiler by the siphon mechanism. In the case of the recirculating reboiler; however, the feed to the reboiler is a stream of the bottom product from the fractionator. This is vaporized as described earlier and the liquid/vapor effluent returned to the tower. The vaporization by this reboiler can exceed 60 % without danger of surging. However, vaporization in this type of reboiler should not exceed 80 %. Its action is directed solely to providing heat to the tower and, because it recycles the same composition stream to the tower bottom, it cannot be considered as a theoretical fractionating tray (although some amount of fractionation does occur in this system).

Note in the description of both the thermosiphon-type reboilers, the heating fluid is shown as flowing tube side. There may be cases where this stream will be routed shell side and the reboil fluid directed tube side. Some guidance to this selection is provided by the following preference for tube side fluid:

1. Corrosive or fouling fluids
2. The less viscous of the two fluids
3. The fluid under the higher pressure
4. Condensing steam

Reboiler Sizing

As in the case of most heat exchangers, the sizing calculation is quite rigorous and complex. Normally process engineers rarely need to compute this in detail. There will be need however to estimate the size of these items for cost purposes or for plot layout studies. This sizing is greatly simplified by applying heat flux quantities to the predetermined reboiler duty. Heat flux is the value of heat transferred per unit time per sqft of surface. The following list gives a range of heat fluxes that have been used in design and observed in operating units.

	Design	Observed
	(Btu/h·sqft)	
Kettle type	12,000	15,000–20,000
Once through	15,000	17,500+
Recirculating	15,000	up to 20,000
Forced circulation	20,000	–

The duty of the reboiler is obtained by the overall heat balance over the tower. This is accomplished by equating the total heat out of a fractionating tower to the heat supplied, making the reboiler duty the unknown in the heat supplied statement. Now the heat out of the fractionator is the total heat in the products leaving plus the condenser duty. The heat supplied to the tower is the heat brought in with the feed and the heat supplied by the reboiler.

Example Calculation

The feed to a fractionator is 87,960 lbs/h of mixed hydrocarbons. It enters the tower as a vapor and liquid stream and has a total enthalpy of 15.134 MMBtu/h. The overhead products are a distillate and a vapor stream at 95°F. The vapor is 1,590 lb/h with an enthalpy of 320 Btu/lb. The distillate is 8,028 lbs/h with an enthalpy of 170 Btu/h. The bottom product from the tower is 78,342 lbs/h and leaves as a liquid at its boiling point at 440 °F. Its enthalpy is 370 Btu/lb. The overhead condenser duty is 4.278 MMBtu/lb. Calculate the reboiler duty.

Calculation

Calculate the reboiler duty from the overall tower heat balance as in the following:

					Enthalpy	
	V/L	°API	°F	lb/h	Btu/lb	MMBtu/h
In						
Feed	V/L	–	300	87,960	–	15.134
Reboiler duty						*x*
Total in				87,960		15.134 + *x*
Out						
Bottom prod	L	–	440	78,342	370	28.986
Overhead dist	L	–	95	8,028	170	1.364
Overhead vapor	V	–	95	1,590	320	0.508
Total out				87,960		35,136

Heat in = heat out

Then:

$$15.134 + x = 35.136$$

$$\text{Reboiler duty } x = 20.002 \text{ MMBtu/h.}$$

Using a heat flux of 15,000 Btu/h sqft, the surface area for the reboiler becomes

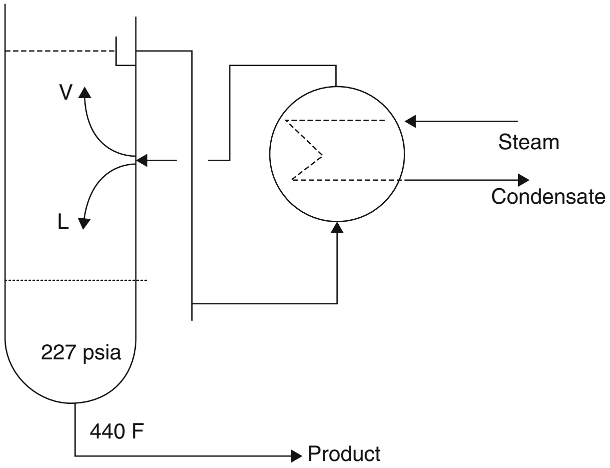
$$\frac{20.002 \times 10^6}{15,000} = 1,333.5 \,\text{sqft.}$$

Estimating the Liquid and Vapor Flow from the Reboiler

It is necessary to know the vapor and liquid flow leaving the reboiler and entering the tower for the following reasons:

- To establish that there is sufficient vapor rising in the tower to strip the bottom product effectively
- To establish the vapor loading to the bottom tray for calculating the tray loading
- To be able to calculate the driving force for flow through the exchanger in the case of thermosiphon reboilers

The calculation of this flow is again based on a heat balance. In this case, it is the heat balance across the reboiler itself. With the duty of the reboiler now established by the overall tower heat balance, as described above, the balance over the reboiler can proceed as follows:



	V/L	°API	°F	lb/h	Enthalpy Btu/lb	MMBtu/h
In						
Liquid from tray 1	L	–	430	78,342 + V	369	28.908 + 369 V

(*continued*)

					Enthalpy	
	V/L	°API	°F	lb/h	Btu/lb	MMBtu/h
Reboiler duty						20.002
Total in				78,342 + V		48.910 + 369 V
Out						
Bottom prod	L	–	440	78,342	370	28.986
Vapor to tray 1	V	–	440	V	458	458 V
Total out				78,342 + V		28.986 + 458 V

The temperature of the bottom tray (430 °F) is estimated from a straight-line temperature profile of the tower. As a rule of thumb, for a 30–40 tray tower, the bottom tray will be about 10 °F lower than the bottom temperature.

$$\begin{aligned}&\text{Again heat in} = \text{heat out.}\\&\text{Then}: 48.910 + 369\ \text{V} = 28.986 + 458\ \text{V}.\\&\text{V} = 223,865\ \text{lbs/h}.\end{aligned}$$

Now the mole weight of the vapor is determined from the bubble point calculation of the bottom product used to determine the tower bottom temperature (see the introductory chapter of this handbook). In the case of the calculation, example given above the bubble point calculation for the bottom product was as follows:

$$\begin{aligned}\text{Pressure at bottom of tower} &= 220 + (30 \times 0.25)\\ &= 227\ \text{psia}.\end{aligned}$$

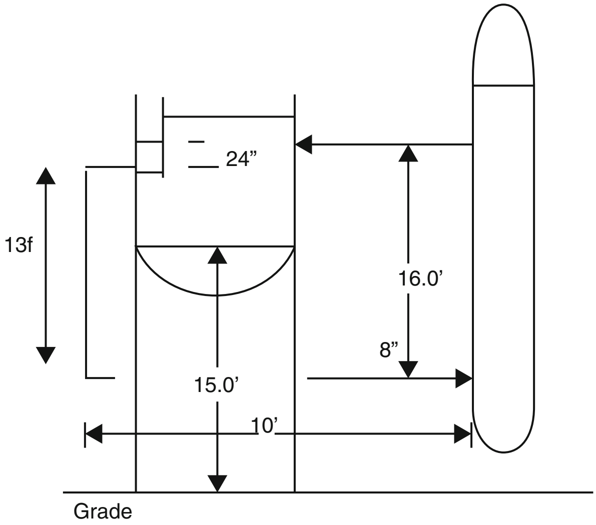
		1st trial = 400°F		2nd trial = 435 °F					
	X_w	K	$Y = XK$	K	$Y = XK$	MW	Weight factor	lbs/gal	vol factor
nC_4	0.017	2.7	0.046	3.1	0.053	58	3.1	4.86	0.64
iC_5	0.047	1.9	0.089	2.2	0.103	72	7.4	5.20	1.42
									(°API 53.1)
nC_5	0.055	1.7	0.094	1.9	0.105	72	7.6	5.25	1.45
C_6	0.345	0.96	0.331	1.3	0.449	81	36.4	6.83	5.33
C_7	0.322	0.44	0.142	0.59	0.190	102	19.4	6.84	2.84
C_8	0.214	0.17	0.036	0.25	0.054	128	6.9	6.94	0.99
Total	1.000		0.738		0.954	84.7	80.8	6.38	12.67

Actual temp = 440 °F

The mole weight of the vapor is that calculated for the "y" column in the above table, which is 84.7.

Calculating the Pressure Head Driving Force Through a Thermosiphon Reboiler

The big advantage of thermosiphon reboilers is that there are no working parts, such as pumps, that can fail. However, a major cause of failure in a thermosiphon reboiler is loss of driving force to move the fluid over or through the tube bundle. This problem mostly occurs during commissioning when the reboiler has been incorrectly positioned relative to the tower nozzles or during start-up where debris left after maintenance blocks one or other of the nozzles. In both these cases, the problem is really the loss of pressure head that drives the fluid to be reboiled through the exchanger. The calculation to determine the theoretical driving force is based on the density of the incoming liquid, the head of that liquid to the inlet nozzle, the density of the outflowing liquid/vapor fluid, and its head. An example of a pressure driving force calculation based on a once-through thermosiphon (as shown in the diagram below) is as follows. The flow data are based on the heat balance given earlier in this item.



The density of the liquid to the reboiler is 38.2 lbs/cuft at 430 °F and the total flow is 302,207 lbs/h (223,865 lbs/h V + 78,342 lbs/h L).

$$\text{Hot cuft/h} = 7{,}911.$$
$$\text{Hot gpm} = 966.$$

The transfer line from the tower to the bottom nozzle of the reboiler is an 8″ schedule 40 seamless steel pipe. The head between the bottom of the tower draw-off pot and the reboiler nozzle is 13 ft. The equivalent horizontal line length including fittings is 15 ft.

From the friction loss tables in Appendix 9 of this chapter, head loss due to friction = 66.4 ft/100 f. of line (viscosity is taken as 1.1 cSt).

Total equivalent line length to the reboiler is 13 + 15 ft = 28 ft.

$$\begin{aligned}\text{Head loss due to friction} &= \frac{28 \times 66.4}{1,\ 000} = 1.85\text{ ft.}\\ \text{Head of liquid in draw off pot} &= 2\text{ ft }(24'').\\ \text{Head of liquid to the reboiler inlet nozzle} &= 13 + 2\text{ ft.} = 15\text{ ft.}\\ \text{Pressure head at the reboiler inlet} &= 15 - 1.85\,\text{ft} = 13.15\,\text{ft}\\ &= \frac{13.15 \times 38.2}{144}\\ &= 3.49\text{ psi.}\end{aligned}$$

The density of the vapor/liquid stream leaving the reboiler is calculated as follows:

$$\frac{\text{Total mass of fluid}}{\text{cuft liquid} + \text{cuft vapor}}. \tag{147}$$

Lbs/cft of liquid (this is bottom product) = 39.4 at 440 °F.

Mole wt of vapor (see bubble point calculation above) = 84.74.

$$\begin{aligned}\text{Cuft/h of liquid} &= \frac{78,342\text{ lbs/h}}{39.9} = 1,963.5.\\ \text{Cuft/h of vapor} &\Rightarrow \frac{223,865}{84.5}\text{lbs/h} = 2,643\text{ moles/h}\\ &= \frac{2,643 \times 378 \times 14.7 \times (460 + 440\ {}^{\circ}\text{F})}{227 \times 520}\\ &= 111,974.6\text{ cuft/h.}\end{aligned}$$

$$\begin{aligned}\text{Density of fluid from reboiler} &= \frac{302,207}{1,963.5 + 111,974.6}\\ &= 2.65\text{ lbs/cuft.}\end{aligned}$$

In this case, the fluid to be reboiled flows on the shell side of the exchanger. The manufacturer's certified shell side pressure drop based on all vapor flow is 1.5 psi. The mixed-phase pressure drop is calculated using Fig. 50, thus

$$m_{\text{v}} = \text{average mass of vapor} = \frac{223,865}{2} = 111,933\text{ lbs/h.}$$

$$m_{\text{l}} = \text{average mass of liquid} = \frac{302,207 + 78,342}{2} = \ 190,275\text{ lbs/h.}$$

$$\rho_{\text{v}} = \text{average density of vapor} = \frac{2.0}{2} == 1.0\text{ lbs/cuft.}$$

$$\rho_{\text{l}} = \text{average density of liquid} = \ \frac{38.8 + 39.9}{2} = 39.35\text{ lbs/cuft.}$$

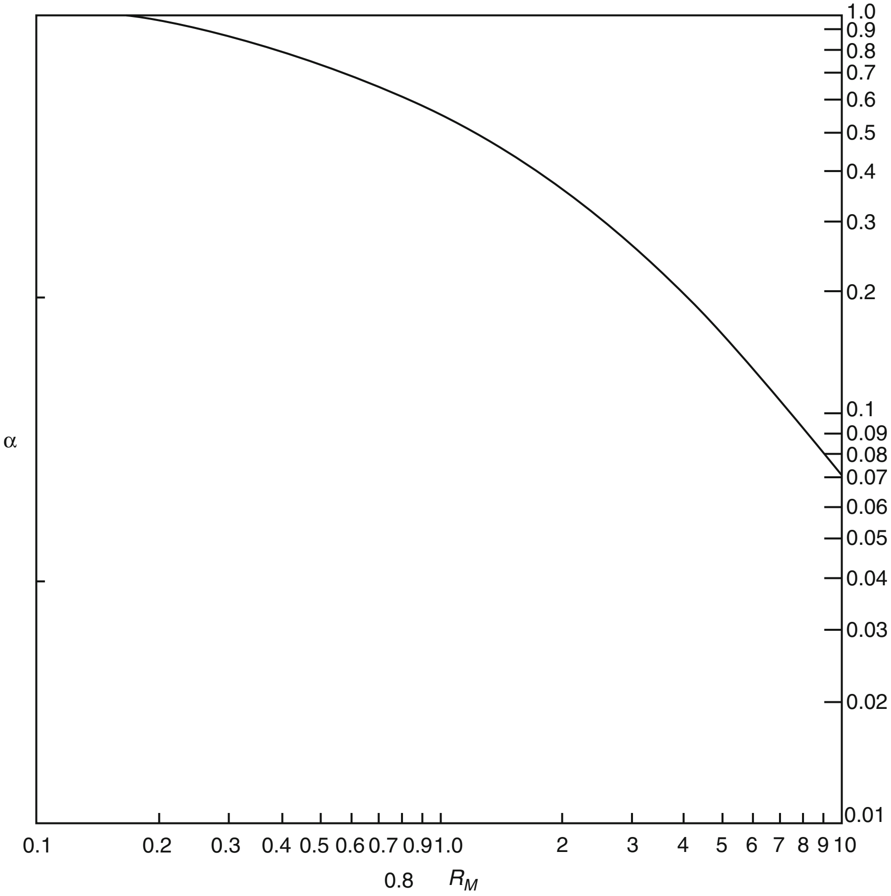


Fig. 50 Two-phase pressure drop factor for flow across staggered tubes

Referring to Fig. 50,

$$\begin{aligned} R_{\mathrm{m}} &= \frac{1}{\dfrac{m_{\mathrm{v}}}{m_{\mathrm{l}}} + \dfrac{\rho_{\mathrm{v}}}{\rho_{\mathrm{l}}}} \\ &= \frac{1}{\dfrac{111,933}{190,275} + \dfrac{1.0}{39.32}} \\ &= 1.63. \end{aligned} \tag{148}$$

From Fig. 50,

$$\begin{aligned} \alpha &= 0.42 \\ \Delta P_{\text{mixed phase}} &= \alpha \times \Delta P_{\text{gas}} \\ &= 0.42 \times 1.5 \text{ psi} \\ &= 0.63 \text{ psi.} \end{aligned} \tag{149}$$

To calculate the total head of liquid from exchanger inlet to outlet nozzle.

Tube length is standard 16 ft.

Assume bottom 20 % of length is all liquid phase at a density of 38.8 lbs/cuft.

$$\text{Then head is } \frac{16 \times 0.2 \times 38.8}{144} = 0.862 \text{ psi.}$$

Remaining head is mixed phase at a density of 2.65 lbs/cuft.

$$\text{Then head is } \frac{16 \times 0.8 \times 2.65}{144} = 0.24 \text{ psi.}$$

Neglecting the small pressure drop due to friction in the 4 f. long return line to tower,

$$\begin{aligned} \text{Friction loss through exchanger} &= 0.630 \text{ psi.} \\ \text{Lower section head} &= 0.862 \text{ psi.} \\ \text{Upper section head} &= 0.240 \text{ psi.} \\ \text{Total} &= 1.732 \text{ psi.} \end{aligned}$$

$$\begin{aligned} \text{Then driving force} &= \text{pressure head available} - \text{pressure head required} \\ &= 3.49 \text{ psi} - 1.732\text{psi} \\ &= 1.758 \text{ psi which is satisfactory for good flow.} \end{aligned}$$

Note the height of the tower above grade is usually fixed by pump suction requirements in the first place. It may be adjusted upward if necessary to accommodate a head to a reboiler. However, this necessity is quite rare. The transfer line to the reboiler should have its horizontal section at least 3.0 f. above grade to allow for maintenance.

Fired Heaters

Types of Fired Heaters

This chapter provides some features and detail of fired heaters.

Most chemical plants and all petroleum refineries contain fired heaters as a means of providing heat energy into a system. Because the equipment utilizes an outside source of fuel, it is usually supported and enhanced by a heat exchange system to minimize the quantity of fuel required.

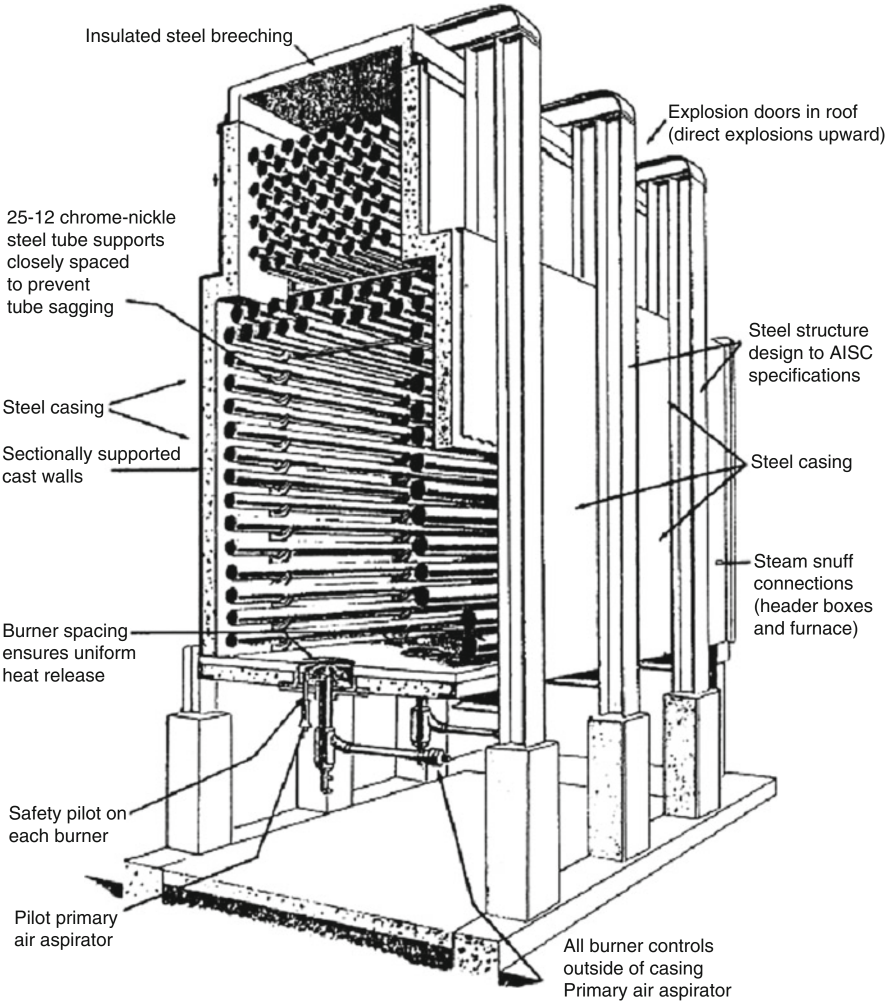


Fig. 51 Horizontal-type heater

Generally fired heaters fall into two major categories:

- Horizontal type
- Vertical type

The horizontal-type heater usually means a box-type heater with the tubes running horizontally along the walls. Vertical type is normally a cylindrical heater containing vertical tubes. Figures 51 and 52 show examples of these two types of heaters.

These figures also give some nomenclature used in describing these items of equipment. Other terms used in connection with fired heaters are as follows:

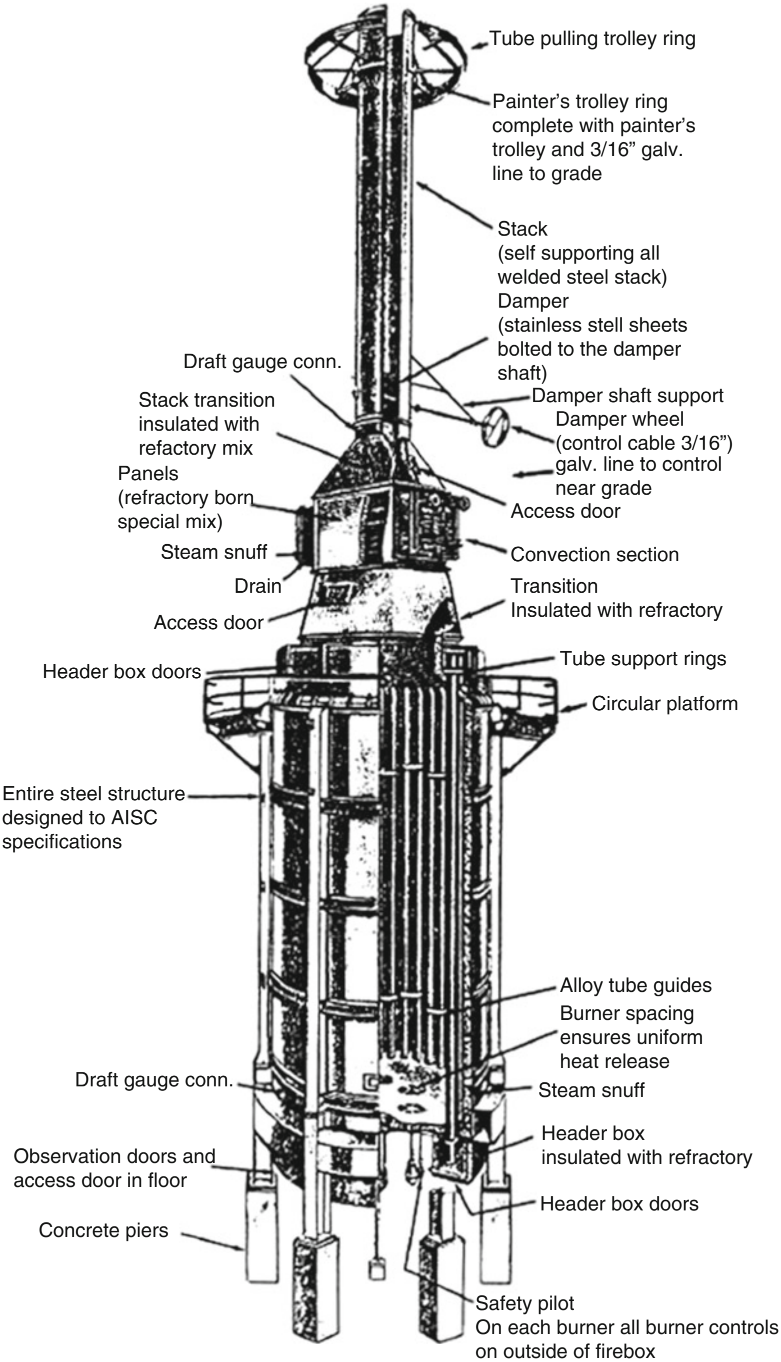


Fig. 52 Vertical-type heater

Headers and return bends are the fittings used to connect individual tubes.

Terminals are the inlet and outlet connections.

Crossovers are the piping used to connect the radiant with the convection section, usually external to the heater.

Manifold is the external piping used to connect the heater passes to the process piping and may be furnished with the heater.

Setting is any and all parts that form:

- Coil supports
- Enclosure (housing)

Casing is the steel shell which encloses the heater.

Bridge wall or partition wall is the refractory wall inside the heater that divides the radiant section into separately fired zones.

Shield tubes or shock tubes are the first two or three rows of tubes in the convection section. They protect or shield the convection tubes from direct radiant heat and normally must have the same metallurgy as the radiant tubes with no fins.

Air plenum is the chamber enclosing burners under the heater and having louvers to control the air flow.

Cylindrical heaters require less plot space and are usually less expensive. They also have better radiant symmetry than the horizontal type.

Horizontal box types are preferred for crude oil heaters, although vertical cylindrical heaters have been used in this service. Vacuum unit heaters should have horizontal tubes to eliminate the static head pressure at the bottom of vertical tubes and to reduce the possibility of two-phase slugging in the large exit tubes.

Occasionally, several different services (“coils”) may be placed in a single heater with a cost saving. This is possible if the services are closely tied to each other in the process. Catalytic reforming preheater and reheaters in one casing are examples. Reactor heater and stripper reboiler in one casing is another example. This arrangement is made possible by using a refractory partition wall to separate the radiant coils. The separate radiant coils may be controlled separately over a wide range of conditions by means of their own controls and burners. If a convection section is used, it is usually common to the several services. If maintenance on one coil is required, the entire heater must be shut down. Also, the range of controllability is less than with separate heaters.

Each of these types may be shop fabricated if size permits. Shop fabrication reduces costs. However, shop fabrication should not be forced to the extent of getting an improperly proportioned heater.

Codes and Standards

Fired heaters have a “live” source of energy. That is, they use a flammable material in order to impart heat energy to a process stream. Because of this, the design, construction, and operation of process fired heaters and boilers are strictly

Table 33 Typical heater tube sizes and center-to-center dimensions from API standard 630

Tube OD, in.		Header C-C, in.	
Primary	Secondary	Group A	Group B
2.375	–	4.00	4.75
2.875	–	5.00	5.25
3.50	–	6.00	–
4.00	–	7.00	6.50
4.50	–	8.00	7.25
–	5.00	9.00	7.75
5.563	–	10.00	8.50
–	6.00	11.00	9.00
6.625	–	12.00	10.00
–	7.625	14.00	12.00
8.625	–	16.00	14.00

controlled by legislative and other codes and standards. This item outlines some of the more important of these codes and standards which need to be recognized by engineers dealing with fired heaters in any way.

Codes and standards directly applicable to fired heaters are listed below. In addition, there are many codes and standards covering such factors as materials, welding, refractories, structural steel, etc., which apply to fired heaters. This discussion reflects the standards at the time of this writing. For detailed design, current versions of the applicable standards should be used.

API RP-530

Calculation of heater tube thickness in refineries

This recommended practice sets forth procedures for calculating the wall thickness of heater tubes for service at elevated temperatures in petroleum refineries.

API Standard 630

Tube and heater dimensions for fired heaters for refinery service

This standard establishes certain standard dimensions for heater tubes and for cast and wrought headers. It also provides guidelines on maximum heat release per heater volume.

Tube sizes and header center-to-center dimensions covered by the standard are in Table 33 as of this writing.

Groove dimensions and tolerances for rolled headers are also given. Much of this standard is also used in chemical and petrochemical plants.

API RP-2002 Fire protection in natural gasoline plants

This practice contains a brief statement about the use of snuffing steam. This system provides the piping of a steam source to the heater firebox which in an emergency can introduce steam into the box to quench any uncontrolled fire. This system may be automatically controlled or activated manually.

API guide for inspection of refinery equipment, chapter IX, fired heaters, and stacks

This reference gives a general description of fired heaters and describes how to inspect them, what damage to look for, and how to report the results of the inspection.

ASME boiler code and boiler codes of the USA

These are applicable in process plants if steam is generated and superheated or boiler feedwater preheated in the convection section. Special materials are required according to ASME Section I. The external piping and pressure relieving devices must also be in accordance with ASME Section I.

Contractors' and company standards

These will be covered in the "Narrative Specification" for the particular job and/or heater. The narrative specification is written by the heat transfer engineer specialists in the Contractors' Mechanical Equipment Group. These specifications detail all of the pertinent aspects required in the manufacture of the equipment. They will encompass all of the requirements that are applicable.

Thermal Rating

Refinery process engineers are seldom if ever required to thermal rate a fired heater or indeed check the thermal rating. This is a procedure that falls in the realm of specialist mechanical engineers with extensive experience in heater design and fabrication. Process engineers are however required to specify the equipment so that it can be designed and installed to meet the requirements of the process heat balance. To do this effectively, it is desirable to know something about the mechanism of heater thermal rating.

A fired heater is essentially a heat exchanger in which most of the heat is transferred by radiation instead of by convection and conduction. Rating involves a heat balance between the heat-releasing and heat-absorbing streams and a rate relationship.

Fuel is burned in a combustion chamber to produce a "flame burst." The theoretical flame burst temperature may vary from 4,000 °F when burning refinery gases with 20 % excess air preheated to 460 °F down to 2,300 °F when burning residual fuel oils with 100 % excess air at 60 °F. Heat is transferred from the flame burst to the gases in the firebox by radiation and mixing of the products of combustion. Heat is then transferred from the firebox gases to the tubes mainly by radiation.

The common practice is to assume a single temperature for the firebox gases for the purpose of radiation calculations. This temperature may be the same as the exit gas temperature from the firebox to the convection section (bridge wall temperature), or it may be different due to the shape of the heater and to the effect of convection heat transfer in the radiant section. Experience with the particular type of heater is required in order to select the effective firebox temperature accurately.

While this chapter does not detail the rating procedure or give an example calculation, the following steps summarize the rating procedure:

Step 1. Calculate net heat release and fuel quantity burned from the specified heat absorption duty and an assumed or specified efficiency.

Step 2. Select excess air percentage and determine flue gas rates.

Step 3. Calculate duty in the radiant section by assuming 70 % of total duty is radiant. This is a typical figure and will be checked later in the calculations. For very high process temperatures, such as in steam-methane reforming heaters, the radiant duty may be as low as 45 % of the total.

Step 4. Calculate the average process fluid temperature in the radiant section and add 100 °F to get the tube wall temperature. The figure of 100 °F is usually a good first guess and can be checked later by using the calculated inside film coefficient and metal resistance. This temperature is sensitive to tube flow rates and fouling.

Step 5. Calculate the radiant surface area using the average allowable flux. Convection surface is usually about equal to the radiant surface.

Step 6. Select a tube size and pass arrangement that will give the required total surface and meet specified pressure drop limitations.

Step 7. Select a center-to-center spacing for the tubes from the API 630 standard or from dimensions of standard fittings from other standards, and calculate firebox dimensions. Long furnaces minimize the number of return bends and thus reduce cost. Shorter and wider fireboxes usually give more uniform heat distribution and lessen the probability of flame impingement on the tubes. For vertical cylindrical heaters, the ratio of radiant tube length to tube circle diameter should not exceed 2.7.

Step 8. The remainder of the calculation involves determining the firebox exit temperature from assumption (3) above, applying an experience factor for the type of furnace to obtain the average firebox temperature, and then checking if this temperature will transfer the required radiant heat.

Step 9. The average heat flux (proportional to radiant surface) and the percent of total duty of the radiant section (which affects average tube wall temperature) are varied until a balance is obtained. The convection section surface and arrangement can now be calculated.

Step 10. The heater is normally designed to allow adequate draft at the burners with at least 125 % of design heat release and an additional 10 % excess air at the maximum and minimum ambient air temperatures.

Heat Flux

Although a process engineer is not normally required to thermally rate a process heater, he is often required to estimate the heater size, for preliminary cost estimates or plot layout and the like. This can be accomplished quite simply by the use of "heat flux." While this figure is quoted as Btu/h sqft, it is not however an overall heat transfer coefficient; it lacks the driving force ΔT for this. Heat flux is the rate of heat transmission through the tubes into the process fluid.

The maximum film temperature and tube metal temperature are a function of heat flux and the inside film heat transfer coefficient.

The heat flux varies around the circumference of the tube, being a maximum on the side facing the fire. The value depends upon the sum of the heat received directly from the firebox radiation and the heat reradiated from the refractory.

Single-fired process heaters are usually specified for a maximum average heat flux of 10,000–12,000 Btu/h sqft. The maximum point heat flux is about 1.8 times greater.

Double-fired heaters are usually specified for about 13,500–18,000 Btu/h sqft *average* heat flux with the maximum point flux being about 1.2 times greater.

The following are typical flux values for heaters in hydrocarbon service:

Horizontal, fired on one side	8,000–12,000
Vertical, fired on one side from bottom	9,000–12,000
Vertical, single row, fired on both sides	13,000–18,000

Heater Efficiency

The efficiency of a fired heater is the ratio of the heat absorbed by the process fluid to the heat released by combustion of the fuel expressed as a percentage.

Heat release may be based on the lower heating value (LHV) of the fuel or higher heating value (HHV). Process heaters are usually based on LHV and boilers on HHV. The HHV efficiency is lower than the LHV efficiency by the ratio of the two heating values.

Heat is wasted from a fired heater in two ways:

- Hot stack gas
- Radiation and convection from the setting

The major loss is by the heat contained in the stack gas. The temperature of the stack gas is determined by the temperature of the incoming process fluid unless an air preheater is used. The closest economical approach to process fluid is about 100 °F. If the major process stream is very hot at the inlet, it may be possible to find a colder process stream to pass through the convection section to improve efficiency, provided plant control and flexibility are adequately provided for. A common method of improving efficiency is to generate and/or superheat steam and preheat boiler feedwater.

The lowest stack temperature that can be used is determined by the dew point of the stack gases. See the section on stack emissions.

Figures 53 and 54 may be used to estimate flue gas heat loss.

The loss to flue gas is expressed as a percentage of the total heat of combustion available from the fuel. These figures also show the effect of excess air on efficiency. Typically excess air for efficiency guarantees is 20 % when firing fuel gas and 30 % when firing oil.

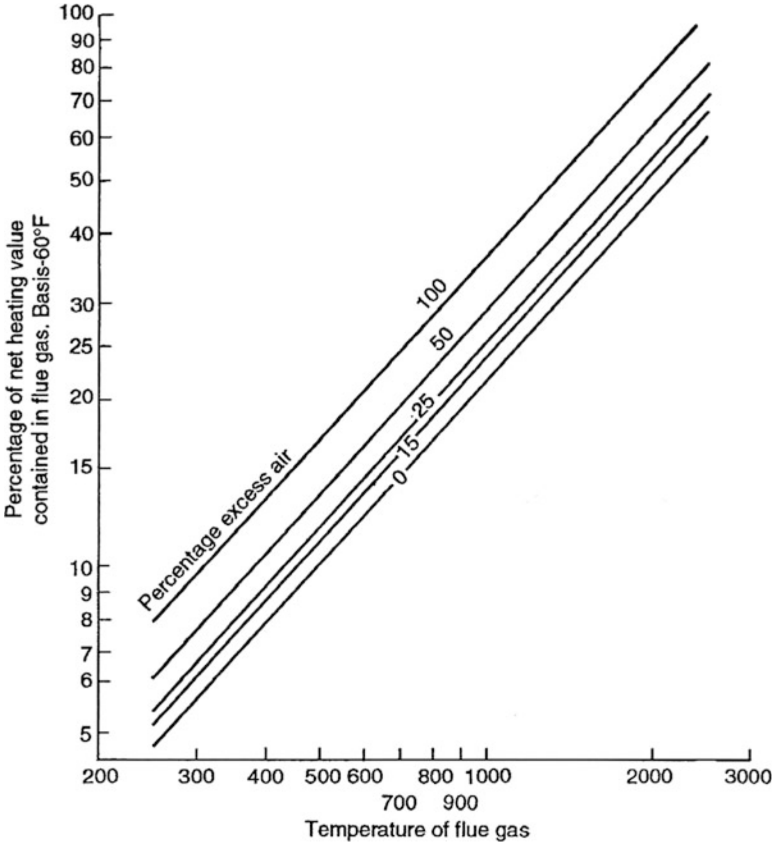


Fig. 53 Percentage of net heating value contained in flue gas when firing fuel gas

Heat loss from the setting, called radiation loss, is about 1½–2 % of the heat release. The range of efficiencies is approximately as follows:

Very high	90 %+. Large boilers and process heaters with air preheaters
High	85 %. Large heaters, low process inlet temps and/or air preheaters
Usual	70–80 %
Low	60 % and less. All radiant

Engineers are often required to check the efficiencies of the process heaters on operating units assigned to them. This can be done using the heats of combustion given in Appendices 10 and 11 to this chapter. The steps used to carry out these calculations are as follows:

Step 1. Obtain details of the heater from the manufacturer’s data sheet or drawings. The data required are:

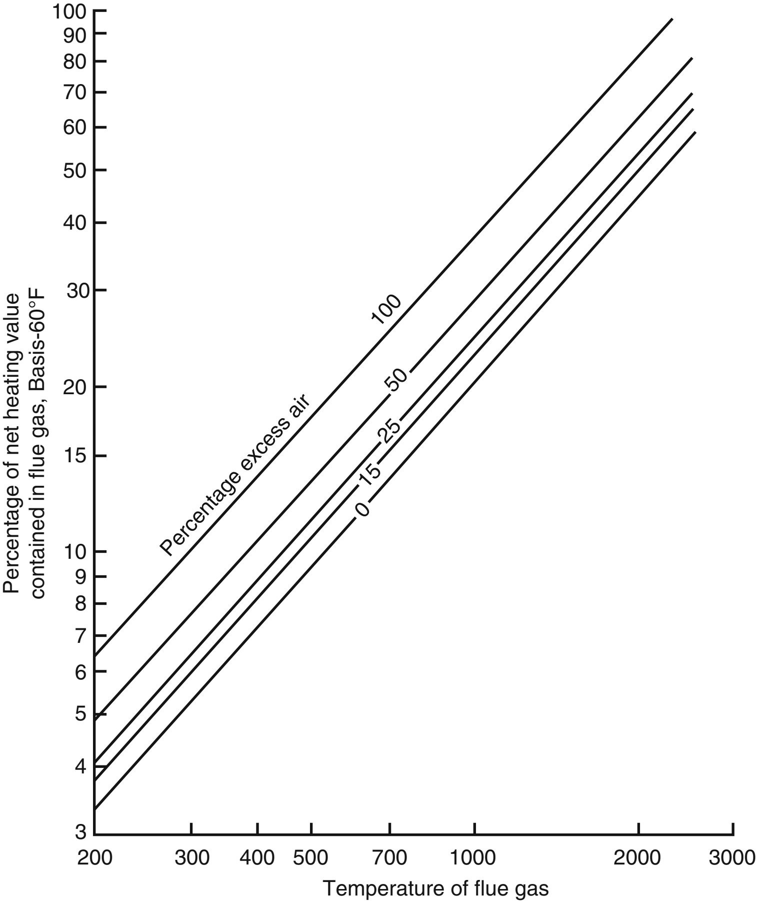


Fig. 54 Percentage of net heating value contained in flue gas when firing fuel oil

- Tube area
- Layout (is it vertical and how are the burners located?)

Step 2. From plant data, obtain coil inlet and outlet temperatures, pressures, and flows. Calculate the outlet flash (i.e., vapor or liquid or a mixture of vapor and liquid) condition, then calculate its enthalpy. Do the same for the inlet flow. Usually this will be a single phase either liquid or vapor.

Step 3. Again from plant data, obtain the quantity of fuel fired and its properties (API gravity in particular).

Step 4. The difference between the enthalpies calculated in step 2 is the enthalpy absorbed by the feed in Btu per hour.

Step 5. Divide this absorbed enthalpy by the tube area to give the heat flux in Btu/h/ft^2. Heat fluxes are generally as follows:

Horizontal, fired one side	8,000–12,000 Btu/h/ft^2
Vertical, fired from bottom on one side	9,000–12,000 Btu/h/ft^2
Vertical, single row, fired on both sides	13,000–18,000 Btu/h/ft^2

If the heat flux falls outside this range, there could be excessive fouling. Check the pressure drop – if this is far above manufacturer's calculated value, then fouling is certainly present. Fouling can be confirmed by an infrared scan of an operating heater.

Step 6. Check the thermal efficiency of the heater by giving the fuel fired a heating value. These are available in Appendices 10 and 11. Use the LHV (lower heating valve) in Btu/lb and multiply it by the lbs/h of the fuel.

Step 7. Divide the heat absorbed by the heat released calculated in step 4 to give the thermal efficiency. For most heaters, this should be between 70 % and 80 %. If it falls below this range, note should be taken of burner operation and the amount of excess air being used.

Burners

The purpose of a burner is to mix fuel and air to ensure complete combustion. There are about 12 basic burner designs. These are based on the factors in Table 34.

Various combinations of the above types are available.

Gas Burners

The two most common types of gas burners are the "premix" and the "raw gas" burners.

Premix burners are preferred because they have better "linearity," i.e., excess air remains more nearly constant at turndown. With this type, most of the air is drawn in through an adjustable "air register" and mixes with the fuel in the furnace firebox. This is called secondary air. A small part of the air is drawn in through the "primary air register" and mixed with the fuel in a tube before it flows into the furnace firebox. A turndown of 10:1 can be achieved with 25 psig hydrocarbon fuels. A more normal turndown is 3:1.

Oil Burners

An oil burner "gun" consists of an inner tube through which the oil flows and an outer tube for the atomizing agent, usually steam. The oil sprays through an orifice into a mixing chamber. Steam also flows through orifices into the mixing chamber. An oil-steam emulsion is formed in the mixing chamber and then flows through orifices in the burner tip and then out into the furnace firebox. The tip, mixing chamber and inner and outer tubes can be disassembled for cleaning.

Oil pressure is normally about 140–150 psig at the burner but can be lower or higher. Lower pressure requires larger burner tips; the pressure of the available atomizing steam may determine the oil pressure.

Table 34 Types of burner design parameters and burners

Categories	Options
Firing direction	Vertical upward
	Vertical downward
	Horizontal
Capacity	High
	Low
Fuel type	Gas
	Oil
	Combination
Flame shape	Normal
	Slant
	Thin, fan-shaped
	Flat
	Adaptable pattern
Hydrogen content	High
	Normal or none
Excess air	Normal
	Low
Type of atomization (oil)	Steam
	Mechanical
	Air-assisted mechanical
Boiler types	Various styles
Low NOx or ultra-low NOx (LN or ULN)	
High intensity	

Atomizing steam should be at least 100 psig at the burner valve and at least 20–30 psi above the oil pressure. Atomizing steam consumption will be about 0.15–0.25 lbs steam/lb oil, but the steam lines should be sized for 0.5.

Combination Burners

This type of burner will burn either gas or oil. It is better if they are not operated to burn both fuels at the same time because the chemistry of gas combustion is different from that of oil combustion. Gases burn by progressive oxidation and oils by cracking. If gas and oil are burned simultaneously in the same burner, the flame volume will be twice that of either fuel alone.

Pilots

Pilots are usually required on oil-fired heaters. Pilots are fired with gas. Natural gas is preferred, but they can be fired on very clean fuel gas.

Pilots are not required when heaters are gas fired only, but most gas-fired heaters today have them. Minimum flow bypasses around the fuel gas control valves are also used to prevent the automatic controls from extinguishing burner flames. Pilots normally are self-contained, with their own aspirated air intake, separate from the main burners.

Excess Air and Burner Operation

The excess air normally used in process-fired heaters is about 15–25 % for gas burners and about 30 % for oil burners. Excess oxygen then runs from 2-5 % for gas burners and about 6% for oil burners. These excess air rates permit a wide variation in heater firing rates which can be effectively controlled by automatic controls without fear of "starving" the heater of combustion air. There has been considerable work lately to reduce this excess air considerably mostly to minimize air pollution. This practice has not been used in process heaters to date. It has however been adopted in the operation of large power station-type heaters with some success.

Normally companies specify that burners be sized to permit operation at up to 125 % of design heat release with a turndown ratio of 3:1. This gives a minimum controllable rate of 40 % of design without having to shut down burners.

Burner Control

Burner controls become very important from safety and operation considerations. Most systems include an instrumentation system with interlocks that prohibit:

- Continuing firing when the process flow in the heater coil fails
- The flow of fuel into the firebox on flame failure

Under normal operating conditions, the amount of fuel that is burnt is controlled by flow controllers operated on the coil outlet temperature. With combination burners, the failure of one type of fuel automatically introduces the second type. Such a switch over can also be effected manually. This aspect is usually activated on pressure control of the respective fuel system, that is, on low pressure being sensed on the fuel being fired automatically switches to the second fuel.

Most companies operate their own specific controls for the heater firing system. Refer also to the discussion of burner management systems in the topic "► Utilities in Petroleum Processing" of this handbook.

Heater Noise

All heaters are noisy and this noise is the result of several mechanisms. Among these is the operation of the burners. Gas burners at critical flow of fuel emit a noise. This can be minimized by designing for low pressure drop in the system. Intake of primary and secondary air is another source of noise. Forced draft burners are generally quieter than natural draft if the air ducting is properly sized and insulated. The design of the fan can also reduce noise in this mechanism. Low-tip-speed fan favors low noise levels. Simple, cost-effective techniques are available to mitigate heater noise, but they cannot eliminate all noise.

Refractories, Stacks, and Stack Emissions

Refractories are used on the inside walls of the heater firebox, floor, and through the convection side of the heater. The purpose of this refractory lining is to conserve the heat by limiting its loss to atmosphere by convection. It is also necessary for personal safety of those working on or about the heater who may accidentally touch the heater walls.

Good insulation has the following qualities:

- It has good high temperature strength.
- It is resistant to abrasion, spalling, chemical reaction, and slagging.
- It has good insulating properties.

Among the most common refractories that meet some if not all of the above criteria are silica refractories, high alumina, and fire clay brick. These have high resistance to spalling and to thermal shock. Their insulating qualities are also good.

Silica refractories tend to form slag with metal oxide dust and ashes. Compounds of sodium and potassium attack most refractories while refractories containing magnesium react with acids and acid gases. Carbon monoxide and other reducing chemicals that may be present in the firebox reduce the life of refractories, particularly fire clay brick and silica.

Dense refractories with low porosity are the strongest but have the poorest insulation qualities. Castable refractories containing a mixture of cement and refractory aggregate are cheap and relatively easy to install. They are not very rugged however. Normally in process heaters, conditions are such that the use of a light insulating refractory will satisfy all that is required from a refractory lining.

Today, many furnaces use refractory fiber in modular blocks and blankets for insulation. This material is lighter, meaning the furnace wall supports much less weight, and it has much better insulating properties than more dense materials. The blanket refractory can be installed in the shop before the furnace is shipped, with limited need for finish work in the field. These refractories do not require curing, which is a big time savings in start-ups. Blanket refractory can be eroded by high flue gas velocities, so it is common to “rigidize” the blanket and block modules in high-velocity areas. The rigidizing is accomplished simply by spraying the refractory with a proprietary solution which, when dried and fired, bonds and stiffens the refractory fibers together so that they are less affected by velocities.

The ASTM, standard part 13, gives more detail on refractories. This standard provides the classification of refractories and describes their characteristics and composition. It also offers a procedure for calculating the heat loss through the insulation and thus its thickness.

Preparing Refractories for Operation

All new hard refractories need to be “cured” after installation and before use. Refractories contain moisture, some due to the installation procedure and some in the form of water of crystallization. Curing the refractory means removing this moisture by applying a slow heating mechanism. New heater manufacturers will usually provide details of the curing procedure they recommend. The procedure must not damage any part of the furnace or process system. The following procedure may however be used as a guide to refractory curing when manufacturers’ procedures are not available:

Step 1. Raise the flue gas temperature at the arch 50 °F/h to a temperature of 400 °F and hold for 8 h at that temperature. Maintain a cooling flow on inside the tubes with minimal pressure – see step 6 below.

Step 2. Then increase the temperature again at 50 °F/h from 400 to 1,000 °F and hold for another 8 h.

Step 3. If necessary continue heating at 100 °F/h to the operating temperature if higher than 1,000 °F. Hold at the operating temperature for a further 8 h.

Step 4. Cool at 100 °F/h to about 500 °F and hold ready for operation.

Step 5. On start-up the heater can be heated up to its operating temperature at a rate of 100 °F/h.

Step 6. During the curing of the refractory, it will normally be necessary to pass some fluid through the heater coils to protect them from overheating. Steam or air may be circulated through the coils for this purpose. In certain cases such as in the catalytic reforming of petroleum stock, it may be necessary to circulate the nitrogen or the hydrogen that was used to purge and pressure test the unit. Air and steam in this process would not be desirable.

Following refractory repairs, it may be necessary to cure the repair material. Normally, if the repairs were minor, you can heat up at 50 °F/h and adequately cure the refractory. If the refractory work was extensive, a regular cure needs to be built into the start-up schedule.

Stacks

Stacks are used to create an updraft of air from the firebox of a heater. The purpose of this is to cause a small negative pressure in the firebox and thus enable the introduction of air from the atmosphere. This negative pressure also allows for the removal of the products of combustion from the firebox. The stack therefore must have sufficient height to achieve these objectives and overcome the frictional pressure drop in the firebox and the stack itself.

The height required for a stack to achieve good draft can be estimated from the following equation:

$$D = 0.187H\left(\rho_a - \rho_g\right) \tag{150}$$

where:

D = draft in inches of water.
H = stack height in feet.
ρ_a = density of atmospheric air in lbs/cuft.
ρ_g = density of stack gases in lbs/cuft at stack conditions.

For stack gas temperature, use 100 °F lower than gases leaving the convection section. Stack gases have a molecular weight close to that of nitrogen. For this calculation, use 28 as the mole weight. Burner draft requirements range from 0.2 to 0.5 in. of water. Use 0.3 in. of water as a good design value.

Stacks must also be designed to handle and disperse stack emissions. This usually results in having to build stack heights greater than that required for obtaining draft. There are available specific computer programs relating plume height of the stack gases above the stack outlet to the probable ground level fallout of the impurities in the gas. These programs also produce a map of the relative concentrations of these impurities at ground level. Such data are usually available from government authority offices in most countries. The predicted ground concentration and map calculated are checked against local legal requirements. The results usually form part of the government approval to build and/or operate a facility.

The stack diameter is based on an acceptable velocity of stack gases in the stack. This is generally taken as 30 ft/s. Some allowance must be made for fractional losses; these are:

1.5 velocity heads for inlet and outlet losses
1.5 velocity head for damper
1.0 velocity head for each 50 f. of stack height

Stack Emissions

The obnoxious compounds in stack gas emissions arise from:

- Impurities in the fuel
- Chemical reactions resulting from the fuel combustion with air

The three major impurities in oil or gas fuels which produce undesirable emissions are:

- Sulfur
- Metals
- Nitrogen

Sulfur

All gas and oil fuels contain sulfur at some level of concentration. When these fuels are burned, the sulfur reacts with air to form SO_2 and SO_3. These compounds are objectionable because they cause:

- Air pollution in the form of smog.
- They contribute to the corrosion of heater tubes and stack.
- SO_3 lowers the dew point of the flue gases resulting in an objectionable visible plume at the stack exit.

Figure 55 shows the effect of sulfur in the feed on the flue gas dew point. This dew point also varies with the amount of excess air and the relative partial pressure of the combustion gases.

There is no precise way of determining the amount of SO_3 that is formed in the flue gas. Nor can it be determined with any degree of accuracy where the SO_3 is

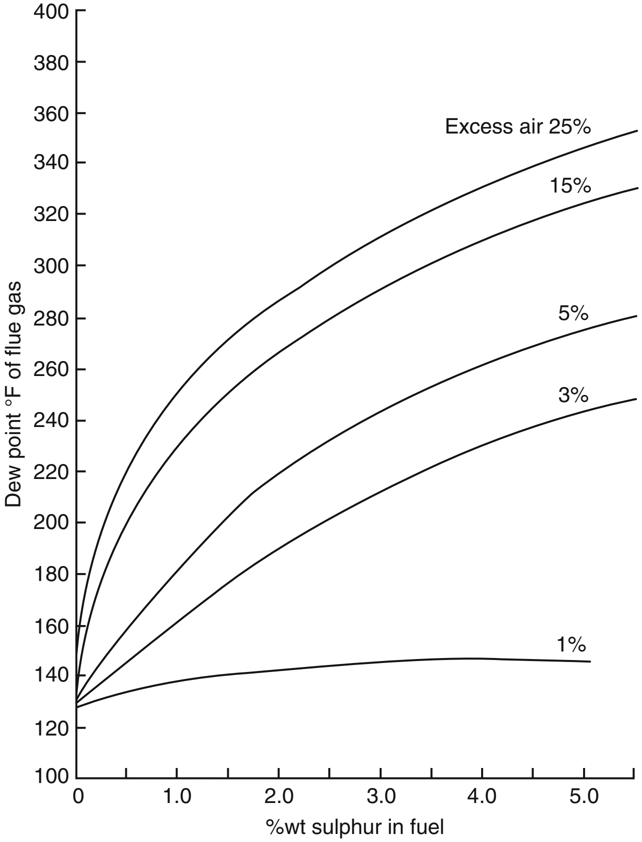


Fig. 55 Dew point of flue gases versus sulfur content

formed in the system. The total amount of the sulfur oxides is determined simply from the sulfur content of the feed. Because of this uncertainty, it is important to restrict the minimum allowable convection side metal temperatures to 350 °F when firing fuels containing sulfur. Also the minimum temperatures to the stack should be 320 °F when firing fuel gas and 400 °F when firing fuel oil. In the case of metal stacks, the use of a noncorrosive lining must be used in the colder section of the stack if the flue gas temperature falls below those stated above.

Metals

The most objectionable metal impurities in fuel oil are sodium and vanadium. These can cause severe corrosion of tubes and refractory lining. By high vanadium content is meant concentrations between 200 and 400 ppm, above 400 ppm is considered very high and should not be used as a fuel. Vanadium in the presence of sodium and oxygen readily forms a corrosive compound:

$$Na_2O \cdot 6V_2O_5.$$

This compound attacks iron or steel to form ferric oxides according to the equation:

$$Na_2O \cdot 6V_2O_5 + Fe \rightarrow Na_2O\,V_2O_4 \cdot 5V_2O_5 + FeO. \quad (152)$$

This vanadium product is oxidized back to the original corrosive compound according to the reaction:

$$Na_2OV_2O_4 \cdot 5V_2O_5 + O_x \rightarrow Na_2O \cdot 6V_2O_5. \quad (153)$$

These reactions occur at temperatures between 1,070 and 1,220 °F with the vanadium compound being continually regenerated to its corrosive state.

Sodium and sulfur also combine to form undesirable corrosive compounds without vanadium being present. This reaction forms sodium iron trisulfate $Na_3Fe(SO_4)_3$ at temperatures of around 1,160 °F. The critical temperature for both vanadium and sodium corrosion is around 1,100 °F. Vanadium is not a major problem at this temperature but becomes so at temperatures above this level.

Nitrogen

Some nitrogen oxides will be formed in combustion gases even if there are no nitrogen compounds in the fuel. The presence of the nitrogen compounds in the fuel significantly increases the nitrogen oxide content of the flue gas. There are six oxides of nitrogen present in flue gases but only two are present in any appreciable amount. These are:

NO nitrogen oxide
NO_2 nitrogen dioxide

Nitrogen oxide is a poisonous gas which readily oxidizes to nitrogen dioxide on entering the atmosphere. Nitrogen dioxide is a yellowish gas which readily combines with the moisture in the air to form nitric acid. In the presence of sunlight and oxygen, nitrogen dioxide also contributes to the formation of other air pollutants. The production of NO_x can be reduced by limiting the amount of excess air, by washing the flue gases with aqueous ammonia, or by catalytically reducing NO_x in the presence of ammonia.

The environmental chapter of this handbook further discusses emissions and emissions control.

Specifying a Fired Heater

Some basic data concerning a fired heater must be made known before the equipment can be designed for fabrication or even costed. These data are provided by a specification sheet or sheets. In the case of a fired heater, as in the case of compressors or exchangers, this specification can run into several sheets or forms. Such sheets will define the unit in terms of:

- Process requirement
- Mechanical detail
- Civil engineering requirement
- Operational requirement
- Environmental requirement

This discussion will deal only with the "process requirement" and the duty of the heater. A typical process originated specification sheet is shown here as Fig. 56. The data provided on this sheet are the minimum that will be necessary for a heater manufacturer or a heater specialist to begin to size the heater or price out the item. Usually these data would also be supported with a vaporization curve of the feed if there is a change of phase taking place in the heater coils. The process engineer developing this specification would also provide details of services required in addition to the main duty of the heater. For example, if it is intended that the convection side of the heater is to be used for steam generation, preheating, or steam superheating, the system envisaged must be properly described by additional diagrams and data.

The example specification sheet in Fig. 56 is completed for a crude oil vacuum distillation unit heater with a steam superheater coil located in the convection side of the heater. The following paragraphs describe the content on a line-by-line basis.

1. Flash curve of the reduced crude feed versus % volume distilled is attached for atmos pressure and at 35 mmHg Abs would be attached.
2. Gravity and mole wt curves for the reduced crude versus mid volume % would be attached.
3. Soot blowers are to be considered in this package. Steam is available at 600 psig and 750 °F.
4. Studded tubes to be considered for the convection side.

Line 1. *Design duty* refers to the total duty required of the unit. In the case of the example given here, it includes the duty required to heat and partially vaporize the oil in the radiant section and the duty required to superheat the steam. The data sheet will be split into two sections to reflect each of these duties.

Service describes the main purpose for which the heater will be used. In this case, it will be used to heat and vaporize hydrocarbons.

Line 2. *No. of heaters*. This is self-explanatory. In this case, there is only one heater required. Should there have been more than one identical unit, this would be reflected here.

Unit. This is the title given to this unit of equipment as it appears on an equipment list. It will correspond to the item number also given in the equipment list. In the case of the example, it is "vac unit preheater."

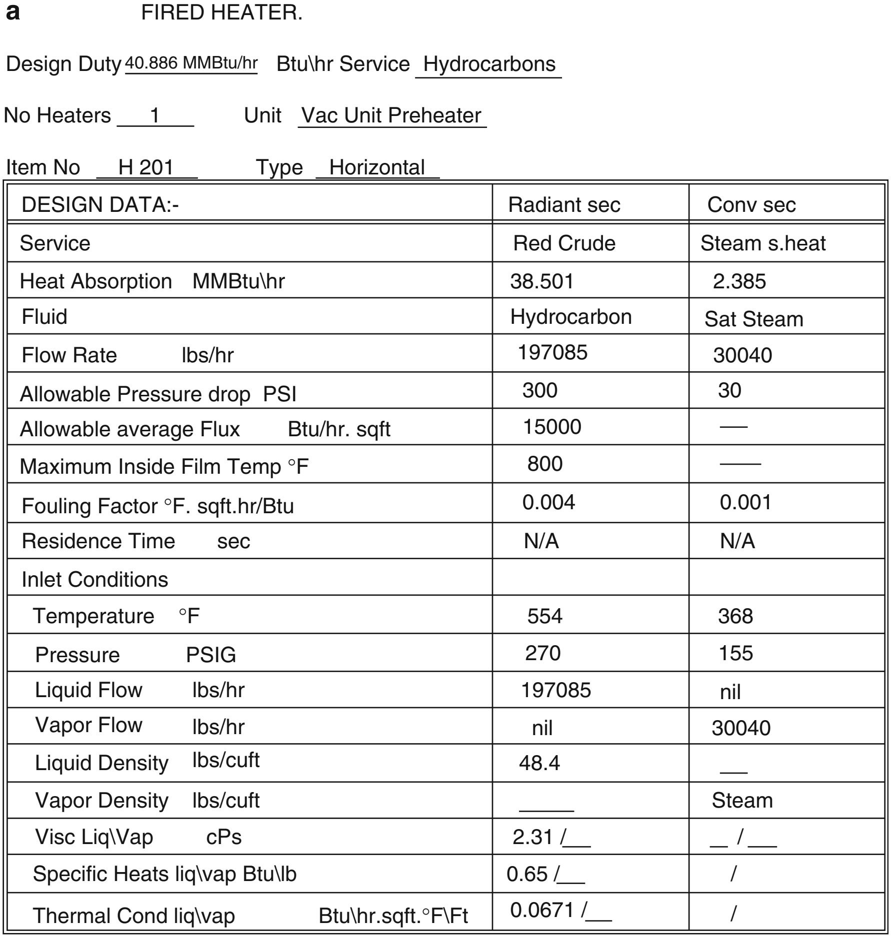
Line 3. *Item No*. This is the reference number given to the item in the equipment list. This reference number and unit title identifies the equipment on all drawings where it appears and all documents used in its purchase, costing, maintenance, etc.

Type. The type of heater (if decided on) is given here. In the case of the example heater, a cabin (horizontal tubes) type has been selected for vacuum services considerations.

Line 4. This is the first line of the specification sheet proper. It commences with the service of the heater or section of the heater. In the case of this example, only two columns have been provided. These are designated for the “Radiant” section and “Convection” section. On most preprinted specification forms, there would be at least four columns.

Line 5. *Heat absorption*. This line divides the duty of the heater into that required from the radiant coils and that required from the convection side. In this example, the oil is routed through the radiant section only while saturated steam from a waste heat boiler is superheated in the convection coils. Both are measured in million Btu/h.

a



FIRED HEATER.

Design Duty 40.886 MMBtu/hr Btu\hr Service Hydrocarbons

No Heaters 1 Unit Vac Unit Preheater

Item No H 201 Type Horizontal

DESIGN DATA:-	Radiant sec	Conv sec
Service	Red Crude	Steam s.heat
Heat Absorption MMBtu\hr	38.501	2.385
Fluid	Hydrocarbon	Sat Steam
Flow Rate lbs/hr	197085	30040
Allowable Pressure drop PSI	300	30
Allowable average Flux Btu/hr. sqft	15000	—
Maximum Inside Film Temp °F	800	——
Fouling Factor °F. sqft.hr/Btu	0.004	0.001
Residence Time sec	N/A	N/A
Inlet Conditions		
Temperature °F	554	368
Pressure PSIG	270	155
Liquid Flow lbs/hr	197085	nil
Vapor Flow lbs/hr	nil	30040
Liquid Density lbs/cuft	48.4	__
Vapor Density lbs/cuft	_____	Steam
Visc Liq\Vap cPs	2.31 /__	__ /__
Specific Heats liq\vap Btu\lb	0.65 /__	/
Thermal Cond liq\vap Btu\hr.sqft.°F\Ft	0.0671 /__	/

Fig. 56 (continued)

Partial vaporization of the oil occurs in the radiant coil. Therefore, a flash curve or a phase diagram of the oil must accompany this specification sheet. In the example, the duty to the oil is calculated from data developed in the material balance and heat balance of the process. Thus:
Temperature of the feed into the heater is 554 °F and that of the coil outlet is 750 °F. From the flash curve at the outlet pressure of 35 mmHg abs (0.68 psia) and the material balance, the weight per h of vapor is calculated to be 127,444 lbs/h and the liquid portion is 69,641 lbs/h. The heat absorbed in the radiant section is

b

DESIGN DATA(Cont)	Rad Sec	Conv Sec
Outlet Conditions.		
Temperature °F	750	500
Pressure (Psia) PSIG	(0.68)	125
Liquid Flow lbs\hr	69641	nil
Vapour Flow lbs\hr	127444	30040
Liquid Density lbs\cuft	47.3	____
Vapour Density lbs\cuft	0.023	0.246
Visc of Liq\Vap cPs	1.4/0.002	__ /__
Specific Heat Liq\Vap Btu\lb	0.64/0.069	__/__
Thermal Cond Liq\Vap Btu\hr.sqft.°F\Ft	0.062/0.023	/
FUEL DATA		
Type (Gas or Oil)	OIL	GAS
LHV Gas Btu\cuft Oil Btu\lb	17560	2320
HHV Gas Btu\cuft Oil Btu\lb	18580	2520
Pressure at Burner PSIG	82	25
Temp at Burner °F	176	68
Mol Wt of Gas		44
Visc of Oil @ Burner cPs	23.3	
Atomising Steam Temp °F Press PSIG	500 125	
Composition of Gas Mol%		
H2		0.2
C1		12.0
C2		28.2
C3		31.3

Fig. 56 (continued)

c

FUEL DATA (Cont)		
Composition of Gas (Cont)		
C4's		
C5's		
C6+		
Properties of Fuel oil		
°API	15.2	
Visc @ 100°F cSt	175	
Visc @ 210°F cSt	12.5	
Flash Pt °F	200	
Vanadium ppm	12	
Sodium ppm	32	
Sulphur %wt	2.4	
Ash %wt	<1.0	

Fig. 56 (**a**–**c**) Typical specification sheet for a fired heater

$$\begin{aligned}\text{Heat in with feed} &= 197{,}085\ \text{lbs/h} \times 268\ \text{Btu/lb (all liquid)}\\ &= 52.819\ \text{mm Btu/h.}\end{aligned}$$

Heat out in feed:

$$\begin{aligned}\text{Liquid portion} &= 69{,}641\ \text{lbs/h} \times 378\ \text{Btu/lb}\\ &= 26.324\ \text{mm Btu/h.}\\ \text{Vapor portion} &= 127{,}444\ \text{lbs/h} \times 510\ \text{Btu/llb}\\ &= 64.996\ \text{MMBtu/h.}\\ \text{Total heat out} &= 91.320\ \text{MMBtu/h.}\\ \text{Duty of radiant sect} &= 91.320 - 52.819\\ &= 38.501\ \text{MMBtu/h.}\end{aligned}$$

For the convection section, the duty is calculated as follows:

Weight of saturated steam at 155 psig is 30,040 lbs/h.
Temperature of 155 psig steam = 368 °F.
From steam tables steam enthalpy = 1,195.9 Btu/lb.
Temperature of steam out = 500 °F.
Pressure of steam out = 125 psig.

From steam tables steam enthalpy = 1,275.3 Btu/lb.
Duty of convection side = 30,040 (1,275.3–1,195.9)
= 2.385 MMBtu/h.

Line 6. *Fluid*. This refers to the material flowing in the coil. In the case of this example, it will be hydrocarbons in the radiant coil and steam in the convection coil.

Line 7. *Flow rate*. This is the total flow rate in lbs per hour entering the respective section of the heater. Thus, for the radiant side, the figure will be 197,085 lbs/h, and for the convection side it will be 30,040 lbs/h.

Line 8. *Allowable pressure drop*. The process engineer enters the required pressure drop calculated from the hydraulic analysis of the system (see Appendix 14 and section "Pressure Drop Calculations)." This pressure drop is measured from the heater side of the inlet manifold downstream of the balancing control valves and the coil outlet downstream of the outlet manifold.

Line 9. *Allowable average flux*. This is usually a standard set by the company for its various heaters. In the example here, this value would be between 13,500 and 18,000 Btu/h sqft (a horizontal heater fired on both sides). It is specified as 15,000 Btu/h sqft for this example and refers only to the radiant section.

Line 10. *Maximum inside film temperature*. It is important to notify the heater manufacturer of any temperature constraint that is required by the process. In the case of this example, temperatures of the oil above 800 °F may lead to the oil cracking. Such a situation could adversely affect the performance of the downstream fractionation equipment, and therefore high temperatures in excess of 800 °F must be avoided. There is no constraint on the convection coil.

Line 11. *Fouling factor*. The fouling factors used in heat exchanger rating can be used here also. In this example, the radiant side would have a fouling factor of about 0.004 °F sqft h/Btu for the oil and 0.001 for the steam.

Line 12. *Residence time*. This becomes important when a chemical reaction of any kind takes place in the heater tubes. In the case of this example, this item does not apply. If the example were a thermal cracking heater or a visbreaker, the appropriate kinetic equations and calculations would be attached to the specification sheet to support this item.

Line 13–30. These are self-explanatory. The only comment here is that the data are quoted at the inlet or outlet conditions of temperature and pressure.

Line 31. *LHV*. The section of the specification sheet that follows deals with the characteristics of the fuel that will be used in the heater. This section is divided into oil and gas which are the usual fuels used in modern day processes. This item requires the "lower heating value" of the fuel. This can be read off charts such as Appendices 10 and 11 of this chapter.

Line 32. *HHV*. This is the other heating value data required by the heater designer. This "higher heating value" data can also be read off charts such as Appendices 10 and 11.

Line 33. *Pressure at burner*. This normally refers to the oil fuel and is measured at the heater fuel oil manifold.

Line 34. *Temperature at the burner*. This item too is self-explanatory and these measurements are also taken at the respective manifolds.

Line 35. *Mol wt of gas*. This refers to the gas stream normally expected to be used. Obviously in practice, this will vary with the process operation from day to day.

Line 36. *Viscosity of the oil at the burner*. This viscosity is quoted at the burner temperature and may be arrived at from the two viscosity figures given later in the specification sheet. This is important for the best design or selection of the burner itself.

Line 37. *Atomizing steam*. This item calls for the temperature and pressure of the steam that will be used for atomizing the oil fuel. This is also required for the best design or selection of the oil burner.

Line 38. *Composition of gas*. This section requires the composition of the gas fuel in terms of mol percent. This is the normal expected fuel gas that will be used in the heater. If there is likely to be a wide variation in the quality of the fuel gas that will be used, this should be noted here as a range of two or even three compositions. This situation is particularly common in petroleum refining.

Line 46. *Properties of fuel oil*. This final section of the specification sheet requires details of the fuel oil that will be used. These details are:
Gravity of the oil at 60 °F (in °API)
Viscosity of the oil at 100 °F and at 210 °F
Flash point in °F

From the two viscosities, the "Refutus" graph can be used to determine the viscosity at any other temperature. This graph can be found in most data books that carry viscosity data. Note the viscosity requested in this section is in centistokes (kinematic viscosity). This is because most suppliers quote in centistokes. To convert to centipoise, multiply by the specific gravity (g/cm^3).

The flash point required is that determined by the Pensky-Marten method and is a measure of the oil's flammability.

This completes the explanation of the main body of the specification sheet. It represents the minimum data required to commence the sizing of the item. The last part of the specification sheet is given to "Remarks." In this section, the engineer should provide all the other data that may influence the design of the heater, e.g., Fig. 57.

Pressure Drop Calculations

Incompressible Flow Pressure Drop in Piping

The technical literature provides numerous methods for calculating pressure drop for incompressible flow. We will look here at a couple of relatively simple methods for estimating pressure drop. More sophisticated methods, sometimes proprietary, are normally used for plant design, but the approaches described here give good

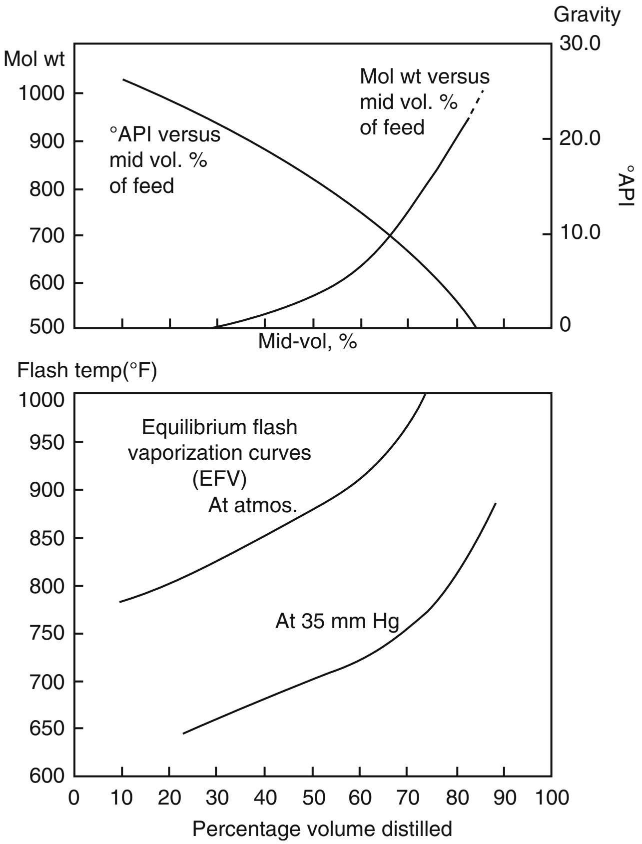


Fig. 57 Fired heater specification sheet attachment

order of magnitude estimates. For now, we will consider only horizontal piping pressure drops. In sections "Fittings and Piping Elements" and "Overall Pressure Drop, Including Elevation and Velocity Changes" we will include the effects of piping elements (fittings, valves, etc.) and elevation changes, respectively.

Appendix 14 illustrates the calculation of pressure drop through a piping system. This calculation is frequently required when specifying or analyzing process systems.

For our sign convention here, we will use a positive pressure drop to indicate a reduction in pressure through a system $(\Delta P = P_{inlet} - P_{outlet})$. A negative pressure drop then indicates the pressure increases through a system, which can occur due to liquid head, for instance). If you use a method for calculating pressure drop other than those described here, be sure you understand the sign convention that method uses. In some texts, the pressure drop is defined as outlet minus inlet.

Appendix 9 Charts

The charts in Appendix 9 of this chapter provide a good, quick method for calculating pressure drop for viscous fluids. This would apply to most hydrocarbons. These are based on the Darcy equation.

To use the charts, you would calculate the volumetric flow rate at actual conditions in US gpm (or barrels per hour, BPH). You also need the kinematic viscosity of the fluid in cSt or SSU and the nominal pipe size in inches. The frictional pressure drop is then read off the chart where the flow rate meets the viscosity for the appropriate pipe size. This dP is for Schedule 40, steel pipe, which is the most widely used. The pressure drop on the charts is in feet of liquid per 1,000 f. of pipe. To convert to psi, multiply the chart value by the fluid density in lb/cft and divide the result by 144 in.^{2}/ft^2. This would give psi/1000 ft.

The dP can be adjusted to other pipe schedules by multiplying the dP from the table by the ratio of d_2^5/d_1^5, where:

d_2 = internal diameter of the actual pipe schedule, inches.
d_1 = diameter of the Schedule 40 pipe used in the table, inches.

General Calculation Method

Another simple approach to estimating incompressible flow dP was adapted from a book by Carl Branan (1976).

In this approach, we again apply the Darcy equation in the form

$$\Delta P_{100} = (W/370)^2\left[1/\left(\rho * d^5\right)\right]\,(f/0.0055) \tag{154}$$

where:

ΔP_{100} = pressure drop per 100 f. of pipe, psi/100 ft.
W = mass flow rate in lb/h.
ρ = fluid density in lb/cft.
d = piping ID in inches.
f = friction factor (assume 0.0055 unless you want to adjust).

The correlation assumes commercial steel pipe, Reynolds number of 10^5 or higher (turbulent flow), and a C factor of 110. This equation can also be used for compressible flows if the pressure drop is less than 10 % of the total pressure.

If you want to apply a friction factor correction:

- Calculate the Reynolds number (we will use *Re* here) for the flow:

$$Re = \rho V D_H/\mu = V D_H/\nu = Q D_H/\nu A \tag{155}$$

where:

$$\begin{aligned} \mathrm{Re} &= \text{Reynolds number (dimensionless)}. \\ \rho &= \text{fluid density in lb/cft}. \\ V &= \text{velocity in ft/s}. \\ D_H &= \text{hydraulic diameter (ID) in ft}. \\ \mu &= \text{dynamic viscosity in lb/ft/s}. \\ \nu &= \mu/\rho = \text{kinematic viscosity in ft}^2\text{/s}. \\ A &= \text{pipe internal cross} - \text{sectional area, ft}^2. \\ Q &= \text{volumetric flow rate in cft/s}. \end{aligned} \tag{156}$$

If you are working with metric numbers, the units for the above parameters are listed below with conversion factors. The Re comes out the same as long as you use consistent units.

$$\begin{aligned} \rho &= \text{fluid density in kg/m}^3\left(1\ \text{kg/m}^3 = \ 0.0624\ \text{lb/cft}\right). \\ V &= \text{velocity in m/s}(1\ \text{m/s} = 3.281\ \text{ft/s}). \\ D_H &= \text{hydraulic diameter(ID) in m}(1\ \text{m} = 3.281\ \text{ft} = 39.37\ \text{in}). \\ \mu &= \text{dynamic viscosity in kg/m/s}(1\ \text{kg/m/s} = 0.672\ \text{lb/ft/s}). \\ \nu &= \text{kinematic viscosity in m}^2\text{/s}\left(1\ \text{m}^2\text{/s} = 10.765\ \text{ft}^2\text{/s}\right). \\ A &= \text{pipe internal cross} - \text{sectional area, m}^2\left(1\ \text{m}^2 = 10.765\ \text{ft}^2\right). \\ Q &= \text{volumetric flow rate in m}^3\text{/s}\left(1\ \text{m}^3\text{/s} = 35.31\ \text{cft/s}\right). \end{aligned}$$

- The friction factor, f, can then be estimated using the Reynolds number and the appropriate equation below:

$$\text{Laminar flow}(Re < 2100) : f = 16/Re. \tag{157}$$

$$\text{Commercial pipe} : f = 0.054/Re^{0.2}. \tag{158}$$

$$\text{Smooth tubes} : f = 0.046/Re^{0.2}. \tag{159}$$

$$\text{Rough pipe} : f = 0.013. \tag{160}$$

To apply the calculation method, follow these steps:

1. Calculate the pipe ID and area in ft and ft^2, respectively, for the size of interest.
2. Calculate the flow rate in lb/h.
3. Calculate the fluid density in lb/cft.
4. Estimate the dynamic viscosity in lb/ft/s.
5. Calculate the fluid velocity in the pipe in ft/s at flowing pressure and temperature.
6. Calculate the Reynolds number for the specific case.
7. Estimate the friction factor using the appropriate equation.
8. Plug the variables into the pressure drop equation to get the psi/100 f. frictional pressure loss.

Example Using the Two Incompressible Fluid Approaches

Let us consider the following:

- Flow rate at P and T = 900 gpm of liquid.
- The flowing density is 62 lb/cft.
- The pipe is new, nominal 10 in., Sch. 40, commercial pipe.
- The kinematic viscosity is 2.1 cSt.
- Estimate the pressure drop per 100 f. for these conditions.

Using Appendix 9 Charts

From the charts in Appendix 9, we find the chart for 10 in. pipe. Read down the left side to 900 gpm and then read across to 2.1 cSt viscosity. The chart value is 4.49 f. of liquid per 1,000 f. of pipe.

Converting to psi/100 ft:

$$4.49\ \text{ft}/1000\,\text{ft} \times 62\ \text{lb/c ft} \times 1/144\ \text{ft}^2/\text{in}^2 \times 100\,\text{ft}/1000\,\text{ft} = 0.193\ \text{psi}/100\ \text{ft}.$$

Using the General Calculation Approach

1. Pipe ID and area in ft and ft^2
   For 10″ Sch. 40 pipe: ID = 10.02″ (0.835 ft) and flow area =0.5475 ft^2.
2. Flow rate in lb/h.

$$900\ \ \text{gpm} \times 0.1337\ \text{cft/gal} \times 60\ \text{min/h} \times 62\ \text{lb/cft} = 447{,}628\ \text{lb/h}.$$

3. Fluid density is given as 62 lb/cft.
4. Estimate the dynamic viscosity in lb/ft/s.

$$2.1\text{c St}/(62/62.4\ \text{SG}) = 2.087\ \text{cP}.$$

$$2.087\ \text{cP} \times \left(6.72 \times 10^{-4}\right) = 0.00140\ \text{lb/ft/s}.$$

5. Fluid velocity at flowing pressure and temperature.

$$447{,}628\ \text{lb/h} \times 1\text{h}/3600\text{s} \times 1\text{cft}/62\ \text{lb} \times 1/0.5474\ \text{ft}^2 = 3.663\ \text{ft/s}.$$

6. Reynolds number.

$$Re = \rho VD/\mu = 62\ \text{lb/cft} \times 3.663\ \text{ft/s} \times 0.835\ \text{ft} \div 0.00140\ \text{lb/ft/s} = 1.35 \times 10^5.$$

7. Friction factor.
   We will use the f equation for commercial pipe, turbulent flow.

$$f = 0.054/Re^{0.2} = 0.054/(1.35 \times 105)^{0.2} = 0.00508.$$

8. Pressure drop calculation.

$$\Delta P_{100} = (447{,}628/370)^2\left[1/\left(62 * (10.02)^5\right)\right]\ (0.00508/0.0055\ ) = 0.216\ \text{psi}/100\ \text{ft}.$$

The pressure drops determined by the two methods compare fairly well:

Using the Appendix 9 charts: 0.193 psi/100 ft
Using the calculation approach: 0.216 psi/100 ft

The difference is about 10 %, which is within the error for these approaches to pressure drop. If it was found that the pressure drop or the velocity was too high or too low, a different pipe diameter would be selected and the calculations repeated until an acceptable combination of conditions was determined.

Compressible Flow Pressure Drop in Piping

For the compressible flow case, we will make the assumption that the flow is essentially isothermal, i.e., the flowing pressure drop does not produce a significant change in the fluid temperature. For most cases, this is valid.

As in the case of incompressible flow, we will consider only horizontal piping pressure drops. In sections "Fittings and Piping Elements" and "Overall Pressure Drop, Including Elevation and Velocity Changes," we will adjust for the effects of piping elements (fittings, valves, etc.) and elevation changes, respectively.

We will again examine two approaches to this calculation: the chart in Appendix 13 in this chapter and a generalized calculation approach.

Appendix 13 Pressure Drop Estimating

The chart in Appendix 13 provides an estimate using the "Weymouth formula." To use the chart, determine the volumetric flow rate in Mscfd (1,000 actual cubic feet per day) and the pipe diameter. Then, starting with the Y-axis, you move across the chart to the appropriate line for the pipe size chosen and read vertically downward to obtain the value of $P_1^2 - P_2^2$. P_1 is the upstream pressure in psia and P_2 is the downstream absolute pressure. The pressure drop is determined from the X-parameter.

The chart is based on a specific gravity of 0.9 (air = 1.0), 90 °F, and 14.65 psia base pressure. The results may need to be adjusted to other conditions, but the chart provides a good first estimate of dP.

General Calculation Method

For a general calculation approach, we will again follow an approach described by Branan in his book (1976).

We will apply the general equation for compressible flow:

$$\Delta P = 2P_1/(P_1 + P_2)\left\{0.323[(fL/d) + \ln(P_1/P_2)/24]SG_1U_1^{\,2}\right\} \tag{161}$$

where:

$$
\begin{aligned}
P_1 &= \text{initial pressure, psia } (\underline{\text{absolute}}).\\
P_2 &= \text{final pressure, psia.}\\
SG_1 &= \text{specific gravity of vapor vs water} = 0.0015\ \mathrm{M\ P_1/T}.\\
d &= \text{pipe ID, in.}\\
U_1 &= \text{upstream velocity, ft/s.}\\
f &= \text{friction factor(assume 0.005 for estimates).}\\
L &= \text{length of pipe, ft.}\\
M &= \text{molecular weight of gas.}\\
T &= \text{upstream temperature, }^\circ\text{R.}
\end{aligned}
\tag{162}
$$

Example Using the Two Compressible Fluid Approaches

Let's consider the following case:

- 10.5 MMscfd of vapor with a molecular weight of 26.0 (scfd are at 60 °F, 1 Atm).
- Piping is 8 in., Sch. 40 nominal commercial pipe.
- Initial temperature is 125 °F.
- Initial pressure is 260 psig.
- Estimate the pressure drop per 100 f. for these conditions.

We will do the estimate using both the Appendix 13 chart and the calculation approaches.

Using Appendix 13 Chart

$$Mcfd(chart) = Mcfd(base) \times P/14.65(SG/0.9\ \times T/550 \times Z/1)^{0.5}. \tag{163}$$

Now:

Our *Mcfd* in this case is 10,500 scfd.
P is 14.7 for our scf basis.
SG of the gas is 26 MW/29 = 0.9.
T for the scf basis is 520 °R.
Assume *Z* = 1.0.

So the Mcfd to use on the chart is

$$
\begin{aligned}
Mcfd(chart) &= 10,500 \times 14.7/14.65 \times (0.9/0.9 \times 520/550 \times 1.0/1)^{0.5}\\
&= 10,244.
\end{aligned}
$$

Picking 10,200 for the Y-axis of the chart and moving across to the line for 8″, Sch. 40 pipe, the value of $P_1^2 - P_2^2$ is ~1,000.

We know P_1 is 274.7, so solving for P_2 gives 272.9 psia. Pressure drop is the difference or 1.8 psi/1,000 f. or 0.18 psi/100 ft.

Using the General Calculation Method

1. $P_1 = 260 + 14.7 = 274.7$ psia.
2. $P_2 = P_1$ – initially assumes negligible pressure drop change. We will test this assumption later.
3. Absolute temperature $= 125\ ^\circ\mathrm{F} + 460\ =\ 585\ ^\circ\mathrm{R} = T_1$.
4. Use 100 f. of pipe as a basis $= L$.
5. Gas-specific gravity versus water.

$$SG_1 = 0.0015(26\ \mathrm{mw})(274.7\ \mathrm{psia})/585\ ^\circ\mathrm{R} = 0.0183.$$

6. Pipe diameter $= 7.981$ in. and flow area $= 0.3474$ sqft.
7. Assume a friction factor of 0.005 for estimating work.
8. Calculate the velocity:

$$\begin{aligned} U_1 &= 10.5 \times 10^6 \times\ (14.7\,\mathrm{psia}/274.7\ \mathrm{psia}) \times (585\ ^\circ\mathrm{R}/520\ ^\circ\mathrm{R}) \\ &\times 1\ \mathrm{day}/24\ \mathrm{h} \times 1\ \mathrm{h}/3600\ \mathrm{s} \div 0.3474\ \mathrm{ft}^2 \\ &= 21.1\ \mathrm{ft/s}. \end{aligned}$$

9. Calculate the pressure drop using the equation:

$$\begin{aligned} \Delta P &= 2P_1/(P_1 + P_2)\left\{0.323[(fL/d) + \ln(P_1/P_2)/24]SG_1{U_1}^2\right\} \\ &= 1(274.7\ \mathrm{psia})/(274.7\ \mathrm{psia} + 274.7\ \mathrm{psia}) \\ &\quad \times \{0.323[((0.005 \times 100\ \mathrm{ft})/7.981) + \ln(274.7\ \mathrm{psia}/274.7\ \mathrm{psia})/24] \\ &\quad \times (0.0183\ \mathrm{SG})(21.1)^2\} =\ 1\{0.323[0.0626 + 0/24](0.0183)(445.2)\} \\ &= 0.17\ \mathrm{psi}/100\ \mathrm{ft}. \end{aligned}$$

This is a small enough pressure drop that there is no need for iteration. If the pressure drop was significant, this dP would have been used for the difference between P_1 *and* P_2 in a second iteration.

Comparing Results of Compressible Flow

The answers we got using the two methods of calculation varied by only 0.01 psi per 100 f. or about 6 %. This is about as accurate as you can expect from these types of estimates. For detailed design work, more sophisticated methods are normally applied to increase accuracy.

You can also break a piping system into shorter segments and perform the dP calculation for each segment to improve accuracy.

Fittings and Piping Elements

We have so far dealt with pressure drops in straight, horizontal piping, but seldom is piping all horizontal or all straight. There are fittings, elbows, and valves. We will look at the simplest approach to allowing for these elements next, starting with pipe fittings, valves, and the like. In the section after this, we will review the impacts of elevation and velocity changes.

The most common and simplest approach to account for fittings in piping uses equivalent lengths defined for each type of element. In this approach, for instance, the equivalent length of an 8 in standard elbow in a line is about 20 ft. The nomograph of Appendix 12 to this chapter provides a fast, easy method of determining the equivalent lengths for many types of fittings and pipe configurations.

An alternative to Appendix 12 is Table 35 translated from the GPSA Engineering Data Book after Branan (1976; GPSA 1987).

To determine the total pressure drop due to valves and fittings:

1. Count the numbers of each type of valve and fitting.
2. Look up the equivalent length of each type of fitting in Appendix 12 or in Table 35.
3. Multiply the number of each type of element by the equivalent length of that element.
4. Add the total equivalent lengths of all the elements. The answer, in the units used here, would be in equivalent feet of pipe.
5. Multiply the equivalent length by the calculated ΔP_{100} for straight pipe that has been calculated using the other described methods for single- or two-phase flows to get the total dP due to the piping elements.
6. The total dP for the pipe elements would be added to the dP for the total straight pipe to get the overall system pressure drop from frictional losses.

We will review an example of this that also includes elevation and velocity changes a little later in the next section.

Overall Pressure Drop, Including Elevation and Velocity Changes

Appendix 14 provides an example of a system pressure drop calculation. Here we will review some background and another approach.

Piping is seldom all at the same elevation and piping diameters can be changed along the way. If we define pressure drop as the difference in pressure between two points, then the overall pressure drop for a system would be defined as

$$\Delta P_{overall} = \Delta P_{friction} + \rho \Delta Z + \rho\left(\Delta U^2/2g_c\right) \tag{164}$$

Table 35 Equivalent lengths of valves and fittings in feet (GPSA 1987)

Nominalpipesize, in.	Gate valve or ball check valve	Angle valve	Swing check valve	Plug cock valve	Gate or ball valve														Equivalent length in terms of smaller diameter pipe									
																			Enlargement					Contraction				
						45° elbow		Short rad 90° elbow		Long rad 90° elbow		Hard tee		Soft tee			90° Mitered bend		Sudden			Std reducer		Sudden			Std reducer	
						Welded	Threaded	Welded	Threaded	Welded	Threaded	Welded	Threaded	Welded	Threaded	2 miters	3 miters	4 miters	d/D = 1/4	d/D = 1/2	d/D = 3/4	d/D = 1/2	d/D = 3/4	d/D = 1/4	d/D = 1/2	d/D = 3/4	d/D = 1/2	d/D = 3/4
$1^1/_2$	55	26	13	7	1	1	2	3	5	2	3	8	9	2	3				5	3	1	4	1	3	2	1	1	
2	70	33	17	14	2	2	3	4	5	3	4	10	11	3	4				7	4	1	5	1	3	3	1	1	
$2^1/_2$	80	40	20	11	2	2		5		3		12		3					8	5	2	6	2	4	3	2	2	
3	100	50	25	17	2	2		6		4		14		4					10	6	2	8	2	5	4	2	2	
4	130	65	32	30	3	3		7		5		19		5					12	8	3	10	3	6	5	3	3	
6	200	100	48	70	4	4		11		8		28		8					18	12	4	14	4	9	7	4	4	1
8	260	125	64	120	6	6		15		9		37		9					25	16	5	19	5	12	9	5	5	2
10	330	160	80	170	7	7		18		12		47		12					31	20	7	24	7	15	12	6	6	2

12	400	190	95	170	9	9		22		14		55		14		28	21	20	37	24	8	28	8	18	14	7	7	2
14	450	210	105	80	10	10		26		16		62		16		32	24	22	42	26	9			20	16	8		
16	500	240	120	145	11	11		29		18		72		18		38	27	24	47	30	10			24	18	9		
18	550	280	140	160	12	12		33		20		82		20		42	30	28	53	35	11			26	20	10		
20	650	300	155	210	14	14		36		23		90		23		46	33	32	60	38	13			30	23	11		
22	688	335	170	225	15	15		40		25		100		25		52	36	34	65	42	14			32	25	12		
24	750	370	185	254	16	16		44		27		110		27		56	39	36	70	46	15			35	27	13		
30				312	21	21		55		40		140		40		70	51	44										
36					25	25		66		47		170		47		84	60	52										
42					30	30		77		55		200		55		98	69	64										
48					35	35		88		65		220		65		112	81	72										
54					40	40		99		70		250		70		126	90	80										
60					45	45		110		80		260		80		190	99	92										

where:

$\Delta P_{overall}$ = overall pressure drop, lb/ft^2 (Note this is per square foot).
$\Delta P_{friction}$ = frictional pressure loss, lb/ft^2 (calculated for pipe and pipe elements using single- or two-phase methods).
ρ = flowing fluid density, lb/cft.
ΔZ = net elevation change, ft.
ΔU = net change in flowing fluid velocity, ft/s.
g_c = gravitational constant, 32.17 f. lb$_m$/(lb$_f$ s^2).

The application of the above equation, including all the various elements, is best illustrated by an example.

Suppose we have the following case:

- 250 gpm water flowing at 60 °F
- 10 in., Sch. 40 pipe
- From the piping layout, we determine:
  - The net elevation change is 25 f. upward.
  - There are three standard elbows in the line.
  - There are two fully open gate valves.
  - The line ends in an empty tank (sudden enlargement).
  - There are 265 f. of straight line.
- What is the total system pressure drop for this configuration?

1. Determine the water density = approximately 62.4 lb/cft.
2. Determine flow rate in lb/s and cft/s:

$$250 \text{ gpm} \times 8.34 \text{ lb/cft} \times 1 \text{ min}/60 \text{ s} = 34.75 \text{ lb/s}.$$
$$34.75 \text{ lb/s}/62.4 \text{ lb/cft} = 0.557 \text{ cft/s}.$$

3. Velocity in line:

$$0.557 \text{ cft/s}/0.5475 \text{ ft}^2 (\text{flow area of } 10'' \text{ pipe}) = 1.02 \text{ ft/s or fps}.$$

4. In this case, we are going from 1.02 fps velocity to zero in the tank, so the ΔU = 1.02 fps and the velocity term of the pressure drop equation is

$$62.4 \text{ lb/ft3} \times (1.02 \text{ ft/s})^2/\left(2 \times 32.17 \text{ ft lb}/\left(\text{lb s}^2\right)\right) = 1.01 \text{ lb/ft}^2.$$

   This is less than 0.1 psi pressure drop; so, it is negligible in this case.

5. The elevation change is +25 ft, so the elevation change term is

$$25 \text{ ft} \times 62.4 \text{ lb/cft} = 1560 \text{ lb/sqft} (10.8 \text{ psi}).$$

6. Using the techniques described earlier for single-phase, incompressible flow, the ΔP_{100} frictional loss for straight pipe is determined to be 0.019 psi or 2.75 lb/ft^2 per 100 f. of pipe. The calculation is not detailed here.
7. Calculating the equivalent line length for frictional loss, we have:

Straight pipe	265 ft
3 std. elbows (26 f. each, Appendix 12)	78 ft
2 open gate valves (6 f. each, Appendix 12)	12 ft
1 sudden enlargement (15 ft, Table 35)	15 ft
Total equivalent line length (sum)	370 ft

8. Frictional pressure loss overall is

$$2.75\ \mathrm{lb/ft^2}/100\ \mathrm{ft} \times 370\ \mathrm{equiv.\ ft}/100 = 10.2\ \mathrm{lb/ft^2} = \Delta P_{friction}.$$

9. Overall system pressure drop is then

$$\begin{aligned}\Delta P_{overall} &= \Delta P_{friction} + \rho \Delta Z + \rho\left(\Delta U^2/2g_c\right)\\ &= 10.2\ \mathrm{lb/ft^2} + 1560\ \mathrm{lb/ft^2} + 0\ \mathrm{lb/ft^2}\\ &= 1570.2\ \mathrm{lb/ft^2}\text{or } 10.9\ \text{psi for the system.}\end{aligned}$$

In this case, the elevation change dominated the overall pressure drop across the system. This would not necessarily be the case if the flow rate were significantly higher or the piping system was more complex and long.

Also, note that if the final destination tank was below the start of the line, the pressure drop would be negative or the pressure would actually be higher at the tank than at the start of the line (which would require introduction of some sort of flow control).

If the tank were not empty, the tank level would have to be added to the elevation change for the calculation.

Two-Phase (Liquid + Vapor) Pressure Drop and Flow Regimes in Piping

So far, we have just dealt with single-phase flows, but most petroleum refining processes involve two-phase, mixed liquid/gas flows. Here we will discuss the general approach to estimating pressure drop for two-phase horizontal flows using the method developed by Ovid Baker and described in an excellent article by Robert Kern (1969). The approach here is a simplification described by A.K. Coker (1990). There are other approaches also available with some simplifications to enable easy computing. We will focus here on Baker's approach, however.

We begin by defining the Baker parameters B_x and B_y:

$$B_x = 531(W_L/W_G)\left[\left((\rho_L\rho_G)^{0.5}\right)/\left({\rho_L}^{0.667}\right)\right]\left[\left({\mu_L}^{0.333}\right)/\sigma_L\right] \tag{165}$$

$$B_y = 2.16(W_G/A)\left[1/\left((\rho_L\rho_G)^{0.5}\right)\right] \tag{166}$$

where:

B_x = Baker chart X-parameter.
B_y = Baker chart Y-parameter.
W_L, W_G = flow rate of liquid and gas phases, respectively, lb/h.
ρ_L, ρ_G = densities of liquid and gas phases, respectively, at op. conditions lb/cft.
μ_L = viscosity of liquid phase in cP at operating conditions.
σ_L = surface tension of liquid at operating conditions in dynes/cm.
A = pipe flow area, ft^2.

A log-log plot of the Baker parameters defines the type of flow occurring in the piping or the flow regime as shown in Fig. 58. Within each flow regime, a different approach to the pressure drop applies.

The types of two-phase flow that are generally identified are:

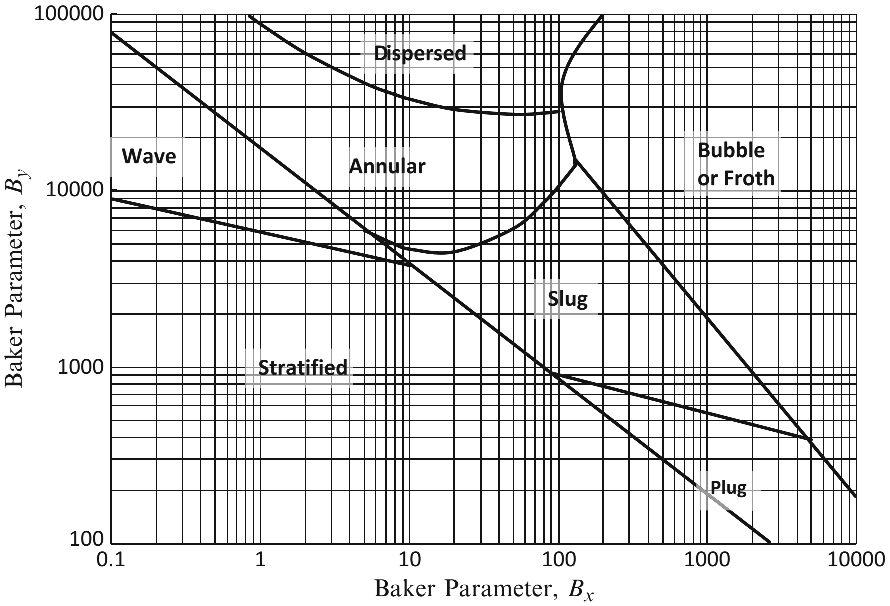


Fig. 58 Two-phase flow regime map for horizontal piping

- Dispersed – In this regime, nearly all the liquid is entrained as a spray in a bulk gas phase. This regime may also be referred to as mist flow. The gas and liquid move at the same velocity. This type of flow works well in upward flow as well as horizontal flow.
- Bubble or froth – Bubbles of gas are dispersed in a primarily liquid phase with the gas moving about the same velocity as the liquid. This regime works for upward or horizontal flows.
- Annular – There is a liquid film flowing along the wall of the pipe with gas or dispersed flow at a higher velocity in the center core of the pipe. If properly sized, operation in this regime is fine for upward or horizontal flows.
- Stratified – This is normally a horizontal flow phenomenon when the gas and liquid separate long horizontal pipes. The gas moves at a higher velocity than the liquid, with the liquid flowing along the bottom of the pipe. The interface between the liquid and gas is relatively smooth. This is a regime that is a concern for vertical flow because it can cause slugging or pipe hammer.
- Wave – This is similar to stratified flow, but the gas velocity is higher, producing a wavy interface between gas and liquid layers. Again, this regime can give rise to problems when flow is vertical.
- Slug – This is a more extreme form of wave flow where the waves are periodically picked up and “slugged” through the pipe. This regime is undesirable as it causes excessive pipe movement and hammer that is potentially damaging.
- Plug – Alternate plugs of liquid and gas move through the pipe. Again, this is an undesirable regime generally, that can result in damage.

Now, to pull this information into a pressure drop value for two-phase flow, we will define some additional parameters:

- The basic two-phase flow equation is

$$\Delta P_{100,2\phi} = \Delta P_{100,G} \times \Phi^2 \tag{167}$$

where:

$\Delta P_{100,2\phi}$ = two-phase pressure drop, convenient units.
$\Delta P_{100,G}$ = pressure drop for the gas phase only, consistent units.
Φ = two-phase flow modulus that depends on the flow regime (see below).

- Lockhart-Martinelli modulus, X

$$X = (\Delta P_L / \Delta P_G)^{0.5} \tag{168}$$

where:

ΔP_L, ΔP_G = pressure drop for each phase in the pipe separately, convenient units (calculate this using the single-phase approach discussed previously).

- Two-phase flow modulus, Φ, depends on flow regime. The relevant empirical equations are:
  - Bubble or froth:

$$\Phi = \left(14.2X^{0.75}\right)/(WL/A)^{0.1}. \tag{169}$$

  - Plug:

$$\Phi = \left(27.315X^{0.855}\right)/(WL/A)^{0.17}. \tag{170}$$

  - Stratified:

$$\Phi = (15400X)/(WL/A)^{0.8}. \tag{171}$$

  - Slug:

$$\Phi = \left(1190X^{0.815}\right)/(WL/A)^{0.5}. \tag{172}$$

  - Annular:

$$\Phi = (4.8 - 0.3125d)X^{(0.343 - 0.021d)}. \tag{173}$$

    For pipe diameters greater than 10″, use 10″ as the basis.
  - Dispersed or spray flow:

$$\Phi = \exp\left[1.4659 + 0.49138\ \ln X + 0.04887(\ln X)^2 - 0.000349(\ln X)^3\right] \tag{174}$$

where:

W = total L + G mass flow in lb/h at operating conditions.
L = equivalent piping length, ft (use 100 for pressure drop per 100 ft).
A = pipe flow area, ft^2.
X = Lockhart-Martinelli modulus as defined above.

- For wavy flow, a slightly different approach is used:

$$H_x = (W_L/W_G)(\mu_L/\mu_G) \tag{175}$$

$$\ln(f_H) = 0.211\ \ln(H_x) - 3.993 \tag{176}$$

$$\Delta P_{100,2\phi} = \left(0.000336 f_H (W_G)^2\right)/\left(d^5 \rho_G\right) \tag{177}$$

where:

W_L, W_G = as defined above, lb/h.
μ_L, μ_G = viscosities of the liquid and gas phases, cP at op. conditions.
d = pipe ID in inches.
ρ_G = gas density, lb/cft.

So for the general two-phase pressure drop calculation, the following approach is defined:

1. Calculate the Baker parameters, B_x and B_y.
2. Determine the flow regime.
3. Calculate the pressure drop per 100 f. for each phase as though that was the only phase flowing in the pipe ($\Delta P_{L,100}$, $\Delta P_{G,100}$). You can use any method previously described or an alternate, preferred method.
4. Calculate the Lockhart-Martinelli modulus, X.
5. Calculate the appropriate flow modulus value, Φ (or follow the wavy flow approach).
6. For flow regimes other than wave flow, use the calculated flow modulus in the equation below to get the final two-phase pressure drop per 100 ft.

$$\Delta P_{100,2_\phi} = \Delta P_{100,G} \times \Phi^2. \tag{167}$$

7. The remaining calculations to get total system pressure drop follow the same pattern as for single phases using equivalent lengths of pipe, elevation changes, and velocity changes. For elevation changes, you will have to estimate the average flowing density. This may be a little more complex for flows where there is significant phase separation.

We will illustrate the two-phase pressure drop calculation with an example.

Two-phase pressure drop example

Let's say we are given the following from a simulation:

- Two-phase flow in an 8 in., Sch. 40 pipe.
- Liquid flow rate = W_L = 59,033 lb/h.
- Vapor flow rate = W_G = 9,336 lb/h.
- Liquid density at flowing conditions = ρ_L = 31.2 lb/cft.
- Vapor density at flowing conditions = ρ_G = 1.85 lb/cft.
- Liquid surface tension at flowing conditions = σ_L = 5.07 dynes/cm.
- Liquid viscosity at flowing conditions = μ_L = 0.11 cP.
- Initial pressure = P_1 = 338 psig.
- Temperature = T = 250 °F.
- Molecular weight of the gas is 40 = M.

Now we follow the solution step-by-step:

1. Calculate the Baker parameters:

(a) $$B_x = 531(W_L/W_G)\left[\left((\rho_L\rho_G)^{0.5}\right)/\left({\rho_L}^{0.667}\right)\right]\left[\left({\mu_L}^{0.333}\right)/\sigma_L\right]$$

$$= 531(59,033/9,336)\left[(31.2 * 1.85)^{0.5}/31.2^{0.667}\right]\left[0.11^{0.333}/5.07\right]$$

$$= 531(6.323)[0.766][0.0945].$$

$$B_x = 243.$$

(b)
$$\begin{aligned} B_y &= 2.16(W_G/A)\left[1/\left((\rho_L\rho_G)^{0.5}\right)\right] \\ &= 2.16\left(9{,}336/0.3474\ \text{ft}^2\right)\left[\ 1/(31.2 * 1.85)^{0.5}\right] \\ &= 2.16(26{,}874)[0.1316]. \\ B_y &= 7{,}639. \end{aligned}$$

2. Looking at the Baker chart (Fig. 58), this puts us on the boundary between slug and bubble/froth flow. Let us say the regime is bubble/froth. (The regimes are not perfectly defined anyway.)
3. Calculate the single-phase pressure drops for both the liquid and gas using one of the previous methods. This calculation is not detailed here, but the resulting pressure drops are

$$\begin{aligned} \Delta P_{L,100} &= 0.025\ \text{psi}/100\ \text{ft for liquid phase.} \\ \Delta P_{G,100} &= 0.0108\ \text{psi}/100\ \text{ft for gas phase.} \end{aligned}$$

4. Calculate the Lockhart-Martinelli flow modulus:

$$X = (0.025/0.011)^{0.5} = 1.51.$$

5. Calculate the two-phase flow modulus using the formula for froth/bubble flow.

$$\begin{aligned} \Phi &= \left(14.2X^{0.75}\right)/(WL/A)^{0.1} \\ &= \left(14.2 * 1.51^{0.75}\right)/[((59{,}033 + 9{,}336) * 100)/0.3474]^{0.1} \\ &= 19.343/5.363. \\ \Phi &= 3.607. \end{aligned}$$

6. Calculate the two-phase pressure drop.

$$\begin{aligned} \Delta P_{100,2\phi} &= \Delta P_{100,G} \times \Phi^2 \\ &= 0.0108 \times (3.607)^2 \\ &= 0.141\ \text{psi}/100\ \text{ft}. \end{aligned}$$

7. No additional data were given, but from here the solution follows the previous discussion for determining overall system pressure drop.

The calculations for two-phase pressure drops are only approximate order of magnitude. For design, more detailed, proprietary methods are normally recommended.

General Comments on Pressure Drops in Beds of Solids

The next few sections of this handbook provide techniques to estimate pressure drop through beds of solids, like reactors or sorbent beds (adsorbents, absorbents). There are a few types of cases to consider:

- Single-phase, cocurrent upflow or downflow
- Two-phase, cocurrent upflow or downflow
- Two-phase counterflow
- Moving solids bed flow

For our purposes here, we will focus on the concurrent flow cases, which are the most common. Discussion of countercurrent pressure drop is beyond the scope of this book. We will only briefly touch on flows where the solids bed moves with some references. The techniques here are also not intended to apply to distillation or absorber tower packings, which are discussed in section "Vessels and Towers" of this chapter.

The approaches described here are for approximate dP only (+/−20 to 30 %). If used for design, it would be advisable to perform some experimental work to fine-tune the parameters required in the calculation. Many licensors have more accurate, proprietary correlations for design. Still, if you have an operating unit with known pressure drops at different rates, this approach could be fine-tuned to reflect the actual dP and can be used for predicting system dP response.

Single-phase flow results are combined together to determine two-phase flow results using various empirical correlations, similar to the way single-phase piping flow pressure drops are combined into two-phase dPs for piping.

Fixed bed dP calculations are largely empirical in nature. The two most critical factors are the void fraction of the bed and the equivalent particle diameter. Unfortunately, these are the two most difficult parameters to determine.

Flow direction plays a role in these techniques. As with piping, if the flow is downward through a bed, the mass of the flowing materials reduces the pressure drop through the bed. Conversely, if the flow is upward, the mass of the fluids increases the pressure drop by fighting gravity.

We will begin with single-phase flow through beds of solids.

Single-Phase Pressure Drop in Beds

The primary equation used for single-phase pressure drop in beds is the Ergun equation. For our purposes here, we will use the form:

$$(\Delta P/L)_{friction} = \left[(\alpha(1-\varepsilon)/Re_B + \beta\right]\left[G^2/\left(g_c D_p \rho\left(\varepsilon^3/(1-\varepsilon)\right)\right)\right] \tag{178}$$

where:

$$\begin{aligned}
(\Delta P/L)_{friction} &= \text{frictional pressure loss in lb/ft}^2 \text{ per foot of bed.}\\
\alpha &= \text{Ergun constant that depends on size, shape, and packing of bed.}\\
\beta &= \text{Ergun constant that depends on size, shape, and packing of bed.}\\
\varepsilon &= \text{void fraction of the bulk bed, dimensionless.}\\
Re_B &= \text{bed Reynolds number} = D_pG/\mu = D_pV_\rho/\mu.\\
G &= \text{mass flux through the bed} = \text{lbs/s} \div \text{empty vessel flow area.}\\
g_c &= \text{gravitational constant} = 32.17\ \text{ft} * \text{lb}/\left(\text{lb} * \text{s}^2\right).\\
D_p &= \text{equivalent particle diameter in feet} = 6/S_v.\\
\rho &= \text{fluid density, lb/cft at operating conditions.}\\
S_v &= \text{particle average surface area/volume, ft}^2\text{/cft}\\
&\quad \text{(for shaped particles, use smoothed/projected particle dimensions).}\\
V &= \text{superficial velocity of fluid in empty vessel, ft/s.}\\
\mu &= \text{fluid viscosity in lb/(ft} * \text{s)}, \left(= \text{cP} \times 6.72 \times 10^{-4}\right).
\end{aligned} \tag{179}$$

Some typical values of α and β are in Table 36.

To obtain the overall pressure drop in a bed, the fluid density must be factored in, so the final overall pressure drop through the bed itself would be

$$(\Delta P/L)_{bed} = (\Delta P/L)_{friction} - / + \rho \tag{180}$$

where:

$(\Delta P/L)_{bed}$ = overall bed pressure drop, lb/ft^2.
$(\Delta P/L)_{friction}$ = frictional pressure drop from above.
ρ = fluid density at flowing conditions, lb/cft (be careful of the sign).
The density is subtracted if flow is downward (negative sign).
The density is added if flow is upward (positive sign).

Table 37 illustrates some typical void fractions for various solids shapes that are randomly packed in a bed. These values should be decreased by 10–15 % if the bed has been dense loaded.

Use of these equations is best illustrated by an example:

Example single-phase bed pressure drop calculation

Consider a downflow reactor in vapor phase. The following parameters are given:

Table 36 Typical values of Ergun α and β for various shapes (for design work, these should be determined experimentally for the specific solid being used)

Size/shape	*α*	*β*
1/16″ extrudate	350	2.83
1/8″ extrudate	350	1.75
3/8″ sphere	118	1.00
3/8″ Raschig ring	266	2.33

Table 37 Typical values of void fraction for various shapes (For design work, these should be determined experimentally for the specific solid being used)

Shape	ε
Cylinder	0.33
Extrudate	0.35
Sphere, ball	0.15
Rings, shapes	~0.42
High void toppings	~0.5

- Catalyst was sock loaded.
- The main catalyst bed is 1/8″ diameter cylindrical extrudate.
- The average L/D (length-to-diameter ratio) for the catalyst is 4.0.
- Reactor internal diameter is 96 in.
- Vapor flow rate is 150,000 lb/h.
- Vapor density is 2.10 lb/cft.
- Vapor viscosity is 0.02 cP.
- Bed depth is 35 ft.
- What is the dP through the reactor bed, assuming negligible density change?

We follow this sequence for the calculation:

1. Assemble the terms required for the Ergun equation:

(a) For 1/8″ extrudate, sock loaded, we pick the following from Tables 36 and 37:

$$\alpha = 350.$$
$$\beta = 1/75.$$
$$\varepsilon = 0.35.$$

(b) Calculate the equivalent particle diameter, D_p:

- Cross-sectional area of particle

$$(0.125\ \text{in.}/12\ \text{in.}/\text{ft})^2 \times \pi/4 = 8.522 \times 10^{-5}\ \text{ft}^2.$$

- Circumference of particle (assume round)

$$(0.125\ \text{in.}/12\ \text{in.}/\text{ft}) \times \pi = 3.272 \times 10^{-2}\ \text{ft}.$$

- Superficial surface area of particle

$$\text{Ends}: 2 \times 8.52 \times 10^{-5}\ \text{ft}^2 = 1.704 \times 10^{-4}\ \text{ft}^2.$$
$$\text{Sides}:\ 3.272 \times 10^{-2}\ \text{ft} \times ((0.125\ \text{in} \times 4.0)/12\ \text{in/ft}) = 1.363 \times 10^{-3}\ \text{ft}^2.$$
$$\text{Total area}: 1.704 \times 10^{-4} + 1.363 \times 10^{-3} = 1.533 \times 10^{-3}\ \text{ft}^2.$$

- Average volume of a particle

$$8.52 \times 10^{-5}\text{ft}^2(\text{end}) \times ((0.125\ \text{in} \times 4.0)/12\ \text{in/ft}) = 3.551 \times 10^{-6}\ \text{cft}.$$

- Surface to volume ratio

$$S_v = 1.533 \times 10^{-3}/\ 3.551 \times 10^{-6} = 4.317 \times 10^2\ \text{ft}^{-1}.$$

- $D_p = 6/S_v = 6/4.317 \times 10^2\ \text{ft}^{-1} = 1.39 \times 10^{-2}\ \text{ft}(\sim 0.167\ \text{in.})$.

(c) Calculate the mass flux for the reactor

Reactor diameter of 96 in. → Flow area = $50.67\,\text{ft}^2$
Flow rate = 150, 000 lb/h or 41.67 lb/s.
Mass flux, $G = (41.67\ \text{lb/s})/\left(50.27\ \text{ft}^2\right) = 0.8289\ \text{lb/ft}^2/\text{s}$.

(d) Convert fluid viscosity to the desired units

$$0.02\ \text{cP} \times 6.72 \times 10^{-4} = 1.34 \times 10^{-5}\text{lb/ft/s} = \mu.$$

(e) Superficial velocity, V

$$V = (150,000\ \text{lb/h})/(2.10\ \text{lb/cft})/\left(50.27\ \text{ft}^2\right)/3600 = 0.395\ \text{ft/s}.$$

2. Calculate the Reynolds number for the bed

$$Re_B = D_pG/\mu = \left(1.39 \times 10^{-2}\text{ft}\right)\left(0.8289\ \text{lb/ft}^2/\text{s}\right)/\left(1.34 \times 10^{-5}\text{lb/ft/s}\right)$$
$$= 859.8.$$

3. Calculate the frictional pressure drop using the Ergun equation

$$(\Delta P/L)_{friction} = \left[(\alpha(1-\varepsilon)/Re_B + \beta\right]\left[G^2/\left(g_cD_p\rho\left(\varepsilon^3/(1-\varepsilon)\right)\right)\right]$$
$$= \Big[(350(1-0.35)/859.8 + 1.75](0.8289)^2/\left((32.17)\left(1.39 \times 10^{-2}\right)(2.10)\right.$$
$$\left.\times\ \left(0.35^3/(1-0.35)\right)\right)] = 22.35\ \text{lb/ft}^2/\text{ft}\ (0.155\ \text{psi/ft depth}).$$

4. Calculate total bed pressure drop

$$\begin{aligned}(\Delta P/L)_{bed} &= (\Delta P/L)_{friction} - \rho \\ &= 22.35\ \mathrm{lb/ft^2/ft} - 2.10\ \mathrm{lb/cft/ft} \\ &= 20.25\ \mathrm{lb/ft^2/ft}(0.141\ \mathrm{psi/ft\ of\ bed}). \\ \text{Total dP} &= 20.25\ \mathrm{lb/ft^2/ft} \times 35\ \mathrm{ft\ depth} = 709\ \mathrm{lb/ft^2}(4.9\ \mathrm{psi}).\end{aligned}$$

This excludes any fouling allowances or internals.

Two-Phase Pressure Drop in Beds

For two-phase pressure drop in solid beds, we will adopt the technique developed by Larkins, White, and Jeffery in 1961. There are other methods, but this approach is relatively simple to apply and it uses the Ergun equations already discussed.

The method developed by Larkins et al. follows these steps:

1. Calculate the $(\Delta P/L)_{friction}$ for each phase (liquid and gas) using the Ergun equation or another approach as though that phase was the only phase flowing in the reactor. This is similar to the approach in two-phase piping pressure drop.
2. Calculate the X modulus, similar to the Lockhart-Martinelli modulus in pipe flows:

$$X = \left[(\Delta P/L)_{fric,L}/(\Delta P/L)_{fric,G}\right]^{0.5}. \tag{181}$$

3. Calculate the frictional two-phase pressure drop in lb/ft^2/ft of bed using the modulus and the following empirical correlation:

$$(\Delta P/L)_{fric,2\phi} = \left[(\Delta P/L)_{fric,L} + (\Delta P/L)_{fric,G}\right]\left[10^{(0.416/(\mathrm{Sq(logX)}+0.666)]}.\right. \tag{182}$$

4. Calculate the liquid saturation factor, S

$$\mathrm{S} = 10^{(-0.774+0.525\mathrm{logX}-0.109\mathrm{Sq(logX)})}. \tag{183}$$

5. Calculate the flowing mixture density at operating conditions, ρ_{mix}

$$\rho_{mix} = {}_{\rho L}S + {}_{\rho G}(1-S). \tag{184}$$

6. Adjust the pressure drop for density of the mixture

$$(\Delta P/L)_{total,2\phi} = (\Delta P/L)_{fric,2\phi} - / + \rho_{mix}\ \mathrm{lb/ft^2/ft\ of\ depth}. \tag{185}$$

As before:

- The sign for the density is negative for downflow.
- The sign of the density is positive for upflow.

So let's consider an example.

Example two-phase bed pressure drop calculation

We will simplify this calculation somewhat by assuming we have already calculated the single-phase frictional losses through the bed for gas and liquid individually. Our input data are then:

$$\begin{aligned}(\Delta P/L)_{fric,L} &= 2.00\ \mathrm{lb/ft^2/ft}(0.014\ \mathrm{psi/ft}).\\ (\Delta P/L)_{fric,G} &= 20.1\ \mathrm{lb/ft^2/ft}(0.14\ \mathrm{psi/ft}).\\ \rho_L &= 40\ \mathrm{lb/cft\ at\ flowing\ conditions.}\\ \rho_G &= 2.0\ \mathrm{lb/cft\ at\ flowing\ conditions.}\end{aligned}$$

So following the step-by-step approach outlined above:

1. Calculate the $(\Delta P/L)_{fric}$ for each phase:
   These were given as 2.00 and 20.1 lb/ft^2/ft depth for liquid and gas phases, respectively.
2. Calculate the X modulus

$$\begin{aligned}X &= \left[(\Delta P/L)_{fric,L}/(\Delta P/L)_{fric,G}\right]^{0.5}\\ &= (2.00/20.1)^{0.5} = 0.315.\end{aligned}$$

3. Calculate the frictional two-phase pressure drop

$$\begin{aligned}(\Delta P/L)_{fric,2_\phi} &= \left[(\Delta P/L)_{fric,L} + (\Delta P/L)_{fric,G}\right]\left[10^{(0.416/(\mathrm{Sq(logX)}+0.666)}\right]\\ &= [(2.00) + (20.1)]\left[10^{(0.416/(\mathrm{Sq(log(0.315))}+0.666)}\right]\\ &= (22.01)\left(10^{0.453}\right) = 62.5\ \mathrm{lb/ft^2/ft\ depth}(0.43\ \mathrm{psi/ft}).\end{aligned}$$

4. Calculate the liquid saturation factor, S

$$\begin{aligned}\mathrm{S} &= 10^{(-0.774+0.525\mathrm{logX}-0.109\mathrm{Sq(logX)})}\\ &= 10^{(-0.774+0.525\mathrm{log}(0.315)-0.109\mathrm{Sq(log(0.315))})}\\ &= 10^{-1.065} = 0.0861.\end{aligned}$$

5. Calculate the flowing mixture density at operating conditions

$$\begin{aligned}\rho_{mix} &= \rho_L S + \rho_G(1 - S)\\ &= 40\ \mathrm{lb/cft}(0.0861) + 2.00\ \mathrm{lb/cft}(1 - 0.0861)\\ &= 5.3\ \mathrm{lb/cft}.\end{aligned}$$

6. Adjust the pressure drop for density of the mixture

$$
\begin{aligned}
(\Delta P/L)_{total,2\phi} &= (\Delta P/L)_{fric,2\phi} - / + \rho_{mix} \\
&= 62.5 - 5.3 = 57.2\ \text{lb/ft}^2/\text{ft depth}(0.40\ \text{psi/ft}).
\end{aligned}
$$

This is a feasible order of magnitude. If the dP per foot was, say, 10 psi or 0.001 psi per foot, these extremes would not be credible for a two-phase system. Practical pressure drops are normally in the 0.1–2.0 psi/ft range. If you get an answer far outside the normal range, check your work and, if it is correct, consider a different vessel/reactor diameter or a different particle size or shape.

The dP per foot is multiplied by the total feet of bed depth to get the final overall dP for the bed.

Estimating Overall Pressure Drop in Beds

In practice, the total pressure drop through a reactor or sorbent bed includes more than just the bed pressure drop itself. For a commercial fixed bed, total dP includes drop generated by the hardware or internals of the reactor. For a typical downflow reactor (see Fig. 59), for instance, the internals include:

- Inlet diffuser or distributor – you can normally assume about 1 psi for this element at full rate and the dP will vary with rates and phase properties.
- Distribution tray (for two phases) – you can assume another 1 psi for this tray at design conditions; again, the dP will vary depending on conditions.
- Quench zones (if required), including bed support grid, mixing system, and redistribution tray – assume 2–4 psi per zone at design rate; again, the dP will vary depending on conditions.
- Outlet collector (elephant stool) – assume 1 psi at design rates.

In addition to the internals, the overall bed dP will be affected by fouling from coke, corrosion products, dust, etc.. i.e., accumulation of solids in the interstitial spaces, thus reducing the void fraction. In design, a typical fouling allowance ranges from 20 % to 100 % of the frictional pressure drop in a bed. Alternately, you can assume a certain loss of void fraction (say 20 %) from start of run to end of run and recalculate the frictional dP for the bed to get the fouled bed dP.

To illustrate how the bed design pressure drop is estimated, consider the following case. Say:

- You have a two bed reactor with two-phase flow.
- The overall bed dPs, clean, are:
  - Bed 1–20 psi
  - Bed 2–35 psi

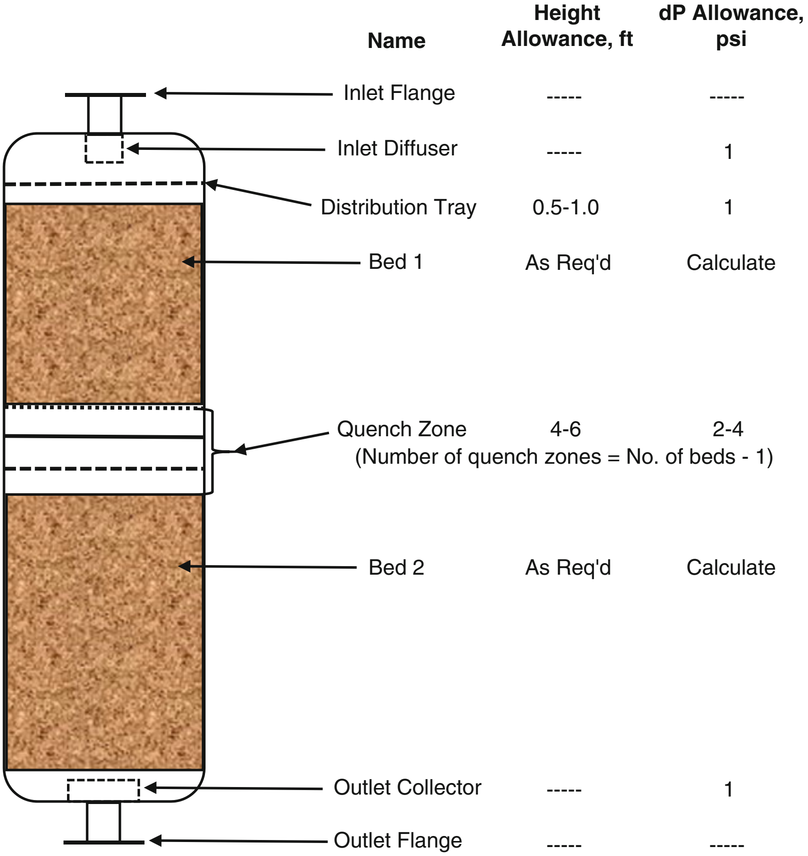


Fig. 59 Typical internals in a two-bed, downflow reactor

These would have been calculated using average vapor and liquid flows, densities, and viscosities in each bed and would include the effects of fluid head.

- The reactor inlet pressure is 627 psig.
- What is the pressure profile in this reactor on an end-of-run design basis?

Solution:

1. Assume a fouling allowance of 50 % dP increase in bed 1 and 20 % increase in bed 2.

2. The reactor will have:
   - One inlet diffuser (assume 1 psi)
   - One top distribution tray (assume 1 psi)
   - One quench zone (assume 2 psi)
   - One outlet collector (assume 1 psi)
3. Set up a table for the pressure profile:

	dP, psi	Psig after element
Inlet to reactor	–	**627 (inlet flange)**
Inlet diffuser	1	626
Top distribution tray	1	625
Bed 1		
Clean bed dP	20	
Fouling (allow 50 %)	10	
Total bed 1	30	595
Quench zone	2	593
Bed 2		
Clean bed dP	35	
Fouling (allow 20 %)	7	
Total bed 2	42	551
Outlet collector	1	550
Overall reactor	**77**	**550 (outlet flange)**

Moving Solids Bed Pressure Drops

Moving solids beds are typically found in fluid catalytic crackers, ebullated and bubbling bed reactors, and certain other solids handling systems in a refinery or petroleum processing facility. The details of pressure drop estimates in these services are beyond the scope of this book. Many of the best methods for dealing with the moving bed dPs are proprietary and are used for design by technology licensors.

One good available reference on these calculations is the book: Hydrodynamics of Gas-Solids Fluidization by Cheremisinoff and Cheremisinoff (1984).

Appendices

Appendix 1: Chord Height, Area, and Length for Distillation Trays and Circular Cross-Sections

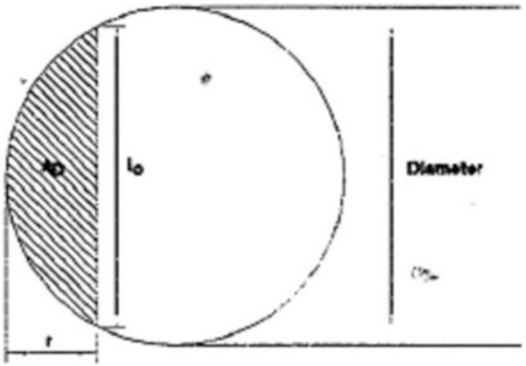
See Table 38.

Table 38 Chord height, area, and length for distillation trays and circular cross-sections

Weir length and downcomer area																	
R*	L*	A*	R*	L*	A*	R*	L*	A*	R*	L*	A*	R*	L*	A*	R*	L*	A*
0.070	0.511	0.306	0.120	0.650	0.680	0.170	0.751	0.113	0.220	0.828	0.163	0.280	$	0.230	0.390	0.977	0.361
1	0.514	0.0315	1	0.652	0.0688	1	0.753	0.114	1	0.829	0.164	5	0.903	0.236	6	0.979	0.367
2	0.517	0.0321	2	0.654	0.0697	2	0.755	0.115	2	0.831	0.165						
3	0.521	0.0328	3	0.657	0.0705	3	0.756	0.116	3	0.832	0.166	0.290	0.908	0.241	0.400	0.980	0.374
4	0.524	0.0335	4	0.659	0.0714	4	0.758	0.117	4	0.834	0.157	5	0.913	0.247	5	0.982	0.380
5	0.527	0.0342	5	0.661	0.722	5	0.760	0.117	5	0.835	0.169	0.300	0.917	0.252	0.410	0.984	0.386
6	0.530	0.0348	6	0.663	0.0731	6	0.762	0.118	6	0.836	0.170	5	0.921	0.258	6	0.986	0.392
7	0.533	0.0355	7	0.665	0.0739	7	0.763	0.119	7	0.838	0.171						
8	0.536	0.0362	8	0.668	0.0748	8	0.765	0.120	8	0.839	0.172	0.310	0.925	0.264	0.420	0.967	0.398
9	0.539	0.0368	9	0.670	0.0756	9	0.766	0.122	9	0.841	0.173	5	0.930	0.2780	5	0.969	0.405
0.080	0.542	0.0375	0.130	0.672	0.0765	0.180	0.768	0.122	0.230	0.842	0.174	0.320	0.933	0.276	0.430	0.991	0.412
1	0.545	0.0382	1	0.674	0.0774	1	0.770	0.123	1	0.843	0.175	5	0.937	0.282	5	0.993	0.418
2	0.548	0.0389	2	0.677	0.0782	2	0.772	0.124	2	0.845	0.176						
3	0.552	0.0396	3	0.679	0.0791	3	0.773	0.125	3	0.846	0.177	0.330	0.941	0.288	0.440	0.994	0.424
4	0.555	0.0403	4	0.682	0.0799	4	0.775	0.126	4	0.848	0.178	5	0.945	0.294	5	995	0.430
5	0.558	0.0410	5	0.684	0.0808	5	0.777	0.127	5	0.849	0.179	0.340	0.948	0.300	0.450	0.996	0.437
6	0.551	0.0418	6	0.686	0.0817	6	0.778	0.128	6	0.850	0.180	5	0.951	0.306			
7	0.554	0.0425	7	0.688	0.0825	7	0.780	0.129	7	0.851	0.181				0.460	0.997	0.450
8	0.567	0.0432	8	0.691	0.0834	8	0.781	0.130	8	0.853	0.182	0.350	0.955	0.312			
9	0.570	0.0439	9	0.693	0.0842	9	0.783	0.131	9	0.854	0.183	5	0.958	0.318	0.470	0.998	0.462
0.090	0.573	0.0446	0.140	0.695	0.0851	0.190	0.784	0.132	0.240	0.855	0.184	0.360	0.961	0.324	0.480	0.998	0.475
1	0.576	0.0454	1	0.697	0.0860	1	0.785	0.133	5	0.860	0.190	5	0.964	0.330			
2	0.578	0.0461	2	0.699	0.0869	2	0.787	0.134							0.490	0.999	0.488
3	0.581	0.0469	3	0.700	0.0878	3	0.789	0.135	0.250	0.866	0.196	0.370	0.967	0.337			
4	0.583	0.0476	4	0.702	0.0887	4	0.790	0.136	5	0.872	0.202	5	0.969	0.343	0.500	1.0	0.50
5	0.586	0.0484	5	0.704	0.0896	5	0.782	0.137	0.260	0.878	0.207	0.380	0.971	0.348			
6	0.589	0.0491	6	0.706	0.0905	6	0.794	0.138	5	0.583	0.213	5	0.977	0.354			

7	0.592	0.0499	7	0.708	0.0914	7	0.795	0.139									
8	0.594	0.0506	8	0.710	0.0923	8	0.797	0.140	0.270	0.888	0.218						
9	0.597	0.0514	9	0.712	0.0932	9	0.798	0.141	5	0.893	224						
0.100	0.600	0.0521	0.150	0.714	0.0941	0.200	0.800	0.142									
1	0.603	0.0529	1	0.716	0.0950	1	802	0.143									
2	0.605	0.0537	2	0.718	0.0959	2	0.803	0.144									
3	0.608	0.0645	3	0.720	0.0969	3	0.805	0.145									
4	0.610	0.0553	4	0.722	0.0978	4	0.806	0.146									
5	0.613	0.0551	5	0.724	0.0987	5	0.808	0.148									
6	0.615	0.0568	6	0.726	0.0996	6	0.809	0.149									
7	0.618	0.0576	7	0.728	0.1005	7	0.810	0.150									
8	0.620	0.0584	8	0.729	0.1015	8	0.812	0.151									
9	0.623	0.0592	9	0.731	0.102	9	0.813	0.152									
0.110	0.625	0.0600	0.160	0.733	0.103	0.210	0.814	0.153									
1	0.628	0.0608	1	0.735	0.104	1	0.816	0.154									
2	0.630	0.0616	2	0.737	0.105	2	0.817	0.155									
3	0.633	0.0624	3	0.738	0.106	3	0.819	0.156									
4	0.635	0.0632	4	0.740	0.107	4	0.820	0.157									
5	0.638	0.0640	5	0.742	0.108	5	0.822	0.158									
6	0.640	0.0648	6	0.744	0.109	6	0.823	0.159									
7	0.043	0.0656	7	0.746	0.110	7	0.824	0.160									
8	0.645	0.0654	6	0.747	0.111	8	0.826	0.161									
9	0.648	0.0672	9	0.749	0.112	9	0.627	0.162									
$R = \frac{*\text{Downcomer Rise}}{\text{Diameter}} = \frac{r}{\text{Dia.}}$						$L = \frac{*\text{Wetr Length}}{\text{Diameter}} = \frac{lo}{\text{Dia.}}$						$A = \frac{*\text{Downcomer Area}}{\text{Tower Area}} = \frac{A_O}{A_S}$					

*This table relates the downcomer area, the weir length, and the height of the circular segment formed by the weir



Appendix 2: Valve Tray Design Details

Valve tray design principles			
Design feature	Suggested value	Alternate values	Comment
1. Valve size and layout			
(a) Value diameter	–		Valve diameter is fined by die vendor
(b) Percent hole area. A_u/A_n	12	8–15	Open area should be set by the designer. In general, the lower and open area, the higher the efficiency and flexibility, and the lower the capacity (due to increased pressure drop). At values of open area toward the upper end of the range (say 15 %), the flexibility and efficiency are approaching sieve tray values. At the lower end of the range, capacity and downcomer filling becomes limited
(c) Valve pitch/diam. ratio	–		Value pitch is normally triangular. However, this variable is usually fixed by the vendor
(d) Valve distribution		–	On trays with flow path length $\geq 5'$ and for liquid rates $>$5,000 GPH/ft (diameter) on trays with flow path length $<5'$, provide 10 % more valves on the inlet half of the tray than on the outlet half
(e) Bubble area. A_u	–		Bubble area should be maximized
(f) Plate efficiency	–		Valve tray efficiency will be about equal to sieve tray efficiency provided there is not a blowing or flooding limitation
(g) Valve blanking	–		This should not generally be necessary unless tower is being sized for future service at much higher rates. Blanking strips can then be used. Blank within buddle area, not around periphery to maintain best efficiency

(*continued*)

Valve tray design principles			
Design feature	Suggested value	Alternate values	Comment
2. Tray spacing, inches	–	12–36	Generally economic to use min. Values given on p. III-E-2 which are set by maintenance requirements. Other considerations are downcomer filling and flexibility. Use of variable spacings to accommodate loading changes from section to section should be considered
3. Number of liquid passes	11	to 2 M	Multi-passing improves liquid handling capacity at the expense of vapor capacity for a given diameter column and tray spacing. Cost is apparently no greater – at least, for tower diameters <8 ft
4. Downcomers and weirs			
(a) Allowable downcomer inlet velocity. ft/s of clear liq.		0.3–0.4	Lower value recommended for absorbers or other systems of known high frothiness
(b) Type downcomer	Chord	Chord. arc	Min. chord length should be 65 % of tray diameter for good liquid distribution. Sloped downcomers can be used for high liquid rates – with maximum outlet velocity =0.6 ft/s. Arc downcomers may be used alternatively to give more bubble area (and higher capacity) but are somewhat more expensive. Min. width should be 6 in. for latter
(c) Inboard downcomer width (inlet and outlet)		Min. 8 in.	Use of a 14–16″ "jump baffle" suspended lengthwise in the center of the inboard downcomer and extending the length of the downcomer is suggested to prevent possible bridging over by froth entering the downcomer form opposite sides. Elevation of the base of jump baffle should be level with outlet weirs. Internal accessway must be provided to allow passage from one side to another during inspection

(*continued*)

Valve tray design principles

Design feature	Suggested value	Alternate values	Comment
(d) Outlet weir height	2″	1–4″	Weir height can be varied with liquid rate to give a total liquid head on the tray (h_g) in the range of 2.5–4″ whenever possible. Lower values suggested for vacuum towers, higher ones for long residence time applications
(e) Clearance under downcomer, in.	1.5″	1″ min	Set clearance to give head loss of approximately 1 in. Higher values can be used if necessary to assure sealing of downcomer
(f) Downcorner seal (inlet or outlet weir height minus downcomer clearance)	Use outlet weir to give min.1/2”seal in plate liquid	Inlet weir or recessed inlet box	In most cases, plate liquid level can be made high enough to seal the downcomer through use of outlet weir only. Inlet weirs add to downcomer buildup; in some cases, they may be desirable for 2-pass trays to ensure equal liquid distribution. Recessed inlets are more expensive but may be necessary in cases where an operating seal would require an excessively high outlet weir
(g) Downcomer filling, % of tray spacing		40–50	Use the lower value for high-pressure towers, absorbers, vacuum towers, known foaming systems, and also for tray spacings of 18″ or lower

Appendix 3: Pressure-Temperature Curves for Hydrocarbon Equilibria

See Figs. 60 and 61.

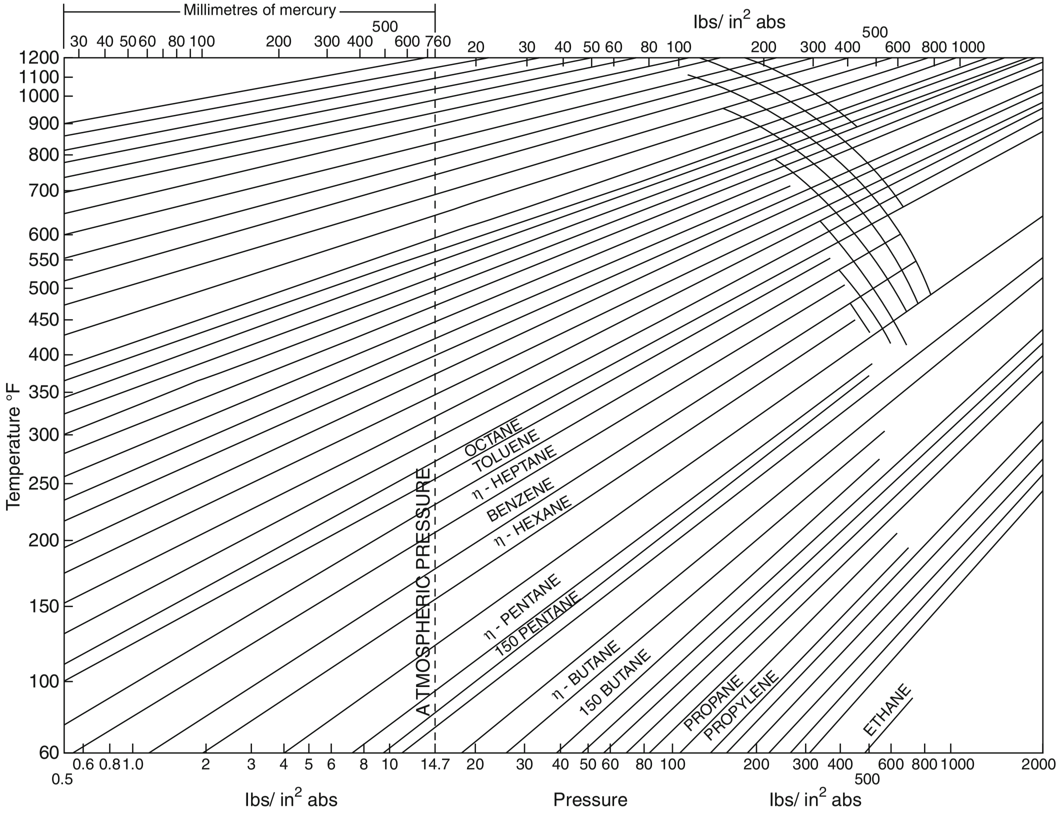


Fig. 60 Pressure-temperature curves for hydrocarbon equilibria (chart 1 of 2)

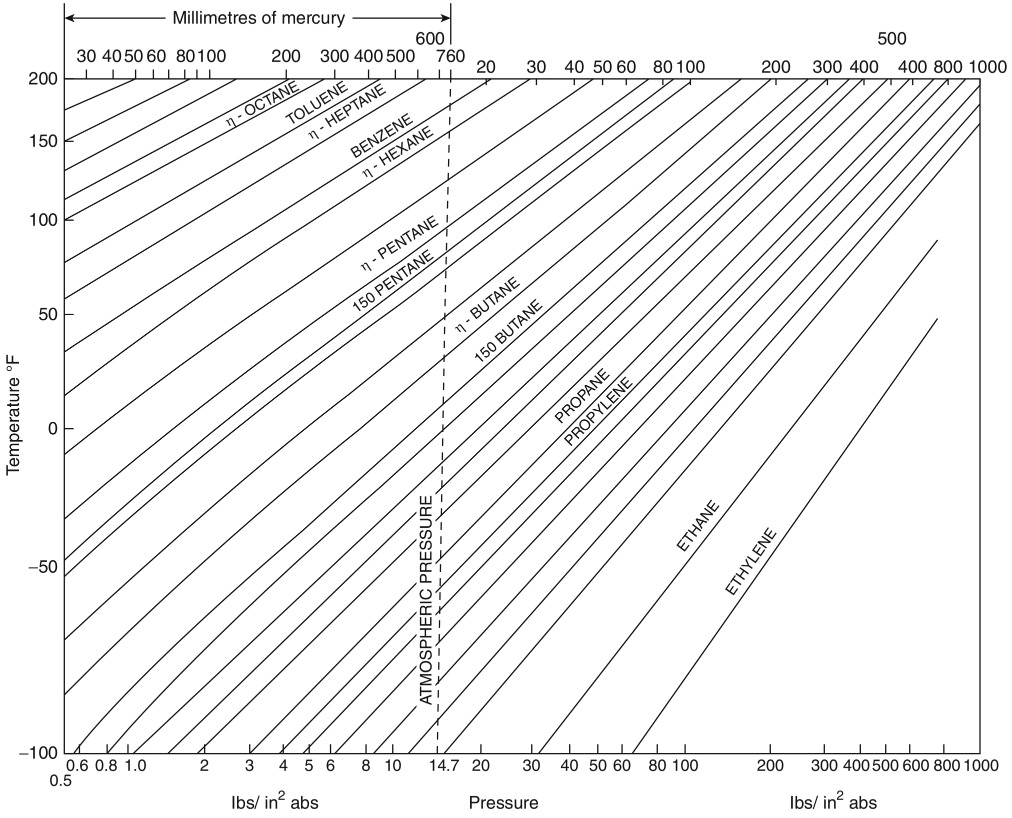
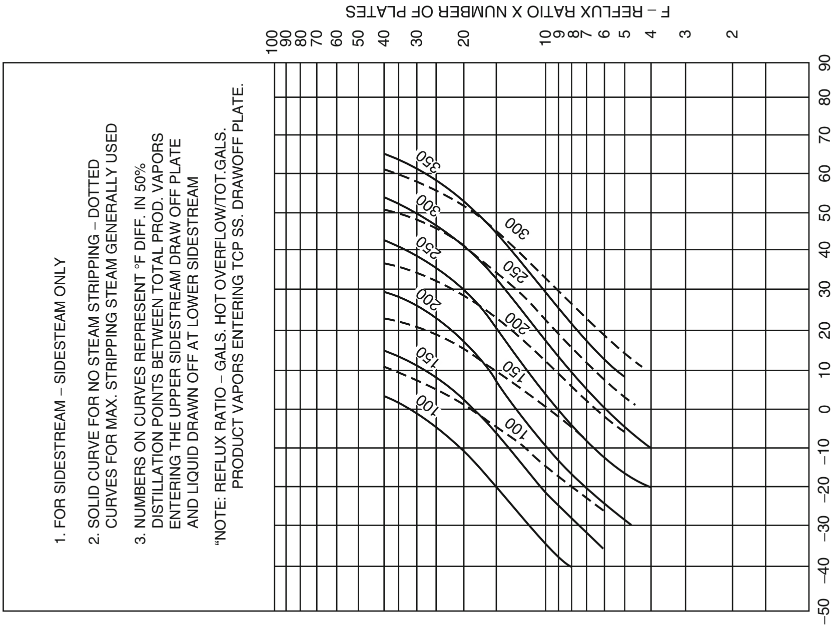
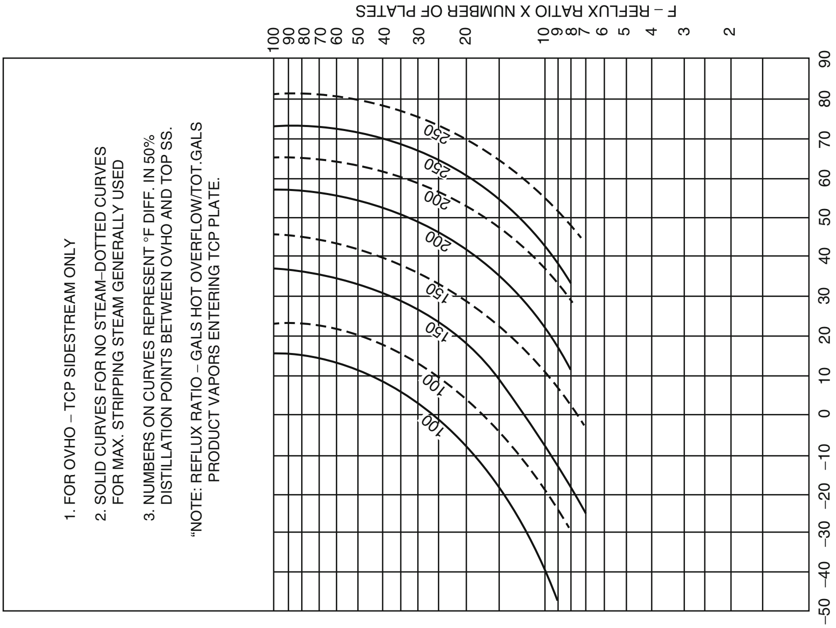


Fig. 61 Pressure-temperature curves for hydrocarbon equilibria (chart 2 or 2)

Appendix 4: ASTM Gaps and Overlaps



Fractionation Curves for Sidestream to Sidestream Poroducts.



Fractionation Curves for Overhead to Top Sidestream Poroducts.

Appendix 5: Values of Coefficient C for Various Materials

Values of coefficient $C = 520\sqrt{k\left(\frac{2}{k+1}\right)^{\frac{k+1}{k-1}}}; k = \frac{C_p}{C_v}$

k	C	k	C	k	C	k	C	k	C	k	C
0.41	219.28	0.71	276.09	1.01	316.56[a]	1.31	347.91	1.61	373.32	1.91	394.56
0.42	221.59	0.72	277.64	1.02	317.74	1.32	348.84	1.62	374.09	1.92	395.21
0.43	223.86	0.73	279.18	1.03	318.90	1.33	349.77	1.63	374.85	1.93	395.86
0.44	226.10	0.74	280.70	1.04	320.05	1.34	350.68	1.64	375.61	1.94	396.50
0.45	228.30	0.75	282.20	1.05	321.19	1.35	351.60	1.65	376.37	1.95	397.14
0.46	230.47	0.76	283.69	1.06	322.32	1.36	352.50	1.66	377.12	1.96	397.78
0.47	232.61	0.77	285.16	1.07	323.44	1.37	353.40	1.67	377.86	1.97	398.41
0.48	234.71	0.78	286.62	1.08	324.55	1.38	354.29	1.68	378.61	1.98	399.05
0.49	236.78	0.79	288.07	1.09	325.65	1.39	355.18	1.69	379.34	1.99	399.67
0.50	238.83	0.80	289.49	1.10	326.75	1.40	356.06	1.70	380.08	2.00	400.30
0.51	240.84	0.81	290.91	1.11	327.83	1.41	356.94	1.71	380.80	2.01	400.92
0.52	242.82	0.82	292.31	1.12	328.91	1.42	357.81	1.72	381.53	2.02	401.53
0.53	244.78	0.83	293.70	1.13	329.98	1.43	358.67	1.73	382.25	2.03	402.15
0.54	246.72	0.84	295.07	1.14	331.04	1.44	359.53	1.74	382.97	2.04	402.76
0.55	248.62	0.85	296.43	1.15	332.09	1.45	360.38	1.75	383.68	2.05	403.37
0.56	250.50	0.86	297.78	1.16	333.14	1.46	361.23	1.76	384.39	2.06	403.97
0.57	252.36	0.87	299.11	1.17	334.17	1.47	362.07	1.77	385.09	2.07	404.58
0.58	254.19	0.88	300.43	1.18	335.20	1.48	362.91	1.78	385.79	2.08	405.18
0.59	256.00	0.89	301.74	1.19	336.22	1.49	363.74	1.79	386.49	2.09	405.77
0.60	257.79	0.90	303.04	1.20	337.24	1.50	364.56	1.80	387.18	2.10	406.37
0.61	259.55	0.91	304.33	1.21	338.24	1.51	365.39	1.81	387.87	2.11	406.96
0.62	261.29	0.92	305.60	1.22	339.24	1.52	366.20	1.82	388.56	2.12	407.55
0.63	263.01	0.93	306.86	1.23	340.23	1.53	367.01	1.83	389.24	2.13	408.13
0.64	264.72	0.94	308.11	1.24	341.22	1.54	367.82	1.84	389.92	2.14	408.71
0.65	266.40	0.95	309.35	1.25	342.19	1.55	368.62	1.85	390.59	2.15	409.29
0.66	268.06	0.96	310.58	1.26	343.16	1.56	369.41	1.86	391.26	2.16	409.87
0.67	269.70	0.97	311.80	1.27	344.13	1.57	370.21	1.87	391.93	2.17	410.44
0.68	271.33	0.98	313.01	1.28	345.08	1.58	370.99	1.88	392.59	2.18	411.01
0.69	272.93	0.99	314.19a	1.29	346.03	1.59	371.77	1.89	393.25	2.19	411.58
0.70	274.52	1.00	315.38a	1.30	346.98	1.60	372.55	1.90	393.91	2.20	412.15

Values of C for gases

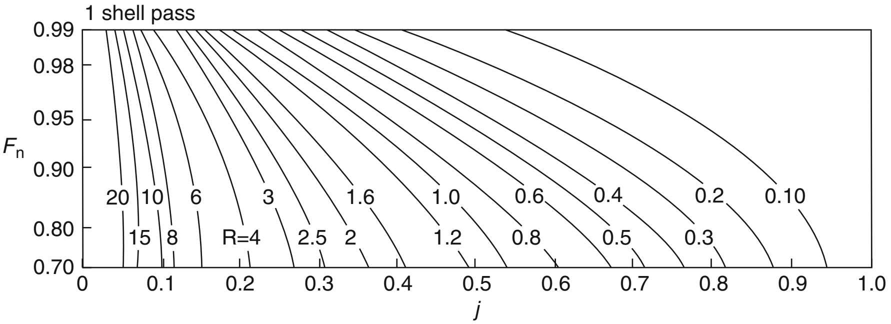
	Mol	k =				Mol	k =		
	wt	C_p/ C_v	C	C/ 356		wt	C_p/C_v	C	C/356
Acetylene	26	1.28	345	0.969	Hydrochloric acid	36.5	1.40	356	1.000
Air	29	1.40	356	1.000	Hydrogen	2	1.40	356	1.000
Ammonia	17	1.33	351	0.986	Hydrogen sulfide	34	1.32	348	0.978
Argon	40	1.66	377	1.059	Isobutane	58	1.11	328	0.921

(*continued*)

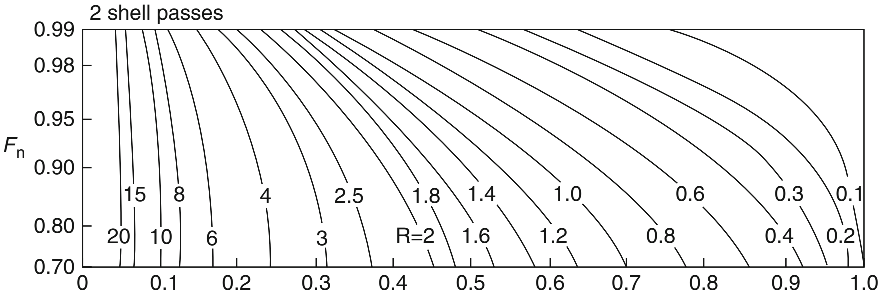
Benzene	78	1.10	327	0.919	Methane	16	1.30	346	0.972
Carbon disulfide	76	1.21	338	0.949	Methyl alcohol	32	1.20	337	0.947
Carbon dioxide	44	1.28	345	0.969	Methyl chloride	50.5	1.20	337	0.947
Carbon monoxide	28	1.40	356	1.000	N-butane	58	1.11	328	0.921
Chlorine	71	1.36	352	0.989	Natural gas	19	1.27	345	0.969
Cyclohexane	84	1.08	324	0.910	Nitrogen	28	1.40	356	1.000
Ethane	30	1.22	339	0.952	Oxygen	32	1.40	356	1.000
Ethylene	28	1.20	337	0.947	Pentane	72	1.09	325	0.913
Helium	4	1.66	377	1.059	Propane	44	1.14	331	0.930
Hexane	86	1.08	324	0.910	Sulfur dioxide	64	1.26	342.	0.961

[a] Interpolated values, since C becomes indeterminate as k approaches 1.00 (Reproduced by permission of Gas Processors Suppliers Association)

Appendix 6: LMTD Correction Factors



$$R = \frac{T_1 - T_2}{t_2 - t_1} \qquad j = \frac{t_2 - t_1}{T_1 - t_2}$$



Appendix 7: Common Overall Heat Transfer Coefficients – U_O

Fluid being cooled	Fluid being heated	$\frac{U_0}{(\text{BTU/h.ft}^2.^\circ\text{F})}$
Exchangers		
C_4s and lighter	Water	75–110
C_4s and lighter	LPG	75
Naphtha	Naphtha	75
Naphtha	Water	80–100
BPT 450 (kero)	Heavy oil (crude)	70–75
Gas oils	Crude	40–50
Gas oils	Water	40–70
Light fuel oil	Crude	20–30
Waxy distillates	Heavy oils	30–40
Slurries	Waxy distillate	40
MEA or DEA	Water	140
MEA or DEA	MEA or DEA	120–130
Water	Water	180–200
Air	Water	20–30
Lt HC vapor	H_2-rich stream	35–40
Lt HC vapor	Naphtha	38
Condensers		
Full-range naphtha	Water	70–80
Amine stripper O/heads	Water	100
C_4s and lighter	Water	90
Reformer effluent (Lt HC)	Water	65

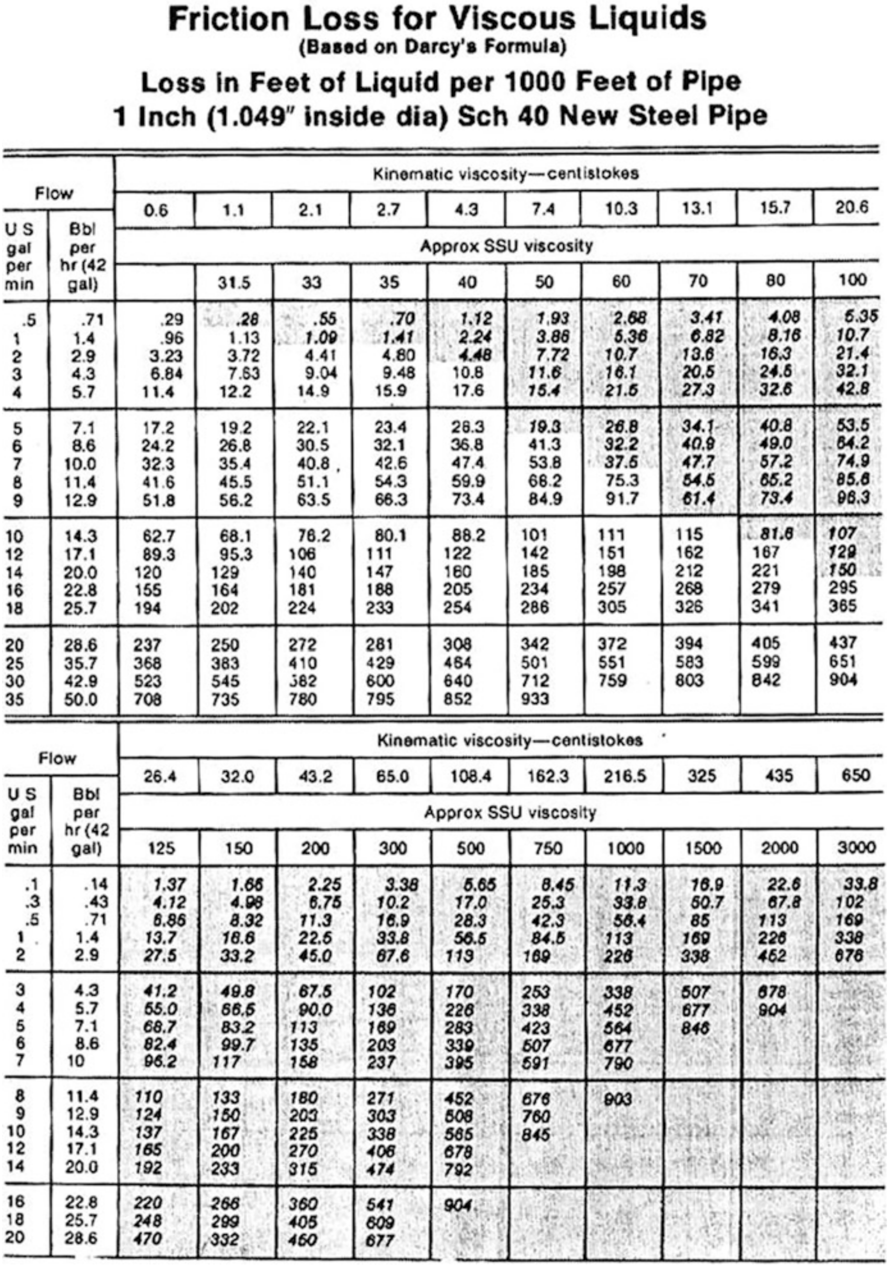
Appendix 8: Standard Heat Exchanger Tube Data

d_0 = OD of tubing (in.)	BWG gauge	l = thickness (ft)	d_i = ID of tubing (in.)	Internal area (in.^{2})	External surface per foot length (ft^2)
$\frac{3}{4}$	10	0.0112	0.482	0.1822	0.1963
$\frac{3}{4}$	12	0.00908	0.532	0.223	0.1963
$\frac{3}{4}$	14	0.00691	0.584	0.268	0.1963
$\frac{3}{4}$	16	0.00542	0.620	0.302	0.1963
$\frac{3}{4}$	18	0.00408	0.652	0.334	0.1963
1	8	0.0137	0.670	0.355	0.2618
1	10	0.0112	0.732	0.421	0.2618
1	12	0.00908	0.782	0.479	0.2618
1	14	0.00691	0.834	0.546	0.2618
1	16	0.00542	0.870	0.594	0.2618
1	18	0.00408	0.902	0.639	0.2618
$1\frac{1}{2}$	10	0.0112	1.232	1.192	0.3927
$1\frac{1}{2}$	12	0.00908	1.282	1.291	0.3927
$1\frac{1}{2}$	14	0.00691	1.334	1.397	0.3927
$1\frac{1}{2}$	16	0.00542	1.37	1.474	0.3927

Appendix 9: Line Friction Loss for Viscous Fluids

See Tables 39, 40, 41, 42, 43, 44, 45, 46, and 47.

Table 39 Line friction loss



Friction Loss for Viscous Liquids

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
1 Inch (1.049″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		0.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
		Approx SSU viscosity									
US gal per min	Bbl per hr (42 gal)		31.5	33	35	40	50	60	70	80	100
.5	.71	.29	*.28*	.55	*.70*	*1.12*	*1.93*	*2.68*	*3.41*	*4.08*	*5.35*
1	1.4	.96	1.13	*1.09*	*1.41*	*2.24*	*3.86*	*5.36*	*6.82*	*8.16*	*10.7*
2	2.9	3.23	3.72	4.41	4.80	*4.48*	*7.72*	*10.7*	*13.6*	*16.3*	*21.4*
3	4.3	6.84	7.63	9.04	9.48	10.8	*11.6*	*16.1*	*20.5*	*24.5*	*32.1*
4	5.7	11.4	12.2	14.9	15.9	17.6	*15.4*	*21.5*	*27.3*	*32.6*	*42.8*
5	7.1	17.2	19.2	22.1	23.4	28.3	*19.3*	*26.8*	*34.1*	*40.8*	*53.5*
6	8.6	24.2	26.8	30.5	32.1	36.8	41.3	*32.2*	*40.9*	*49.0*	*64.2*
7	10.0	32.3	35.4	40.8	42.6	47.4	53.8	*37.5*	*47.7*	*57.2*	*74.9*
8	11.4	41.6	45.5	51.1	54.3	59.9	68.2	75.3	*54.5*	*65.2*	*85.6*
9	12.9	51.8	56.2	63.5	66.3	73.4	84.9	91.7	*61.4*	*73.4*	*96.3*
10	14.3	62.7	68.1	76.2	80.1	88.2	101	111	115	*81.6*	*107*
12	17.1	89.3	95.3	106	111	122	142	151	162	167	*129*
14	20.0	120	129	140	147	160	185	198	212	221	*150*
16	22.8	155	164	181	188	205	234	257	268	279	295
18	25.7	194	202	224	233	254	286	305	326	341	365
20	28.6	237	250	272	281	308	342	372	394	405	437
25	35.7	368	383	410	429	464	501	551	583	599	651
30	42.9	523	545	582	600	640	712	759	803	842	904
35	50.0	708	735	780	795	852	933				

Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
		Approx SSU viscosity									
US gal per min	Bbl per hr (42 gal)	125	150	200	300	500	750	1000	1500	2000	3000
.1	.14	*1.37*	*1.66*	*2.25*	*3.38*	*5.65*	*8.45*	*11.3*	*16.9*	*22.6*	*33.8*
.3	.43	*4.12*	*4.98*	*6.75*	*10.2*	*17.0*	*25.3*	*33.8*	*50.7*	*67.8*	*102*
.5	.71	*6.86*	*8.32*	*11.3*	*16.9*	*28.3*	*42.3*	*56.4*	*85*	*113*	*169*
1	1.4	*13.7*	*16.6*	*22.5*	*33.8*	*56.5*	*84.5*	*113*	*169*	*226*	*338*
2	2.9	*27.5*	*33.2*	*45.0*	*67.6*	*113*	*169*	*226*	*338*	*452*	*676*
3	4.3	*41.2*	*49.8*	*67.5*	*102*	*170*	*253*	*338*	*507*	*678*	
4	5.7	*55.0*	*66.5*	*90.0*	*136*	*226*	*338*	*452*	*677*	*904*	
5	7.1	*68.7*	*83.2*	*113*	*169*	*283*	*423*	*564*	*846*		
6	8.6	*82.4*	*99.7*	*135*	*203*	*339*	*507*	*677*			
7	10	*96.2*	*117*	*158*	*237*	*395*	*591*	*790*			
8	11.4	*110*	*133*	*180*	*271*	*452*	*676*	*903*			
9	12.9	*124*	*150*	*203*	*303*	*508*	*760*				
10	14.3	*137*	*167*	*225*	*338*	*565*	*845*				
12	17.1	*165*	*200*	*270*	*406*	*678*					
14	20.0	*192*	*233*	*315*	*474*	*792*					
16	22.8	*220*	*266*	*360*	*541*	*904*					
18	25.7	*248*	*299*	*405*	*609*						
20	28.6	*470*	*332*	*450*	*677*						

Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe

1½ Inch (1.610″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		0.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
US gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
1	1.4	.13	*.10*	*.20*	*.25*	*.41*	*.69*	*.97*	*1.23*	*1.47*	*1.93*
2	2.9	.42	.49	*.39*	*.51*	*.83*	*1.39*	*1.93*	*2.46*	*2.94*	*3.86*
3	4.3	.86	.98	1.17	1.25	*1.24*	*2.08*	*2.89*	*3.68*	*4.41*	*5.79*
4	5.7	1.43	1.63	1.92	2.07	*1.65*	*2.78*	*3.86*	*4.91*	*5.88*	*7.72*
5	7.1	2.11	2.42	2.83	3.05	*2.06*	*3.47*	*4.82*	*6.14*	*7.35*	*9.65*
6	8.6	2.90	3.36	3.89	4.18	4.69	*4.17*	*5.79*	*7.37*	*8.82*	*11.6*
8	11.4	4.97	5.60	6.44	6.87	7.77	9.02	*7.72*	*9.83*	*11.8*	*15.5*
10	14.3	7.51	8.34	9.58	10.1	11.6	13.2	*9.65*	*12.3*	*14.7*	*19.3*
12	17.1	10.4	11.6	13.4	14.0	15.6	17.9	19.8	*14.7*	*17.6*	*23.2*
15	21.4	16.0	17.4	19.6	20.7	23.2	26.5	29.1	31.1	*21.0*	*29.0*
20	28.6	27.2	29.5	32.9	34.6	38.2	43.9	47.6	51.1	53.8	*38.6*
25	35.7	41.4	44.8	49.5	51.8	57.5	64.6	70.1	75.2	78.9	84.7
30	42.9	58.8	63.0	69.1	72.0	79.0	89.3	97.1	103	109	116.5
40	57.1	102	107	117	122	132	150	160	170	178	191
50	71.4	157	164	176	183	198	222	237	251	263	281
60	85.7	224	233	249	259	279	306	330	347	362	388
70	100	300	312	333	343	369	402	436	457	477	508
80	114	389	403	427	440	470	516	551	580	602	643
90	129	498	508	536	550	585	634	681	715	746	792
100	143	601	624	656	670	714	774	820	863	898	949

Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
US gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
1	1.4	*2.47*	*3.00*	*4.14*	*6.09*	*10.2*	*15.2*	*20.3*	*30.4*	*40.8*	*69.0*
2	2.9	*4.95*	*6.00*	*8.28*	*12.2*	*20.3*	*30.4*	*40.6*	*60.8*	*81.5*	*122*
3	4.3	*7.42*	*9.00*	*12.4*	*18.3*	*30.4*	*45.6*	*60.9*	*91.3*	*122*	*183*
4	5.7	*9.90*	*12.0*	*16.6*	*24.4*	*40.6*	*60.8*	*81.2*	*122*	*163*	*244*
5	7.1	*12.4*	*15.0*	*20.7*	*30.4*	*50.7*	*76.0*	*102*	*152*	*204*	*304*
6	8.6	*14.9*	*18.0*	*24.8*	*36.5*	*60.8*	*91.2*	*122*	*183*	*244*	*365*
8	11.4	*19.8*	*24.0*	*33.1*	*48.7*	*81.2*	*122*	*163*	*243*	*326*	*487*
10	14.3	*24.7*	*30.0*	*41.4*	*60.9*	*102*	*152*	*203*	*304*	*408*	*609*
12	17.1	*29.7*	*36.0*	*49.7*	*73.2*	*122*	*182*	*244*	*365*	*490*	*732*
15	21.4	*37.1*	*45.0*	*62.2*	*91.4*	*152*	*228*	*304*	*457*	*612*	*914*
20	28.6	*49.5*	*60.0*	*82.8*	*122*	*203*	*304*	*406*	*608*	*815*	
25	35.7	*61.9*	*75.0*	*103*	*152*	*254*	*380*	*507*	*760*		
30	42.9	124	*90.0*	*124*	*183*	*304*	*456*	*609*	*913*		
40	57.1	204	216	*166*	*244*	*406*	*608*	*812*			
50	71.4	302	317	342	*304*	*507*	*760*				

Table 40 Line friction loss

Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
2 Inch (2.067″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
U S gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
1	1.4	.04	*.04*	*.07*	*.09*	*.15*	*.26*	*.36*	*.45*	*.54*	*.71*
2	2.9	.13	.15	*.16*	*.19*	*.30*	*.51*	*.71*	*.90*	*1.08*	*1.42*
4	5.7	.43	.50	.58	.63	*.59*	*1.02*	*1.42*	*1.81*	*2.17*	*2.84*
6	8.6	.87	1.00	1.20	1.27	1.46	*1.53*	*2.13*	*2.71*	*3.25*	*4.26*
8	11.4	1.47	1.68	1.97	2.13	2.38	*2.04*	*2.84*	*3.61*	*4.33*	*5.68*
10	14.3	2.20	2.55	2.90	3.09	3.52	*2.56*	*3.56*	*4.52*	*5.42*	*7.11*
12	17.1	3.06	3.46	3.97	4.23	4.78	5.57	*4.27*	*5.43*	*6.51*	*8.53*
14	20.0	4.07	4.51	5.22	5.51	6.26	7.28	*4.98*	*6.33*	*7.59*	*9.96*
16	22.8	5.17	5.79	6.65	7.01	7.92	9.16	9.95	*7.23*	*8.67*	*11.4*
18	25.7	6.44	7.16	8.18	8.63	9.67	11.2	12.6	13.1	*9.76*	*12.8*
20	28.6	7.82	8.64	9.77	10.4	11.6	13.5	14.8	15.5	*10.8*	*14.2*
25	35.7	11.9	13.0	14.7	15.4	17.2	19.9	21.6	22.8	24.1	*17.8*
30	42.9	17.0	18.2	20.4	21.5	23.8	27.2	29.9	31.2	33.0	35.6
35	50.0	22.3	24.1	27.0	28.2	31.2	35.6	38.6	40.4	43.4	47.3
40	57.1	28.8	31.0	34.2	36.0	39.6	44.6	48.8	52.9	54.1	60.7
50	71.4	44.1	47.2	52.0	54.0	59.2	66.4	72.0	76.9	78.4	86.2
60	85.7	62.7	66.5	72.2	74.2	82.3	91.8	98.6	105	111	119
70	100	84.1	83.5	95.8	99.4	108	120	130	137	145	156
80	114	109	114	123	127	138	154	166	174	182	195
90	129	137	143	154	158	171	192	204	215	225	239
100	143	167	176	188	193	208	230	244	260	269	289
110	157	202	211	225	231	246	275	290	307	319	335
120	171	238	249	265	273	290	321	341	358	375	396
130	186	277	290	307	316	335	372	392	411	432	459
140	200	320	347	352	364	383	424	449	472	491	521
150	214	366	382	403	415	437	479	510	529	553	586
160	228	414	431	457	469	494	536	572	595	621	659
170	243	467	485	513	522	553	601	639	665	694	729
180	257	524	543	572	583	619	665	714	743	767	804
190	271	584	602	634	649	688	733	792	825	846	884
200	286	643	666	699	716	756	808	851	901	927	977
210	300	709	731	768	786	826	880	935	975		
220	314	778	798	838	858	902	958				
230	328	851	873	912	934	982					
240	343	922	945	988							

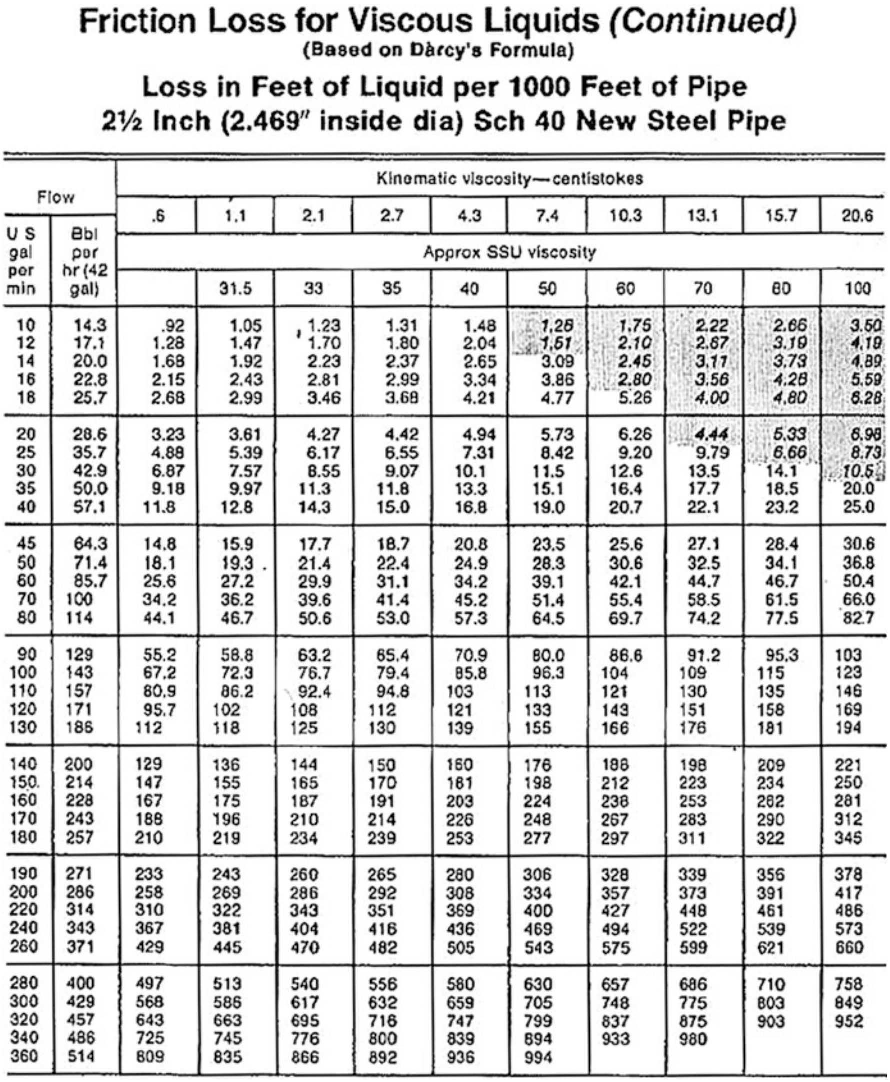
Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
2 Inch (2.067″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
US gal per min	Bbl per hr (42 gal)	26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
		Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
1	1.4	*.91*	*1.10*	*1.49*	*2.24*	*3.74*	*6.60*	*7.48*	*11.2*	*15.0*	*22.4*
2	2.9	*1.82*	*2.21*	*2.98*	*4.48*	*7.49*	*11.2*	*15.0*	*22.4*	*30.0*	*44.9*
3	4.3	*2.73*	*3.31*	*4.47*	*6.73*	*11.2*	*16.8*	*22.4*	*33.0*	*45.0*	*67.4*
4	5.7	*3.64*	*4.42*	*5.96*	*8.98*	*15.4*	*22.4*	*29.9*	*44.8*	*60.0*	*89.9*
5	7.1	*4.56*	*5.52*	*7.45*	*11.2*	*18.7*	*28.0*	*37.4*	*56.0*	*75.0*	*112*
6	8.6	*5.47*	*6.63*	*8.95*	*13.5*	*22.5*	*33.6*	*44.8*	*67.2*	*90.0*	*135*
7	10.0	*6.38*	*7.73*	*10.4*	*15.7*	*26.2*	*39.2*	*52.3*	*78.4*	*105*	*157*
8	11.4	*7.29*	*8.84*	*11.9*	*18.0*	*30.0*	*34.8*	*59.8*	*89.6*	*120*	*180*
9	12.9	*8.20*	*9.94*	*13.4*	*20.2*	*33.7*	*50.4*	*67.3*	*101*	*135*	*202*
10	14.3	*9.11*	*11.0*	*14.9*	*22.4*	*37.4*	*56.0*	*74.8*	*112*	*150*	*224*
12	17.1	*10.9*	*13.3*	*18.9*	*26.9*	*44.9*	*67.3*	*89.7*	*135*	*180*	*269*
14	20.0	*12.7*	*15.5*	*20.9*	*31.4*	*52.4*	*78.4*	*105*	*157*	*210*	*314*
16	22.8	*14.6*	*17.7*	*23.9*	*35.9*	*59.9*	*89.6*	*120*	*179*	*240*	*359*
18	25.7	*16.4*	*19.9*	*26.8*	*40.3*	*67.4*	*101*	*135*	*202*	*270*	*404*
20	28.6	*18.2*	*22.1*	*29.8*	*44.9*	*74.9*	*112*	*150*	*224*	*300*	*449*
25	35.7	*22.8*	*27.6*	*37.3*	*56.1*	*93.6*	*140*	*187*	*280*	*375*	*562*
30	42.9	*27.3*	*33.1*	*44.7*	*67.3*	*112*	*168*	*224*	*336*	*450*	*674*
35	50.0	*31.9*	*38.7*	*52.2*	*78.5*	*131*	*196*	*262*	*392*	*525*	*786*
40	57.1	63.0	*44.2*	*59.6*	*89.8*	*150*	*224*	*299*	*448*	*600*	*899*
45	64.3	70.8	80.2	*67.1*	*101*	*168*	*252*	*336*	*503*	*675*	
50	71.4	92.8	97.1	*74.5*	*112*	*187*	*280*	*374*	*560*	*750*	
60	85.7	127	134	146	*135*	*225*	*336*	*448*	*672*	*900*	
70	100	162	176	189	*157*	*262*	*392*	*523*	*784*		
80	114	208	219	238	*180*	*300*	*448*	*598*	*896*		
90	129	257	270	293	327	*337*	*504*	*673*			
100	143	309	322	352	388	*374*	*560*	*748*			
110	157	364	379	412	465	*412*	*617*	*823*			
120	171	423	445	463	537	*449*	*673*	*898*			
130	186	487	510	549	618	*487*	*728*				
140	200	548	580	627	703	*524*	*784*				
150	214	622	655	705	792	909	*840*				
160	228	697	737	792	887		*896*				
170	243	775	808	882			*952*				
180	257	858	871	962							
190	271	947	986								

Table 41 Line friction loss



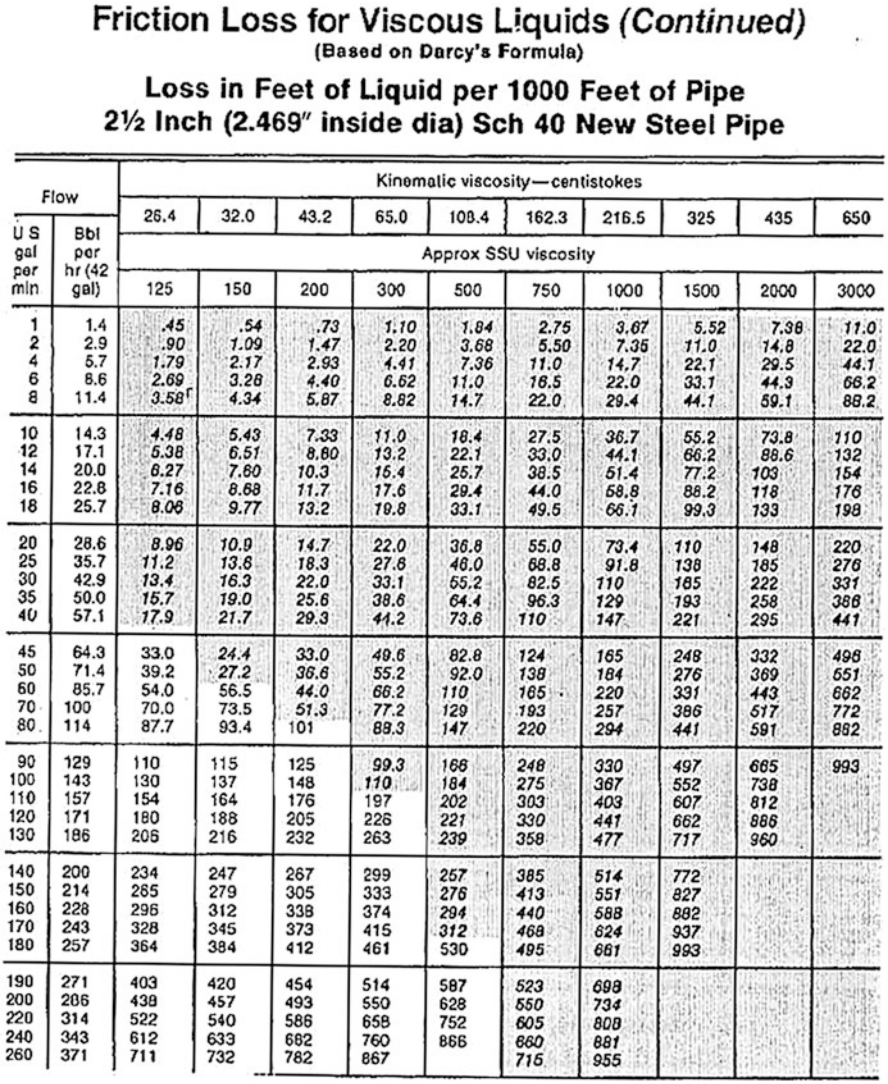
Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe

2½ Inch (2.469″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
		Approx SSU viscosity									
US gal per min	Bbl per hr (42 gal)		31.5	33	35	40	50	60	70	80	100
10	14.3	.92	1.05	1.23	1.31	1.48	*1.26*	*1.75*	*2.22*	*2.66*	*3.50*
12	17.1	1.28	1.47	1.70	1.80	2.04	*1.61*	*2.10*	*2.67*	*3.19*	*4.19*
14	20.0	1.68	1.92	2.23	2.37	2.65	3.09	*2.45*	*3.11*	*3.73*	*4.89*
16	22.8	2.15	2.43	2.81	2.99	3.34	3.86	*2.80*	*3.56*	*4.28*	*5.59*
18	25.7	2.68	2.99	3.46	3.68	4.21	4.77	5.26	*4.00*	*4.80*	*6.28*
20	28.6	3.23	3.61	4.27	4.42	4.94	5.73	6.26	*4.44*	*5.33*	*6.98*
25	35.7	4.88	5.39	6.17	6.55	7.31	8.42	9.20	9.79	*6.66*	*8.73*
30	42.9	6.87	7.57	8.55	9.07	10.1	11.5	12.6	13.5	14.1	*10.5*
35	50.0	9.18	9.97	11.3	11.8	13.3	15.1	16.4	17.7	18.5	20.0
40	57.1	11.8	12.8	14.3	15.0	16.8	19.0	20.7	22.1	23.2	25.0
45	64.3	14.8	15.9	17.7	18.7	20.8	23.5	25.6	27.1	28.4	30.6
50	71.4	18.1	19.3	21.4	22.4	24.9	28.3	30.6	32.5	34.1	36.8
60	85.7	25.6	27.2	29.9	31.1	34.2	39.1	42.1	44.7	46.7	50.4
70	100	34.2	36.2	39.6	41.4	45.2	51.4	55.4	58.5	61.5	66.0
80	114	44.1	46.7	50.6	53.0	57.3	64.5	69.7	74.2	77.5	82.7
90	129	55.2	58.8	63.2	65.4	70.9	80.0	86.6	91.2	95.3	103
100	143	67.2	72.3	76.7	79.4	85.8	96.3	104	109	115	123
110	157	80.9	86.2	92.4	94.8	103	113	121	130	135	146
120	171	95.7	102	108	112	121	133	143	151	158	169
130	186	112	118	125	130	139	155	166	176	181	194
140	200	129	136	144	150	160	176	186	198	209	221
150	214	147	155	165	170	181	198	212	223	234	250
160	228	167	175	187	191	203	224	238	253	262	281
170	243	188	196	210	214	226	248	267	283	290	312
180	257	210	219	234	239	253	277	297	311	322	345
190	271	233	243	260	265	280	306	328	339	356	378
200	286	258	269	286	292	308	334	357	373	391	417
220	314	310	322	343	351	369	400	427	448	461	486
240	343	367	381	404	416	436	469	494	522	539	573
260	371	429	445	470	482	505	543	575	599	621	660
280	400	497	513	540	556	580	630	657	686	710	758
300	429	568	586	617	632	659	705	748	775	803	849
320	457	643	663	695	716	747	799	837	875	903	952
340	486	725	745	776	800	839	894	933	980		
360	514	809	835	866	892	936	994				



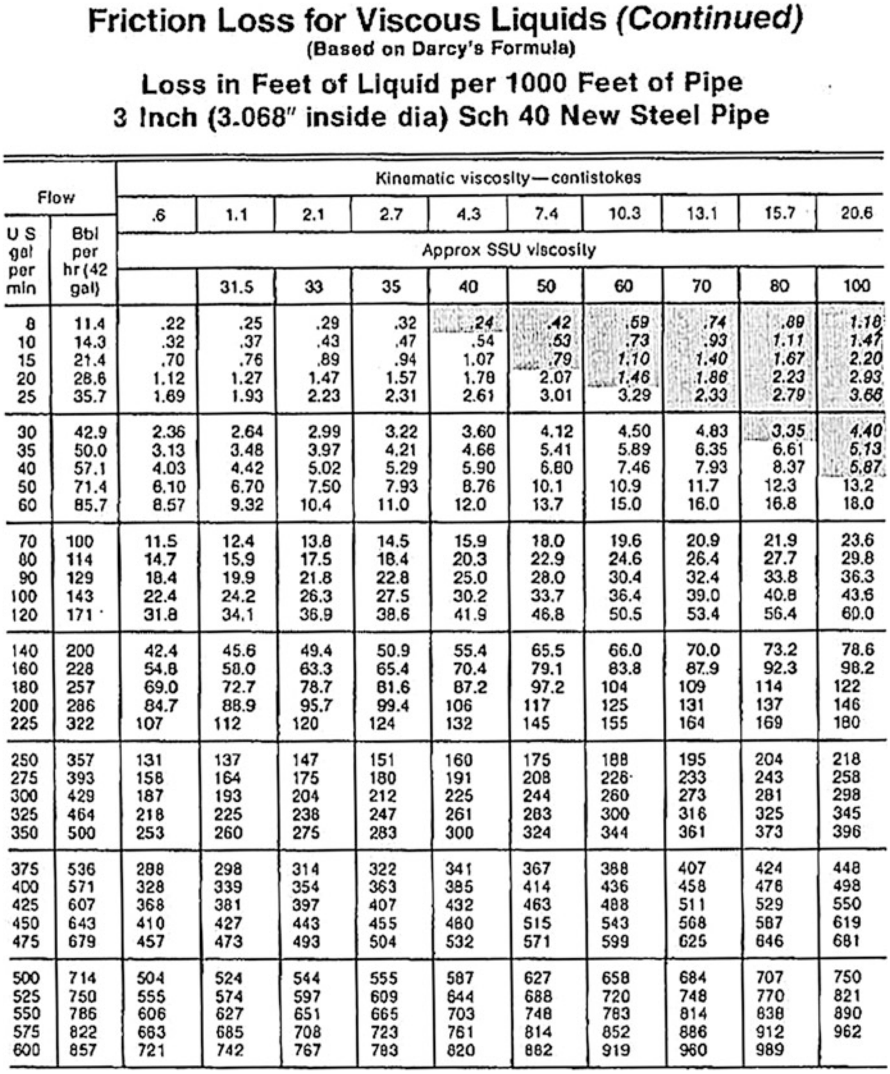
Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
2½ Inch (2.469″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
US gal per min	Bbl per hr (42 gal)	26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
		Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
1	1.4	*.45*	*.54*	*.73*	*1.10*	*1.84*	*2.75*	*3.67*	*5.52*	*7.38*	*11.0*
2	2.9	*.90*	*1.09*	*1.47*	*2.20*	*3.68*	*5.50*	*7.35*	*11.0*	*14.8*	*22.0*
4	5.7	*1.79*	*2.17*	*2.93*	*4.41*	*7.36*	*11.0*	*14.7*	*22.1*	*29.5*	*44.1*
6	8.6	*2.69*	*3.28*	*4.40*	*6.62*	*11.0*	*16.5*	*22.0*	*33.1*	*44.3*	*66.2*
8	11.4	*3.58*	*4.34*	*5.87*	*8.82*	*14.7*	*22.0*	*29.4*	*44.1*	*59.1*	*88.2*
10	14.3	*4.48*	*5.43*	*7.33*	*11.0*	*18.4*	*27.5*	*36.7*	*55.2*	*73.8*	*110*
12	17.1	*5.38*	*6.51*	*8.80*	*13.2*	*22.1*	*33.0*	*44.1*	*66.2*	*88.6*	*132*
14	20.0	*6.27*	*7.60*	*10.3*	*15.4*	*25.7*	*38.5*	*51.4*	*77.2*	*103*	*154*
16	22.8	*7.16*	*8.68*	*11.7*	*17.6*	*29.4*	*44.0*	*58.8*	*88.2*	*118*	*176*
18	25.7	*8.06*	*9.77*	*13.2*	*19.8*	*33.1*	*49.5*	*66.1*	*99.3*	*133*	*198*
20	28.6	*8.96*	*10.9*	*14.7*	*22.0*	*36.8*	*55.0*	*73.4*	*110*	*148*	*220*
25	35.7	*11.2*	*13.6*	*18.3*	*27.6*	*46.0*	*68.8*	*91.8*	*138*	*185*	*276*
30	42.9	*13.4*	*16.3*	*22.0*	*33.1*	*55.2*	*82.5*	*110*	*165*	*222*	*331*
35	50.0	*15.7*	*19.0*	*25.6*	*38.6*	*64.4*	*96.3*	*129*	*193*	*258*	*386*
40	57.1	*17.9*	*21.7*	*29.3*	*44.2*	*73.6*	*110*	*147*	*221*	*295*	*441*
45	64.3	33.0	*24.4*	*33.0*	*49.6*	*82.8*	*124*	*165*	*248*	*332*	*496*
50	71.4	39.2	*27.2*	*36.6*	*55.2*	*92.0*	*138*	*184*	*276*	*369*	*551*
60	85.7	54.0	56.5	*44.0*	*66.2*	*110*	*165*	*220*	*331*	*443*	*662*
70	100	70.0	73.5	*51.3*	*77.2*	*129*	*193*	*257*	*386*	*517*	*772*
80	114	87.7	93.4	101	*88.3*	*147*	*220*	*294*	*441*	*591*	*882*
90	129	110	115	125	*99.3*	*166*	*248*	*330*	*497*	*665*	*993*
100	143	130	137	148	*110*	*184*	*275*	*367*	*552*	*738*	
110	157	154	164	176	197	*202*	*303*	*403*	*607*	*812*	
120	171	180	188	205	226	*221*	*330*	*441*	*662*	*886*	
130	186	206	216	232	263	*239*	*358*	*477*	*717*	*960*	
140	200	234	247	267	299	*257*	*385*	*514*	*772*		
150	214	265	279	305	333	*276*	*413*	*551*	*827*		
160	228	296	312	338	374	*294*	*440*	*588*	*882*		
170	243	328	345	373	415	*312*	*468*	*624*	*937*		
180	257	364	384	412	461	530	*495*	*661*	*993*		
190	271	403	420	454	514	587	*523*	*698*			
200	286	438	457	493	550	628	*550*	*734*			
220	314	522	540	586	658	752	*605*	*808*			
240	343	612	633	682	760	866	*660*	*881*			
260	371	711	732	782	867		*715*	*955*			

Table 42 Line friction loss



Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
3 Inch (3.068″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
U S gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
8	11.4	.22	.25	.29	.32	*.24*	*.42*	*.59*	*.74*	*.89*	*1.18*
10	14.3	.32	.37	.43	.47	.54	*.53*	*.73*	*.93*	*1.11*	*1.47*
15	21.4	.70	.76	.89	.94	1.07	*.79*	*1.10*	*1.40*	*1.67*	*2.20*
20	28.6	1.12	1.27	1.47	1.57	1.78	2.07	*1.46*	*1.86*	*2.23*	*2.93*
25	35.7	1.69	1.93	2.23	2.31	2.61	3.01	3.29	*2.33*	*2.79*	*3.66*
30	42.9	2.36	2.64	2.99	3.22	3.60	4.12	4.50	4.83	*3.35*	*4.40*
35	50.0	3.13	3.48	3.97	4.21	4.66	5.41	5.89	6.35	6.61	*5.13*
40	57.1	4.03	4.42	5.02	5.29	5.90	6.80	7.46	7.93	8.37	*5.87*
50	71.4	6.10	6.70	7.50	7.93	8.76	10.1	10.9	11.7	12.3	13.2
60	85.7	8.57	9.32	10.4	11.0	12.0	13.7	15.0	16.0	16.8	18.0
70	100	11.5	12.4	13.8	14.5	15.9	18.0	19.6	20.9	21.9	23.6
80	114	14.7	15.9	17.5	18.4	20.3	22.9	24.6	26.4	27.7	29.8
90	129	18.4	19.9	21.8	22.8	25.0	28.0	30.4	32.4	33.8	36.3
100	143	22.4	24.2	26.3	27.5	30.2	33.7	36.4	39.0	40.8	43.6
120	171	31.8	34.1	36.9	38.6	41.9	46.8	50.5	53.4	56.4	60.0
140	200	42.4	45.6	49.4	50.9	55.4	65.5	66.0	70.0	73.2	78.6
160	228	54.8	58.0	63.3	65.4	70.4	79.1	83.8	87.9	92.3	98.2
180	257	69.0	72.7	78.7	81.6	87.2	97.2	104	109	114	122
200	286	84.7	88.9	95.7	99.4	106	117	125	131	137	146
225	322	107	112	120	124	132	145	155	164	169	180
250	357	131	137	147	151	160	175	188	195	204	218
275	393	158	164	175	180	191	208	226	233	243	258
300	429	187	193	204	212	225	244	260	273	281	298
325	464	218	225	238	247	261	283	300	316	325	345
350	500	253	260	275	283	300	324	344	361	373	396
375	536	288	298	314	322	341	367	388	407	424	448
400	571	328	339	354	363	385	414	436	458	476	498
425	607	368	381	397	407	432	463	488	511	529	550
450	643	410	427	443	455	480	515	543	568	587	619
475	679	457	473	493	504	532	571	599	625	646	681
500	714	504	524	544	555	587	627	658	684	707	750
525	750	555	574	597	609	644	688	720	748	770	821
550	786	606	627	651	665	703	748	783	814	838	890
575	822	663	685	708	723	761	814	852	886	912	962
600	857	721	742	767	783	820	882	919	960	989	

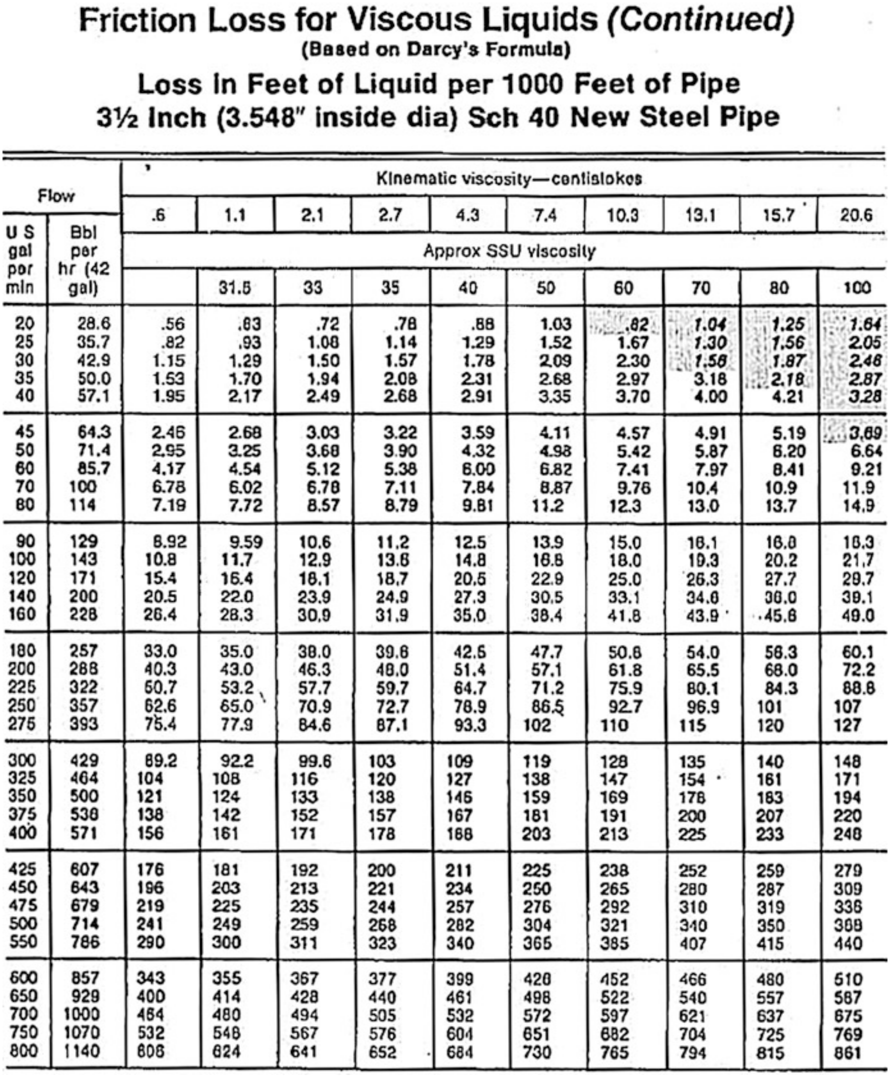
Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
3 Inch (3.068″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
U S gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
4	5.7	.75	.91	1.23	1.85	3.08	4.62	6.16	9.25	12.4	18.5
6	8.6	1.13	1.37	1.84	2.77	4.62	6.92	9.24	13.9	18.5	27.7
8	11.4	1.50	1.82	2.45	3.70	6.16	9.23	12.3	18.5	24.7	36.9
10	14.3	1.88	2.28	3.06	4.62	7.70	11.5	15.4	23.1	30.9	46.2
12	17.1	2.25	2.73	3.68	5.55	9.24	13.8	18.5	27.7	37.1	55.5
14	20.0	2.63	3.18	4.29	6.47	10.8	16.2	21.5	32.3	43.3	64.7
16	22.8	3.00	3.64	4.90	7.39	12.3	18.5	24.6	37.0	49.5	73.9
18	25.7	3.38	4.09	5.52	8.31	13.9	20.8	27.7	41.6	55.6	83.2
20	28.6	3.76	4.55	6.13	9.24	15.4	23.1	30.8	46.2	61.8	92.4
25	35.7	4.69	5.69	7.67	11.5	19.3	28.8	38.5	57.7	77.3	116
30	42.9	5.63	6.83	9.20	13.9	23.1	34.6	46.2	69.3	92.7	139
35	50.0	6.57	7.97	10.7	16.2	27.0	40.3	53.8	80.9	108	162
40	51.1	7.61	9.10	12.3	18.5	30.8	46.2	61.6	92.5	124	185
50	71.4	9.39	11.4	15.3	23.1	38.5	57.7	77.0	116	154	231
60	85.7	19.2	13.7	18.4	27.7	46.2	69.2	92.4	139	185	277
70	100	25.3	26.8	21.6	32.3	53.9	80.8	108	162	216	323
80	114	31.6	33.6	24.7	37.0	61.6	92.3	123	185	247	369
90	129	38.9	40.9	44.6	41.6	69.3	104	139	208	278	416
100	143	46.1	49.5	53.0	46.2	77.0	115	154	231	309	462
120	171	64.0	67.6	72.9	55.5	92.4	138	185	277	371	555
140	200	83.9	89.1	94.9	108	108	162	215	323	433	647
160	228	106	111	120	135	123	185	246	370	495	739
180	257	131	137	148	164	139	208	277	416	556	832
200	286	157	163	179	198	154	231	308	462	618	924
225	322	191	204	223	242	279	260	346	520	698	
250	357	229	242	261	291	332	288	385	577	773	
275	393	271	285	311	343	396	317	423	636	850	
300	429	316	331	361	398	456	346	462	693	927	
325	464	364	381	416	458	527	375	500	751		
350	500	415	436	467	523	593	672	538	809		
375	536	469	493	528	586	672	746	577	867		
400	571	526	550	592	656	751	843	616	925		
425	607	587	612	656	728	834	937	654	982		
450	643	652	675	728	802	928					
475	679	718	744	801	689						

Table 43 Line friction loss



Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss In Feet of Liquid per 1000 Feet of Pipe

3½ Inch (3.548″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
US gal per min	Bbl per hr (42 gal)	.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
		Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
20	28.6	.56	.63	.72	.78	.88	1.03	.82	*1.04*	*1.25*	*1.64*
25	35.7	.82	.93	1.08	1.14	1.29	1.52	1.67	*1.30*	*1.56*	*2.05*
30	42.9	1.15	1.29	1.50	1.57	1.78	2.09	2.30	*1.56*	*1.87*	*2.46*
35	50.0	1.53	1.70	1.94	2.08	2.31	2.68	2.97	3.18	*2.18*	*2.87*
40	57.1	1.95	2.17	2.49	2.68	2.91	3.35	3.70	4.00	4.21	*3.28*
45	64.3	2.46	2.68	3.03	3.22	3.59	4.11	4.57	4.91	5.19	*3.69*
50	71.4	2.95	3.25	3.68	3.90	4.32	4.98	5.42	5.87	6.20	6.64
60	85.7	4.17	4.54	5.12	5.38	6.00	6.82	7.41	7.97	8.41	9.21
70	100	6.78	6.02	6.78	7.11	7.84	8.87	9.76	10.4	10.9	11.9
80	114	7.19	7.72	8.57	8.79	9.81	11.2	12.3	13.0	13.7	14.9
90	129	8.92	9.59	10.6	11.2	12.5	13.9	15.0	16.1	16.8	18.3
100	143	10.8	11.7	12.9	13.6	14.8	16.8	18.0	19.3	20.2	21.7
120	171	15.4	16.4	18.1	18.7	20.5	22.9	25.0	26.3	27.7	29.7
140	200	20.5	22.0	23.9	24.9	27.3	30.5	33.1	34.6	36.0	39.1
160	228	26.4	28.3	30.9	31.9	35.0	38.4	41.8	43.9	45.6	49.0
180	257	33.0	35.0	38.0	39.6	42.5	47.7	50.6	54.0	58.3	60.1
200	288	40.3	43.0	46.3	48.0	51.4	57.1	61.8	65.5	68.0	72.2
225	322	50.7	53.2	57.7	59.7	64.7	71.2	75.9	80.1	84.3	88.8
250	357	62.6	65.0	70.9	72.7	78.9	86.5	92.7	96.9	101	107
275	393	75.4	77.9	84.6	87.1	93.3	102	110	115	120	127
300	429	89.2	92.2	99.6	103	109	119	128	135	140	148
325	464	104	108	116	120	127	138	147	154	161	171
350	500	121	124	133	138	146	159	169	178	183	194
375	538	138	142	152	157	167	181	191	200	207	220
400	571	156	161	171	178	188	203	213	225	233	248
425	607	176	181	192	200	211	225	238	252	259	279
450	643	196	203	213	221	234	250	265	280	287	309
475	679	219	225	235	244	257	276	292	310	319	336
500	714	241	249	259	268	282	304	321	340	350	388
550	786	290	300	311	323	340	365	385	407	415	440
600	857	343	355	367	377	399	428	452	466	480	510
650	929	400	414	428	440	461	498	522	540	557	587
700	1000	464	480	494	505	532	572	597	621	637	675
750	1070	532	548	567	576	604	651	682	704	725	769
800	1140	606	624	641	652	684	730	765	794	815	861

Friction Loss for Viscous Liquids *(Continued)*

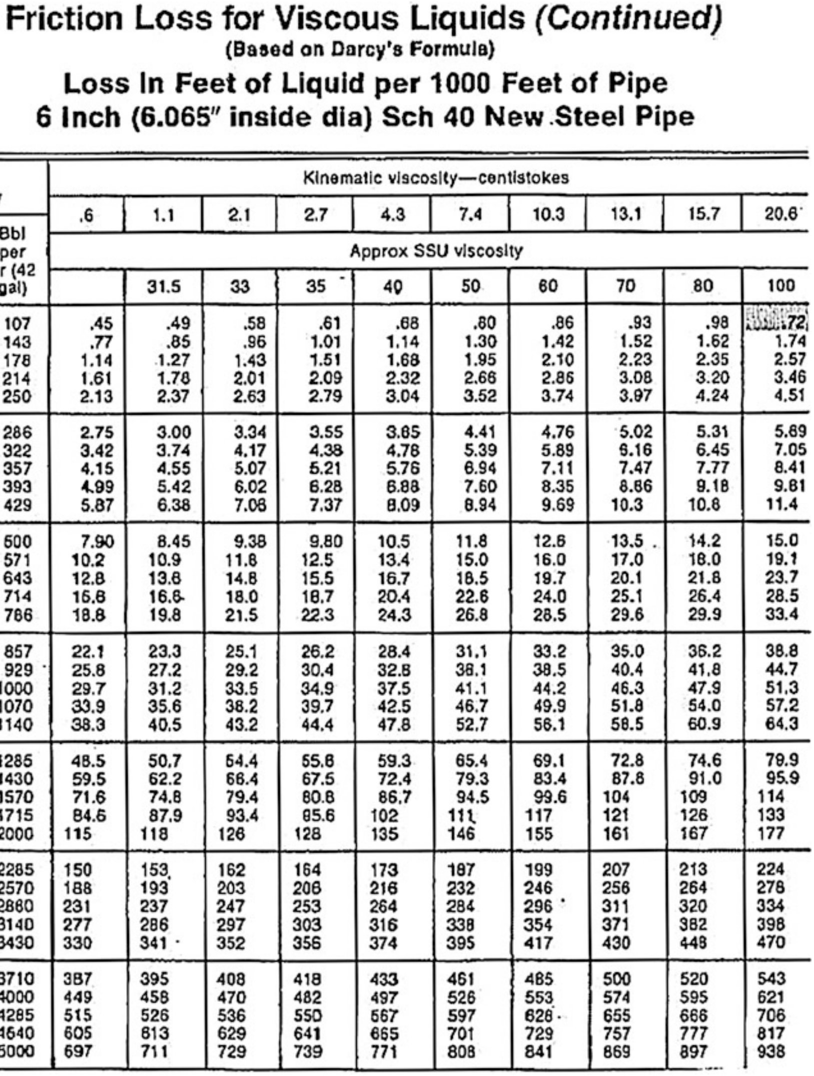
(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe

3½ Inch (3.548″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
U S gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
10	14.3	1.05	1.27	1.72	2.58	4.32	6.46	8.62	12.9	16.9	25.8
15	21.4	1.57	1.91	2.58	3.88	6.47	9.68	12.9	19.4	25.4	38.8
20	28.6	2.10	2.54	3.44	5.17	8.63	12.9	17.3	25.8	33.8	51.7
25	35.7	2.62	3.18	4.29	6.47	10.8	16.1	21.6	32.3	42.3	64.7
30	42.9	3.15	3.82	5.15	7.78	13.0	19.4	25.9	38.8	50.7	77.6
35	50.0	3.67	4.45	6.01	9.05	15.1	22.6	30.2	45.3	59.2	90.6
40	57.1	4.20	5.09	6.87	10.3	17.3	25.8	34.5	51.7	67.6	103
45	64.3	4.72	5.73	7.73	11.6	19.4	29.0	38.8	58.2	76.1	116
50	71.4	5.25	6.36	8.59	12.9	21.6	32.3	43.1	64.7	84.5	129
60	85.7	6.30	7.64	10.3	15.5	25.9	38.8	51.8	77.6	101	155
70	100	12.8	8.91	12.0	18.1	30.2	45.2	60.4	90.6	118	181
80	114	16.1	16.9	13.7	20.7	34.5	51.6	69.0	103	135	207
90	129	19.6	20.8	15.5	23.3	38.8	58.1	77.6	116	152	233
100	143	23.6	24.8	17.2	25.9	43.2	64.6	86.2	129	169	258
120	171	31.9	34.0	37.1	31.0	51.8	77.5	104	155	203	310
140	200	41.5	43.8	48.2	36.2	60.4	90.4	121	181	236	362
160	228	52.3	55.3	60.5	67.7	69.1	103	138	207	270	413
180	257	64.6	67.3	73.9	83.4	77.7	116	155	233	304	466
200	286	77.3	81.5	87.9	99.9	86.3	129	173	258	338	517
225	322	94.4	99.8	108	122	97.1	145	194	291	380	520
250	357	114	120	129	146	108	161	210	323	422	647
275	393	134	141	153	172	199	177	237	356	465	711
300	429	157	164	178	198	233	194	259	388	507	776
325	464	181	188	205	227	266	210	280	420	549	840
350	500	206	215	233	258	301	226	302	452	592	906
375	536	234	245	262	291	339	242	323	485	634	970
400	571	261	274	291	326	379	423	345	517	676	
425	607	291	303	325	363	419	473	367	550	718	
450	643	322	337	359	402	462	525	388	582	761	
475	679	353	368	395	440	505	572	410	614	803	
500	714	389	403	433	482	551	626	431	647	845	
550	786	459	481	514	566	648	733	795	712	930	
600	857	538	566	600	658	749	851	923	776		
650	929	620	648	690	755	865	978		841		
700	1000	708	735	789	863	987			906		

Table 44 Line friction loss



Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss In Feet of Liquid per 1000 Feet of Pipe
6 Inch (6.065″ inside dia) Sch 40 New Steel Pipe

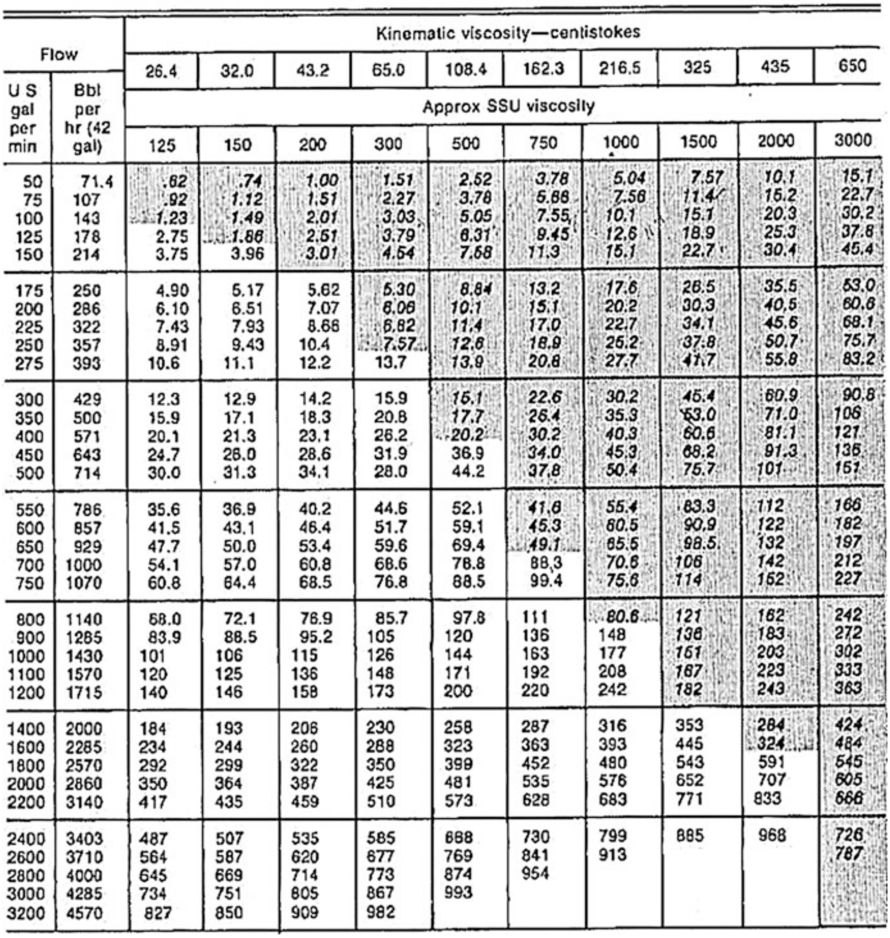
Flow		Kinematic viscosity—centistokes									
		.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
		Approx SSU viscosity									
U S gal per min	Bbl per hr (42 gal)		31.5	33	35	40	50	60	70	80	100
75	107	.45	.49	.58	.61	.68	.80	.86	.93	.98	.72
100	143	.77	.85	.96	1.01	1.14	1.30	1.42	1.52	1.62	1.74
125	178	1.14	1.27	1.43	1.51	1.68	1.95	2.10	2.23	2.35	2.57
150	214	1.61	1.78	2.01	2.09	2.32	2.66	2.86	3.08	3.20	3.46
175	250	2.13	2.37	2.63	2.79	3.04	3.52	3.74	3.97	4.24	4.51
200	286	2.75	3.00	3.34	3.55	3.85	4.41	4.76	5.02	5.31	5.89
225	322	3.42	3.74	4.17	4.38	4.78	5.39	5.89	6.16	6.45	7.05
250	357	4.15	4.55	5.07	5.21	5.76	6.94	7.11	7.47	7.77	8.41
275	393	4.99	5.42	6.02	6.28	6.88	7.60	8.35	8.86	9.18	9.81
300	429	5.87	6.38	7.08	7.37	8.09	8.94	9.69	10.3	10.8	11.4
350	600	7.90	8.45	9.38	9.80	10.5	11.8	12.8	13.5	14.2	15.0
400	571	10.2	10.9	11.8	12.5	13.4	15.0	16.0	17.0	18.0	19.1
450	643	12.8	13.8	14.8	15.5	16.7	18.5	19.7	20.1	21.8	23.7
500	714	16.8	16.6	18.0	18.7	20.4	22.6	24.0	25.1	26.4	28.5
550	786	18.8	19.8	21.5	22.3	24.3	26.8	28.5	29.6	29.9	33.4
600	857	22.1	23.3	25.1	26.2	28.4	31.1	33.2	35.0	36.2	38.8
650	929	25.8	27.2	29.2	30.4	32.8	36.1	38.5	40.4	41.8	44.7
700	1000	29.7	31.2	33.5	34.9	37.5	41.1	44.2	46.3	47.9	51.3
750	1070	33.9	35.6	38.2	39.7	42.5	46.7	49.9	51.8	54.0	57.2
800	1140	38.3	40.5	43.2	44.4	47.8	52.7	56.1	58.5	60.9	64.3
900	1285	48.5	50.7	54.4	55.8	59.3	65.4	69.1	72.8	74.6	78.9
1000	1430	59.5	62.2	66.4	67.5	72.4	79.3	83.4	87.8	91.0	95.9
1100	1570	71.6	74.8	79.4	80.8	86.7	94.5	99.6	104	109	114
1200	1715	84.6	87.9	93.4	85.6	102	111	117	121	126	133
1400	2000	115	118	126	128	135	146	155	161	167	177
1600	2285	150	153	162	164	173	187	199	207	213	224
1800	2570	188	193	203	206	216	232	246	256	264	278
2000	2860	231	237	247	253	264	284	296	311	320	334
2200	3140	277	286	297	303	316	338	354	371	382	398
2400	3430	330	341	352	356	374	395	417	430	448	470
2800	3710	387	395	408	418	433	461	485	500	520	543
2800	4000	449	458	470	482	497	526	553	574	595	621
3000	4285	515	526	536	550	567	597	628	655	666	706
3250	4640	605	613	629	641	665	701	729	757	777	817
3500	5000	697	711	729	739	771	808	841	869	897	938

Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

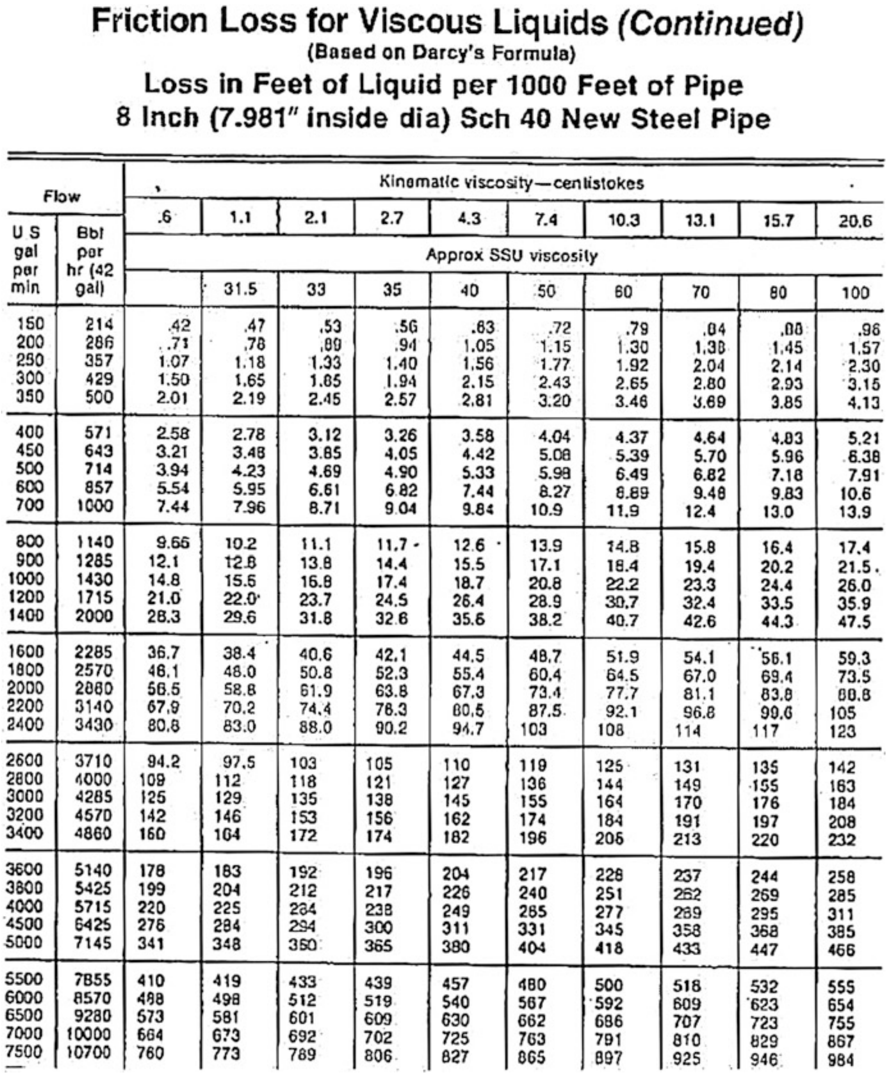
Loss in Feet of Liquid per 1000 Feet of Pipe

6 Inch (6.065″ inside dia) Sch 40 New Steel Pipe



Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
US gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
50	71.4	*.62*	*.74*	*1.00*	*1.51*	*2.52*	*3.78*	*5.04*	*7.57*	*10.1*	*15.1*
75	107	*.92*	*1.12*	*1.51*	*2.27*	*3.78*	*5.66*	*7.56*	*11.4*	*15.2*	*22.7*
100	143	*1.23*	*1.49*	*2.01*	*3.03*	*5.05*	*7.55*	*10.1*	*15.1*	*20.3*	*30.2*
125	178	2.75	*1.86*	*2.51*	*3.79*	*6.31*	*9.45*	*12.6*	*18.9*	*25.3*	*37.8*
150	214	3.75	3.96	*3.01*	*4.54*	*7.58*	*11.3*	*15.1*	*22.7*	*30.4*	*45.4*
175	250	4.90	5.17	5.62	*5.30*	*8.84*	*13.2*	*17.6*	*26.5*	*35.5*	*53.0*
200	286	6.10	6.51	7.07	*6.06*	*10.1*	*15.1*	*20.2*	*30.3*	*40.5*	*60.6*
225	322	7.43	7.93	8.66	*6.82*	*11.4*	*17.0*	*22.7*	*34.1*	*45.6*	*68.1*
250	357	8.91	9.43	10.4	*7.57*	*12.6*	*18.9*	*25.2*	*37.8*	*50.7*	*75.7*
275	393	10.6	11.1	12.2	13.7	*13.9*	*20.8*	*27.7*	*41.7*	*55.8*	*83.2*
300	429	12.3	12.9	14.2	15.9	*15.1*	*22.6*	*30.2*	*45.4*	*60.9*	*90.8*
350	500	15.9	17.1	18.3	20.8	*17.7*	*26.4*	*35.3*	*53.0*	*71.0*	*106*
400	571	20.1	21.3	23.1	26.2	*20.2*	*30.2*	*40.3*	*60.6*	*81.1*	*121*
450	643	24.7	26.0	28.6	31.9	36.9	*34.0*	*45.3*	*68.2*	*91.3*	*136*
500	714	30.0	31.3	34.1	28.0	44.2	*37.8*	*50.4*	*75.7*	*101*	*151*
550	786	35.6	36.9	40.2	44.6	52.1	*41.6*	*55.4*	*83.3*	*112*	*166*
600	857	41.5	43.1	46.4	51.7	59.1	*45.3*	*60.5*	*90.9*	*122*	*182*
650	929	47.7	50.0	53.4	59.6	69.4	*49.1*	*65.5*	*98.5*	*132*	*197*
700	1000	54.1	57.0	60.8	68.6	78.8	88.3	*70.6*	*106*	*142*	*212*
750	1070	60.8	64.4	68.5	76.8	88.5	99.4	*75.6*	*114*	*152*	*227*
800	1140	68.0	72.1	76.9	85.7	97.8	111	*80.6*	*121*	*162*	*242*
900	1285	83.9	88.5	95.2	105	120	136	148	*136*	*183*	*272*
1000	1430	101	106	115	126	144	163	177	*151*	*203*	*302*
1100	1570	120	125	136	148	171	192	208	*167*	*223*	*333*
1200	1715	140	146	158	173	200	220	242	*182*	*243*	*363*
1400	2000	184	193	206	230	258	287	316	353	*284*	*424*
1600	2285	234	244	260	288	323	363	393	445	*324*	*484*
1800	2570	292	299	322	350	399	452	480	543	591	*545*
2000	2860	350	364	387	425	481	535	576	652	707	*605*
2200	3140	417	435	459	510	573	628	683	771	833	*666*
2400	3403	487	507	535	585	688	730	799	885	968	*726*
2600	3710	564	587	620	677	769	841	913			*787*
2800	4000	645	669	714	773	874	954				
3000	4285	734	751	805	867	993					
3200	4570	827	850	909	982						

Table 45 Line friction loss



Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe

8 Inch (7.981″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
U S gal per min	Bbl per hr (42 gal)	.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
		Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
150	214	.42	.47	.53	.56	.63	.72	.79	.84	.88	.96
200	286	.71	.78	.89	.94	1.05	1.15	1.30	1.38	1.45	1.57
250	357	1.07	1.18	1.33	1.40	1.56	1.77	1.92	2.04	2.14	2.30
300	429	1.50	1.65	1.85	1.94	2.15	2.43	2.65	2.80	2.93	3.15
350	500	2.01	2.19	2.45	2.57	2.81	3.20	3.46	3.69	3.85	4.13
400	571	2.58	2.78	3.12	3.26	3.58	4.04	4.37	4.64	4.83	5.21
450	643	3.21	3.48	3.85	4.05	4.42	5.08	5.39	5.70	5.96	6.38
500	714	3.94	4.23	4.69	4.90	5.33	5.98	6.49	6.82	7.18	7.91
600	857	5.54	5.95	6.61	6.82	7.44	8.27	8.89	9.48	9.83	10.6
700	1000	7.44	7.96	8.71	9.04	9.84	10.9	11.9	12.4	13.0	13.9
800	1140	9.66	10.2	11.1	11.7	12.6	13.9	14.8	15.8	16.4	17.4
900	1285	12.1	12.8	13.8	14.4	15.5	17.1	18.4	19.4	20.2	21.5
1000	1430	14.8	15.6	16.8	17.4	18.7	20.8	22.2	23.3	24.4	26.0
1200	1715	21.0	22.0	23.7	24.5	26.4	28.9	30.7	32.4	33.5	35.9
1400	2000	28.3	29.6	31.8	32.6	35.6	38.2	40.7	42.6	44.3	47.5
1600	2285	36.7	38.4	40.6	42.1	44.5	48.7	51.9	54.1	56.1	59.3
1800	2570	46.1	48.0	50.8	52.3	55.4	60.4	64.5	67.0	69.4	73.5
2000	2860	56.5	58.8	61.9	63.8	67.3	73.4	77.7	81.1	83.8	88.8
2200	3140	67.9	70.2	74.4	76.3	80.5	87.5	92.1	96.8	99.6	105
2400	3430	80.8	83.0	88.0	90.2	94.7	103	108	114	117	123
2600	3710	94.2	97.5	103	105	110	119	125	131	135	142
2800	4000	109	112	118	121	127	136	144	149	155	163
3000	4285	125	129	135	138	145	155	164	170	176	184
3200	4570	142	146	153	156	162	174	184	191	197	208
3400	4860	160	164	172	174	182	196	206	213	220	232
3600	5140	178	183	192	196	204	217	228	237	244	258
3800	5425	199	204	212	217	226	240	251	262	269	285
4000	5715	220	225	234	238	249	265	277	289	295	311
4500	6425	276	284	294	300	311	331	345	358	368	385
5000	7145	341	348	360	365	380	404	418	433	447	466
5500	7855	410	419	433	439	457	480	500	518	532	555
6000	8570	488	498	512	519	540	567	592	609	623	654
6500	9280	573	581	601	609	630	662	686	707	723	755
7000	10000	664	673	692	702	725	763	791	810	829	867
7500	10700	760	773	789	806	827	865	897	925	946	984

Friction Loss for Viscous Liquids *(Continued)*

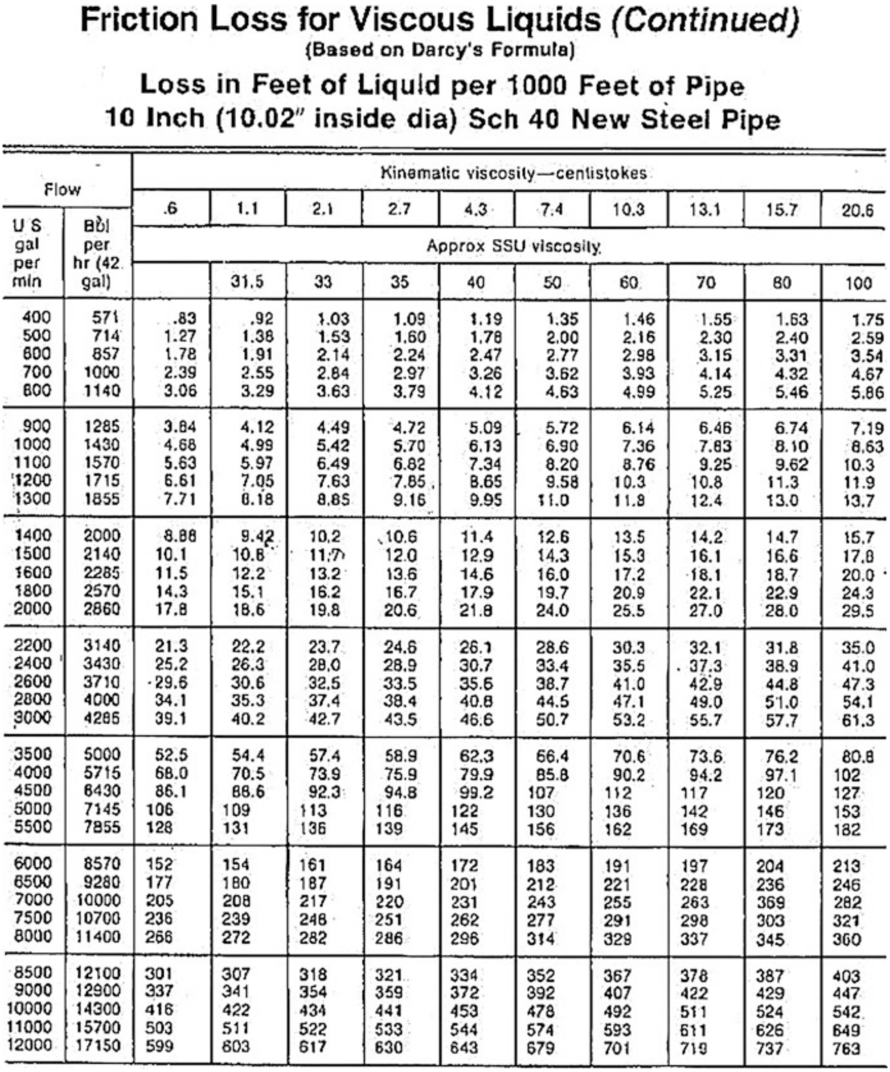
(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe

8 Inch (7.981″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
US gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
50	71.4	.21	.25	.34	.50	.84	1.26	1.68	2.52	3.38	5.05
100	143	.41	.50	.67	1.01	1.68	2.52	3.36	5.04	6.76	10.1
150	214	1.03	.75	1.01	1.51	2.52	3.78	5.04	7.56	10.1	15.1
200	286	1.67	1.78	1.34	2.02	3.37	5.04	6.72	10.1	13.6	20.2
250	357	2.46	2.60	2.85	2.52	4.21	6.30	8.40	12.6	16.9	25.3
300	429	3.37	3.56	3.89	3.03	5.05	7.56	10.1	15.1	20.3	30.3
350	500	4.39	4.63	5.04	5.69	5.89	8.82	11.8	17.7	23.6	35.3
400	571	5.54	5.83	6.35	7.18	6.73	10.1	13.5	20.2	27.0	40.4
450	643	6.79	7.16	7.75	8.76	7.58	11.3	15.1	22.7	30.4	45.4
500	714	8.17	8.58	9.32	10.4	8.42	12.6	16.8	25.2	33.8	50.5
550	786	9.65	10.1	11.0	12.3	9.26	13.9	18.5	27.8	37.2	55.5
600	857	11.2	11.8	12.8	14.3	16.6	15.1	20.2	30.3	40.5	60.6
700	1000	14.7	15.5	16.7	18.6	21.7	17.6	23.5	35.3	47.3	70.6
800	1140	18.6	19.4	21.0	23.4	27.1	20.1	26.9	40.3	54.0	80.7
900	1285	22.9	24.0	25.9	28.7	33.1	37.4	30.2	45.4	60.8	90.8
1000	1430	27.4	28.8	31.0	34.4	38.7	44.9	33.6	50.4	67.6	101
1200	1715	37.8	39.4	42.8	47.3	54.3	60.9	66.4	60.5	81.0	121
1400	2000	49.7	52.0	56.1	62.0	70.8	78.3	88.7	70.6	94.5	141
1600	2285	63.2	65.7	70.6	78.0	89.3	98.4	108	80.7	108	161
1800	2570	77.9	81.3	86.9	96.2	110	122	132	150	122	182
2000	2860	93.4	98.0	105	116	132	147	159	180	135	202
2200	3140	111	116	124	137	155	173	186	211	149	222
2400	3430	130	135	145	159	181	201	217	244	266	242
2600	3710	149	155	168	183	208	231	250	279	306	262
2800	4000	170	178	191	210	238	262	283	317	347	282
3000	4285	193	201	215	236	267	296	319	357	389	303
3200	4570	217	225	240	265	299	332	357	396	433	323
3400	4860	242	251	268	294	333	369	397	441	480	343
3600	5140	268	284	296	326	369	407	438	488	529	598
3800	5425	296	307	328	359	404	447	482	536	582	656
4000	5715	325	337	358	394	441	488	526	586	635	718
4500	6425	405	417	442	485	543	601	646	718	777	876
5000	7145	488	505	536	582	656	726	776	860	932	
5500	7855	578	605	634	689	773	855	913			
6000	8570	678	706	744	810	910	993				

Table 46 Line friction loss



Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
10 Inch (10.02″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		.6	1.1	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
U S gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
400	571	.83	.92	1.03	1.09	1.19	1.35	1.46	1.55	1.63	1.75
500	714	1.27	1.38	1.53	1.60	1.78	2.00	2.16	2.30	2.40	2.59
600	857	1.78	1.91	2.14	2.24	2.47	2.77	2.98	3.15	3.31	3.54
700	1000	2.39	2.55	2.84	2.97	3.26	3.62	3.93	4.14	4.32	4.67
800	1140	3.06	3.29	3.63	3.79	4.12	4.63	4.99	5.25	5.46	5.86
900	1285	3.84	4.12	4.49	4.72	5.09	5.72	6.14	6.46	6.74	7.19
1000	1430	4.68	4.99	5.42	5.70	6.13	6.90	7.36	7.83	8.10	8.63
1100	1570	5.63	5.97	6.49	6.82	7.34	8.20	8.76	9.25	9.62	10.3
1200	1715	6.61	7.05	7.63	7.85	8.65	9.58	10.3	10.8	11.3	11.9
1300	1855	7.71	8.18	8.85	9.16	9.95	11.0	11.8	12.4	13.0	13.7
1400	2000	8.88	9.42	10.2	10.6	11.4	12.6	13.5	14.2	14.7	15.7
1500	2140	10.1	10.8	11.7	12.0	12.9	14.3	15.3	16.1	16.6	17.8
1600	2285	11.5	12.2	13.2	13.6	14.6	16.0	17.2	18.1	18.7	20.0
1800	2570	14.3	15.1	16.2	16.7	17.9	19.7	20.9	22.1	22.9	24.3
2000	2860	17.8	18.6	19.8	20.6	21.8	24.0	25.5	27.0	28.0	29.5
2200	3140	21.3	22.2	23.7	24.6	26.1	28.6	30.3	32.1	31.8	35.0
2400	3430	25.2	26.3	28.0	28.9	30.7	33.4	35.5	37.3	38.9	41.0
2600	3710	29.6	30.6	32.5	33.5	35.6	38.7	41.0	42.9	44.8	47.3
2800	4000	34.1	35.3	37.4	38.4	40.8	44.5	47.1	49.0	51.0	54.1
3000	4285	39.1	40.2	42.7	43.5	46.6	50.7	53.2	55.7	57.7	61.3
3500	5000	52.5	54.4	57.4	58.9	62.3	66.4	70.6	73.6	76.2	80.8
4000	5715	68.0	70.5	73.9	75.9	79.9	85.8	90.2	94.2	97.1	102
4500	6430	86.1	88.6	92.3	94.8	99.2	107	112	117	120	127
5000	7145	106	109	113	116	122	130	136	142	146	153
5500	7855	128	131	136	139	145	156	162	169	173	182
6000	8570	152	154	161	164	172	183	191	197	204	213
6500	9280	177	180	187	191	201	212	221	228	236	246
7000	10000	205	208	217	220	231	243	255	263	369	282
7500	10700	236	239	248	251	262	277	291	298	303	321
8000	11400	266	272	282	286	296	314	329	337	345	360
8500	12100	301	307	318	321	334	352	367	378	387	403
9000	12900	337	341	354	359	372	392	407	422	429	447
10000	14300	416	422	434	441	453	478	492	511	524	542
11000	15700	503	511	522	533	544	574	593	611	626	649
12000	17150	599	603	617	630	643	679	701	719	737	763

Friction Loss for Viscous Liquids *(Continued)*

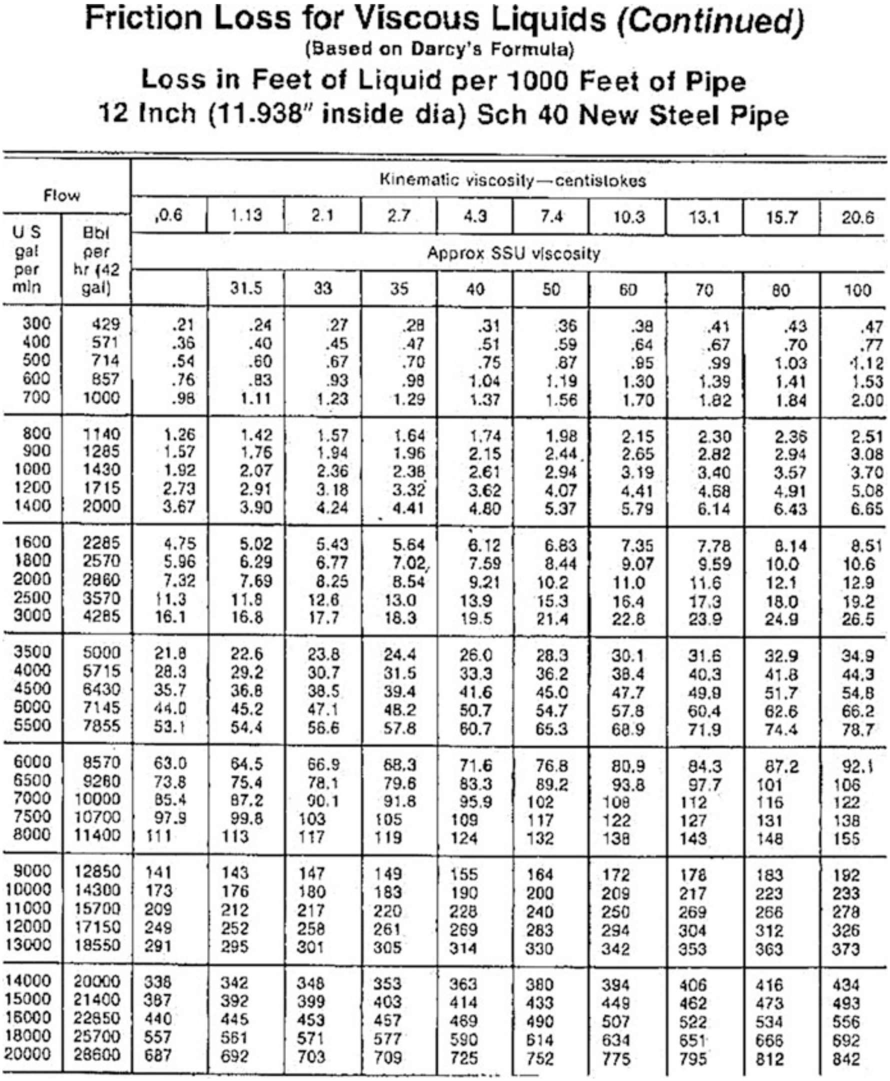
(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe

10 Inch (10.02″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
		Approx SSU viscosity									
U S gal per min	Bbl per hr (42 gal)	125	150	200	300	500	750	1000	1500	2000	3000
150	214	*.25*	*.30*	*.40*	*.61*	*1.02*	*1.52*	*2.03*	*3.04*	*4.08*	*6.09*
200	286	.68	*.40*	*.54*	*.81*	*1.35*	*2.03*	*2.71*	*4.06*	*5.43*	*8.12*
300	429	1.15	1.22	1.33	*1.22*	*2.03*	*3.04*	*4.06*	*6.09*	*8.15*	*12.2*
400	571	1.83	1.98	2.17	*1.62*	*2.71*	*4.08*	*5.41*	*8.12*	*10.9*	*16.2*
500	714	2.75	2.91	3.18	3.60	*3.39*	*5.07*	*6.77*	*10.1*	*13.6*	*20.3*
600	857	3.78	3.97	4.34	4.89	*4.06*	*6.08*	*8.12*	*12.2*	*16.3*	*24.4*
700	1000	4.94	5.19	5.66	6.37	*4.74*	*7.10*	*9.47*	*14.2*	*19.0*	*28.4*
800	1140	6.21	6.55	7.10	7.97	9.31	*8.12*	*10.8*	*16.2*	*21.7*	*32.5*
900	1285	7.66	8.04	8.71	9.76	11.4	*9.13*	*12.2*	*18.3*	*24.5*	*36.5*
1000	1430	9.21	9.61	10.5	11.7	13.6	*10.1*	*13.5*	*20.3*	*27.2*	*40.6*
1100	1570	10.9	11.4	12.3	13.8	16.0	18.0	*14.9*	*22.3*	*29.9*	*44.6*
1200	1715	12.6	13.4	14.4	16.0	18.6	21.0	*16.2*	*24.4*	*32.6*	*48.7*
1300	1855	14.5	15.4	16.4	18.4	21.2	24.0	*17.6*	*26.4*	*35.3*	*52.8*
1400	2000	16.6	17.5	18.7	20.9	24.1	27.2	*18.9*	*28.4*	*38.0*	*56.8*
1500	2140	18.7	19.6	21.2	23.6	27.2	30.6	33.3	*30.4*	*40.8*	*60.9*
1600	2285	21.0	21.9	23.7	26.3	30.4	34.1	37.2	*32.4*	*43.5*	*64.9*
1800	2570	26.0	27.3	29.2	32.2	37.1	41.7	45.5	*36.5*	*48.9*	*73.1*
2000	2860	31.3	32.7	35.0	38.6	44.4	49.8	54.4	*40.6*	*54.3*	*81.2*
2200	3140	37.0	38.6	41.3	45.8	52.3	58.8	64.0	71.9	*59.8*	*89.3*
2400	3430	43.1	45.1	48.3	53.4	60.9	68.3	74.2	83.8	*65.2*	*97.4*
2600	3710	49.8	52.1	55.4	61.4	70.0	78.3	85.0	96.2	*70.7*	*105*
2800	4000	56.8	59.2	63.5	70.1	79.7	88.9	96.1	109	*76.1*	*114*
3000	4285	64.3	66.8	71.8	78.8	89.8	99.8	108	122	133	*122*
3500	5000	84.9	88.3	94.4	103	117	131	142	159	180	*142*
4000	5715	108	112	119	131	149	165	178	199	217	*162*
4500	6430	133	139	147	162	182	202	218	244	266	300
5000	7145	160	168	179	195	218	241	262	293	318	360
5500	7855	191	199	212	231	258	286	309	345	373	423
6000	8570	223	232	247	268	302	334	359	398	435	489
6500	9280	258	267	286	310	348	384	411	460	499	560
7000	10000	296	305	326	355	396	438	468	522	566	637
7500	10700	335	347	369	402	447	492	529	589	638	766
8000	11400	377	389	414	452	505	550	594	659	710	797
9000	12900	469	482	512	557	624	679	729	809	.869	976
10000	14300	567	582	619	686	743	817	872	964		

Table 47 Line friction loss



Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
12 Inch (11.938″ inside dia) Sch 40 New Steel Pipe

Flow		Kinematic viscosity—centistokes									
U S gal per min	Bbl per hr (42 gal)	0.6	1.13	2.1	2.7	4.3	7.4	10.3	13.1	15.7	20.6
		Approx SSU viscosity									
			31.5	33	35	40	50	60	70	80	100
300	429	.21	.24	.27	.28	.31	.36	.38	.41	.43	.47
400	571	.36	.40	.45	.47	.51	.59	.64	.67	.70	.77
500	714	.54	.60	.67	.70	.75	.87	.95	.99	1.03	1.12
600	857	.76	.83	.93	.98	1.04	1.19	1.30	1.39	1.41	1.53
700	1000	.98	1.11	1.23	1.29	1.37	1.56	1.70	1.82	1.84	2.00
800	1140	1.26	1.42	1.57	1.64	1.74	1.98	2.15	2.30	2.36	2.51
900	1285	1.57	1.76	1.94	1.96	2.15	2.44	2.65	2.82	2.94	3.08
1000	1430	1.92	2.07	2.36	2.38	2.61	2.94	3.19	3.40	3.57	3.70
1200	1715	2.73	2.91	3.18	3.32	3.62	4.07	4.41	4.68	4.91	5.08
1400	2000	3.67	3.90	4.24	4.41	4.80	5.37	5.79	6.14	6.43	6.65
1600	2285	4.75	5.02	5.43	5.64	6.12	6.83	7.35	7.78	8.14	8.51
1800	2570	5.96	6.29	6.77	7.02	7.59	8.44	9.07	9.59	10.0	10.6
2000	2860	7.32	7.69	8.25	8.54	9.21	10.2	11.0	11.6	12.1	12.9
2500	3570	11.3	11.8	12.6	13.0	13.9	15.3	16.4	17.3	18.0	19.2
3000	4285	16.1	16.8	17.7	18.3	19.5	21.4	22.8	23.9	24.9	26.5
3500	5000	21.8	22.6	23.8	24.4	26.0	28.3	30.1	31.6	32.9	34.9
4000	5715	28.3	29.2	30.7	31.5	33.3	36.2	38.4	40.3	41.8	44.3
4500	6430	35.7	36.8	38.5	39.4	41.6	45.0	47.7	49.8	51.7	54.8
5000	7145	44.0	45.2	47.1	48.2	50.7	54.7	57.8	60.4	62.6	66.2
5500	7855	53.1	54.4	56.6	57.8	60.7	65.3	68.9	71.9	74.4	78.7
6000	8570	63.0	64.5	66.9	68.3	71.6	76.8	80.9	84.3	87.2	92.1
6500	9280	73.8	75.4	78.1	79.6	83.3	89.2	93.8	97.7	101	106
7000	10000	85.4	87.2	90.1	91.8	95.9	102	108	112	116	122
7500	10700	97.9	99.8	103	105	109	117	122	127	131	138
8000	11400	111	113	117	119	124	132	138	143	148	155
9000	12850	141	143	147	149	155	164	172	178	183	192
10000	14300	173	176	180	183	190	200	209	217	223	233
11000	15700	209	212	217	220	228	240	250	269	266	278
12000	17150	249	252	258	261	269	283	294	304	312	326
13000	18550	291	295	301	305	314	330	342	353	363	373
14000	20000	338	342	348	353	363	380	394	406	416	434
15000	21400	387	392	399	403	414	433	449	462	473	493
16000	22850	440	445	453	457	469	490	507	522	534	556
18000	25700	557	561	571	577	590	614	634	651	666	692
20000	28600	687	692	703	709	725	752	775	795	812	842

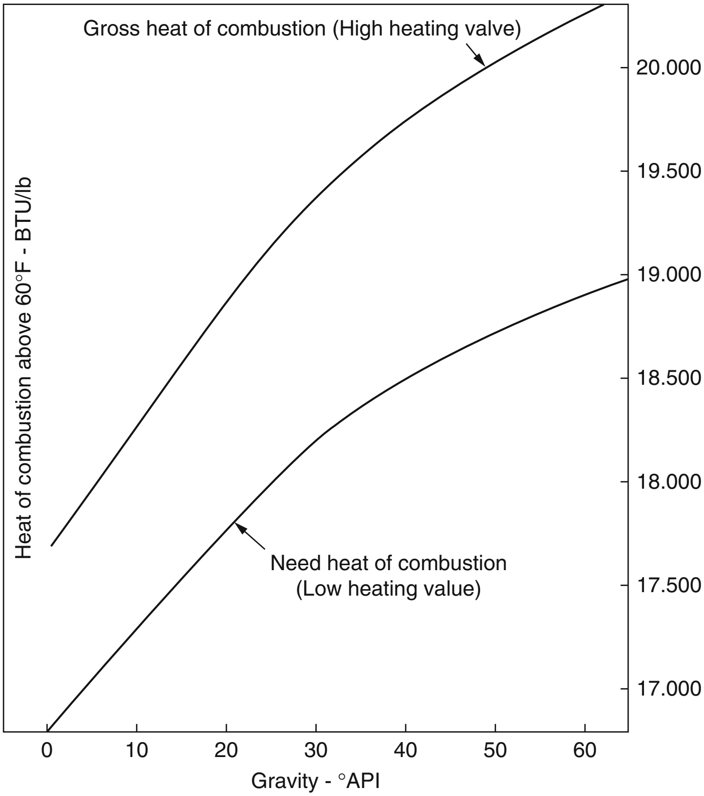
Friction Loss for Viscous Liquids *(Continued)*

(Based on Darcy's Formula)

Loss in Feet of Liquid per 1000 Feet of Pipe
12 Inch (11.938″ inside dia) Sch 40 New Steel Pipe

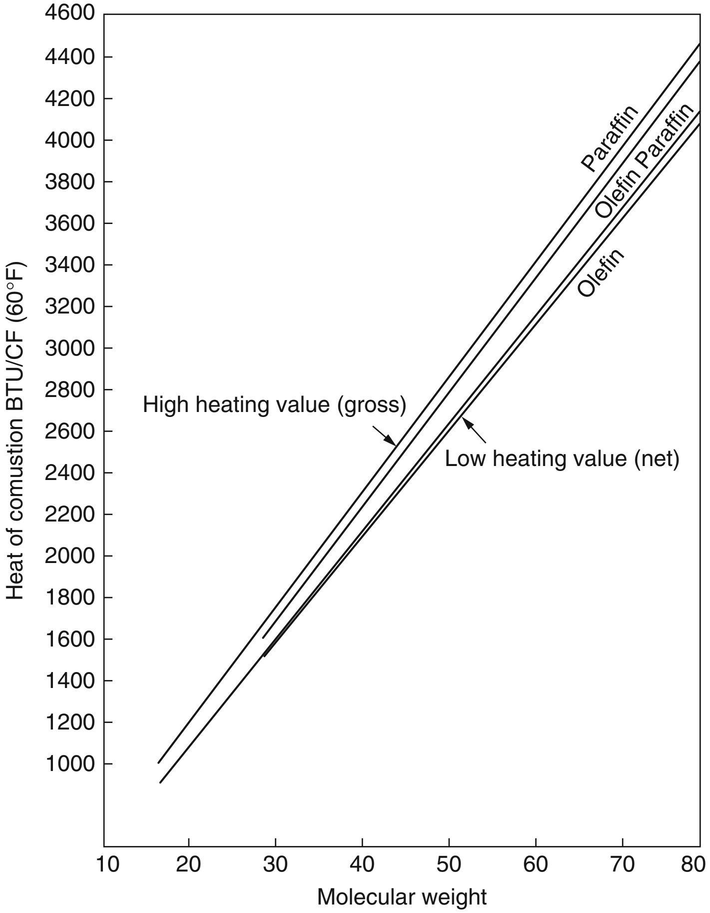
Flow		Kinematic viscosity—centistokes									
		26.4	32.0	43.2	65.0	108.4	162.3	216.5	325	435	650
U S gal per min	Bbl per hr (42 gal)	Approx SSU viscosity									
		125	150	200	300	500	750	1000	1500	2000	3000
100	143	.08	.10	.13	.20	.34	.51	.68	1.00	1.35	2.00
200	286	.16	.19	.27	.40	.67	1.00	1.37	2.05	2.74	4.01
300	429	.49	.53	.41	.62	1.01	1.51	2.00	3.06	4.11	6.16
400	571	.81	.86	.94	.82	1.34	2.02	2.68	3.98	5.46	8.21
500	714	1.22	1.25	1.37	1.02	1.71	2.50	3.37	5.01	6.84	10.3
600	857	1.66	1.71	1.87	2.12	1.97	3.02	4.05	6.03	7.99	12.3
700	1000	2.15	2.30	2.43	2.75	2.37	3.66	4.88	7.05	9.36	13.9
800	1140	2.70	2.88	3.05	3.45	2.83	4.04	5.38	8.09	10.7	15.9
900	1285	3.31	3.52	3.74	4.21	4.93	4.44	6.05	9.30	12.1	18.0
1000	1430	3.97	4.22	4.48	5.04	5.89	5.13	6.84	10.0	13.6	20.0
1200	1715	5.43	5.77	6.33	6.88	8.01	5.91	7.89	12.1	16.2	24.1
1400	2000	7.10	7.53	8.24	8.98	10.4	11.8	9.47	14.6	18.9	28.2
1600	2285	8.98	9.48	10.4	11.3	13.1	14.8	10.6	16.2	21.7	32.4
1800	2570	11.0	11.6	12.7	13.8	16.0	18.0	19.7	17.7	24.2	36.5
2000	2860	13.2	14.0	15.2	16.6	19.1	21.5	23.6	20.5	27.4	40.1
2500	3570	19.6	20.6	22.4	25.3	28.0	31.5	34.3	25.7	34.2	51.3
3000	4285	27.2	28.4	30.8	34.6	38.4	43.0	46.8	53.1	41.1	61.6
3500	5000	36.2	37.3	40.3	45.2	50.2	56.0	60.9	68.8	47.9	71.9
4000	5715	43.4	47.3	51.0	57.0	63.2	70.5	76.5	86.3	94.5	82.1
4500	6430	57.6	58.3	62.8	69.9	77.6	86.4	93.6	105	115	92.4
5000	7145	69.8	70.3	75.6	84.1	93.3	104	112	126	138	103.
5500	7855	82.8	83.6	89.5	99.4	110	122	132	148	162	183
6000	8570	96.8	98.2	104	116	128	142	154	172	188	212
6500	9280	112	114	120	133	148	164	176	197	215	243
7000	10000	128	131	137	152	174	186	201	224	244	275
7500	10700	145	148	155	172	196	210	226	253	274	310
8000	11400	163	167	174	192	220	235	253	282	306	345
9000	12850	202	208	215	237	270	289	311	346	375	422
10000	14300	204	253	260	286	325	347	373	415	450	505
11000	15700	290	301	309	338	384	411	441	490	530	594
12000	17150	341	354	361	395	448	479	514	569	616	689
13000	18550	394	409	417	456	516	551	591	655	707	790
14000	20000	452	469	477	521	588	628	673	745	804	898
15000	21400	513	532	541	589	664	710	760	840	906	
16000	22850	578	598	608	662	745	796	851	940		

Appendix 10: Heats of Combustion for Fuel Oils

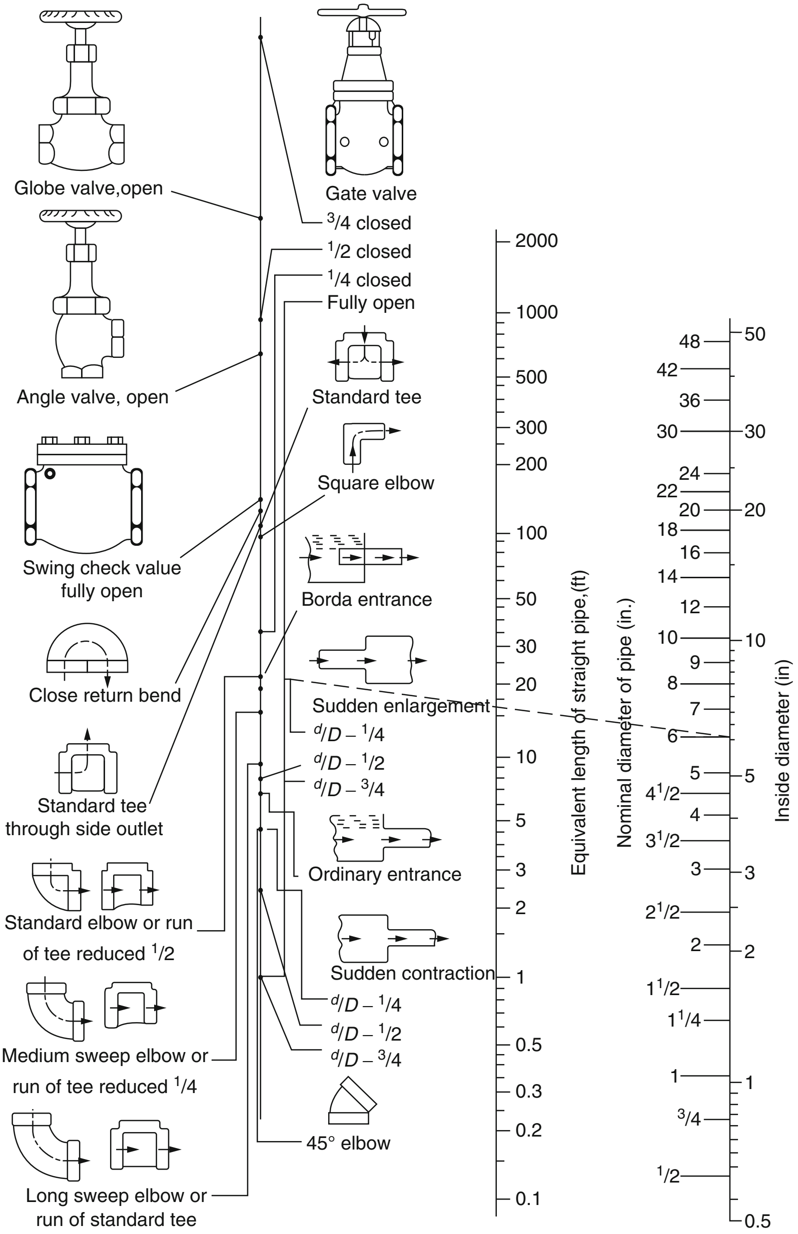


Impurities in average fuels			
°API	%S	%inerts	Total impurity
Residual fuel oil and crudes			
0	2.95	1.15	4.10
5	2.35	1.00	3.35
10	1.80	0.95	2.75
15	1.35	0.65	2.20
20	1.00	0.75	1.75
Crude oils			
25	0.70	0.70	1.40
30	0.40	0.65	1.10
35	0.30	0.60	0.90

Appendix 11: Heats of Combustion for Fuel Gases

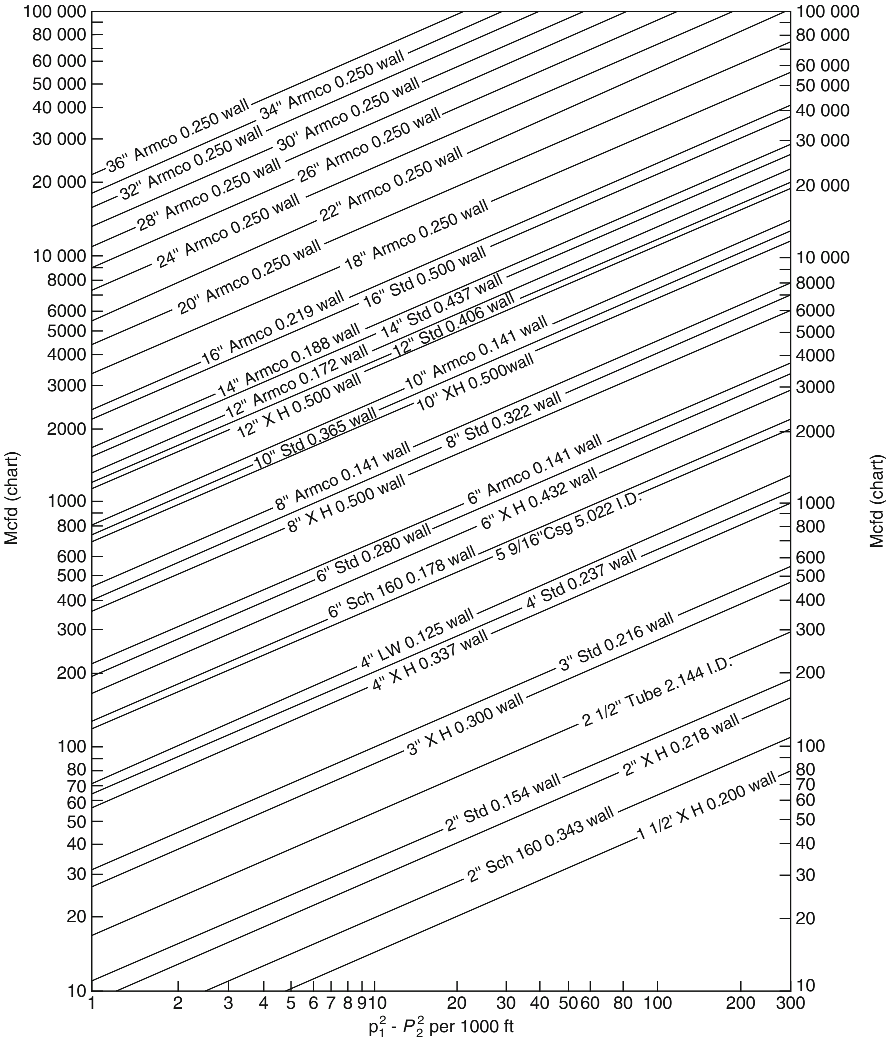


Appendix 12: Resistances of Valves and Fittings



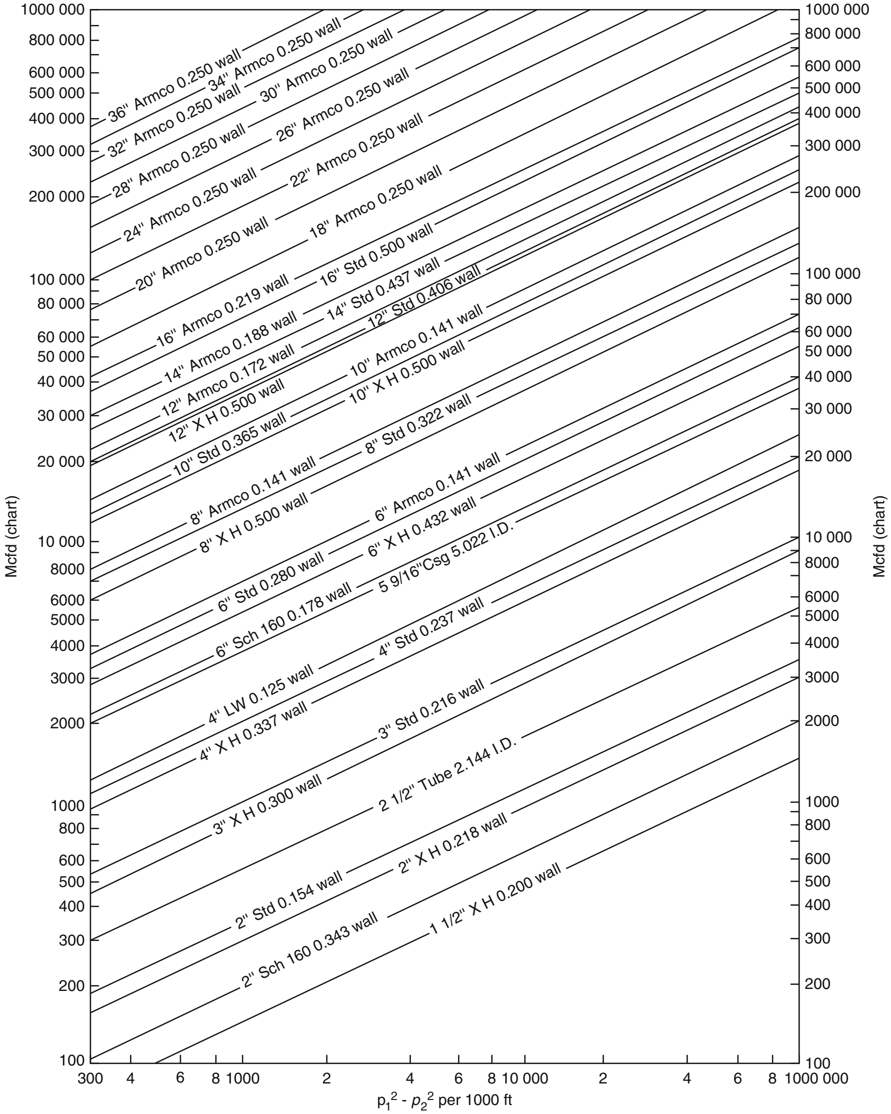
Appendix 13: Flow Pressure Drop for gas Streams

See Figs. 62 and 63.



1. Chart–Mcfd–based on 'Weymouth Formule' where specific gravity = 0.9 (air = 1), flowing temperature = 90°F and pressure base = 14.65 psia
2. Simplified Mcfd = 1.59 $d^{2/3}$ $(P_1^2 - P_2^2/1000 \text{ ft})^{1/2}$

Fig. 62 Flow pressure drop for gas streams



3. For conditions other than in (1) correct Mcfd for chart use as follows:

$$\text{Mcfd(chart)} = \frac{P}{14.65}\left(\frac{SG}{0.9} \times \frac{T}{550} \times \frac{Z}{1}\right)^{1/2} \times \text{Mcfd}$$

Z = Compressibility factor as determined from 'Natural Gas Under Pressure' in the GPSA Engineering Data Book
P = Pressure base other than 14.65 psia
T = Flowing temperature in degrees Rankine (460 + °F)

Fig. 63 Flow pressure drop for gas streams

Appendix 14: Example Hydraulic Analysis of a Process System

The following calculation is an example of a typical system that process engineers' encounter in a design of a plant or in checking out an operating plant's process flow. The attached diagram, Fig. 64, is used as the basis for this example.

Example Calculation Basis

Total flow to P-103 A and B = 519,904 lbs/h.
API gravity = 20.7 = SG of 0.930 at 60 °F.
Stream temperature = 545 °F.
SG at 545°F = 0.755 = 6.287 lbs/gal.
Gallons per minute at temperature = 519,904/(6.287 × 60) = 1,378 gpm.
Viscosity of the oil at 545°F = 1.2 cSt.
Suction line to P-103 A and B is 10″; Sch. 40.

From Appendix 9 of this chapter:

Friction loss in feet/1,000 f. of pipe is 9.3 f. (equivalent to 0.30 psi/100 ft).

Suction Line Equivalent Length

The following information would normally be obtained from a piping general arrangement drawing (a piping GA). For this calculation, this information is fictional:

- Number of standard elbows in the line = 8.
- Number of gate valves (all open) in the line = 3.
- Total straight length of 10″ line = 85 ft.

From Appendix 12 of this chapter:

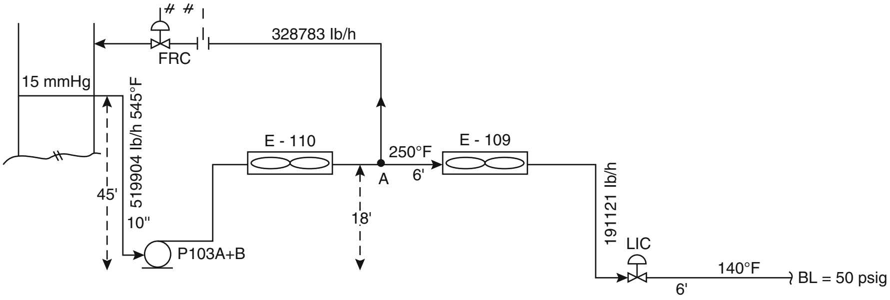


Fig. 64 Example system pressure drop calculation flow sheet

The equivalent length for 10″ elbows is 22 ft per elbow
= 22 × 8 = 176 ft.

The equivalent length for open 10″ gate valves is 5 ft per valve.
= 5 × 3 = 15 ft.

$$\text{Total equivalent line length} : 85 + 176 + 15 = 276\ \text{ft.}$$

Head loss to pump suction due to friction
$= (9.3 \times 276)/1000 = 2.57$ ft.

In terms of pounds per square inch this is
$= (2.57 \times 62.2 \times 0.755)/144 = 0.83$ psi.

Pump Suction Pressure

Source pressure at vacuum tower draw off = 15 mmHg = 0.29 psia.
Static head = 45 ft. $= (45 \times 62.2 \times 0.755)/144 = 14.7$ psi.
Line loss = 0.83 psi.
Total pressure at pump suction flange $= 0.29 + 14.7 - 0.83 = 14.2$ psia
$= -0.5$ psig.

Calculating the Pressures at the Pump Discharge

Destination pressure at battery limits = 50 psig.
Temperature of the oil at battery limits = 140 °F.
Viscosity of the oil at 140 °F = 20 cSt.
SG of the oil at 140 °F = 0.900; lbs/gal = 7.495.

From a material balance or from plant data: Flow of oil = 191,121 lbs/h.

$$\text{Flow rate} = 191,121/(7.495 \times 60) = 425\ \text{gpm.}$$

Line Pressure Drop from E-109 to Battery Limits

Equivalent length of line:

Straight line = 126 ft.
Number of elbows = 18 equiv. length = 18 × 16 = 288 ft.
Number of gate valves = 6 equiv. length = 6 × 3.5 = 21 ft.
Number of Tee's = 1 equiv. length = 1 × 30 = 30 ft.
Total equivalent length = 465 ft.

Line to battery limit (BL) is a 6″ Schedule 40. Then, from Appendix 9, loss due to friction is 21.4 ft/1,000 f. which is equivalent to 0.83 psi/100 ft.

Then line friction loss is

$$(21.4 \times 245)/1{,}000 = 9.95 \text{ ft.}$$

or

$$(9.95 \times 62.2 \times 0.900)/144 = 3.86 \text{ psi.}$$

Control Valve Pressure Drop

There is a battery limit level control valve (LICV) between E-109 and the BL. It is required to calculate the pressure drop for this valve at design flow. The valve pressure drop will be estimated as 20 % of the circuit frictional pressure drop plus 10 % of the static head of the receiving vessel.

The oil discharges into a surge drum of another downstream unit. This drum is pressurized by a blanket of inert gas. The net static head to this drum is 15 f. above valve outlet flange. This is equivalent to 6 psi.

The total line pressure drop for the whole circuit is estimated at three times that calculated above. (This will be checked and may be revised when the analysis of the whole circuit is complete.) This pressure drop therefore is 3 × 3.86 = 11.58 psi for line losses. In addition to this line loss, there are also two air coolers which have pressure drops as follows:

E-109 = 6 psi (from data sheets).
E-110 = 8 psi.

Then total system pressure drop is estimated as 11.58 + 14 = 25.58 psi.

And control valve pressure drop is

$$(0.1 \times 6.0) + (0.2 \times 25.58) = 5.2 \text{ psi.}$$

Calculate Pressure at Point "A" Which Is the Reflux Stream Take Off

Equivalent length of line between point "A" and inlet to E-109 is as follows:

Straight line = 121 ft.
4 elbows = 4 × 16 = 64 ft.
2 valves = 2 × 3.5 = 7 ft.
Total 6″ sched 40 line equiv. = 192 ft.

Temperature of stream at this point is 250 °F.

Viscosity at 250 °F =3.5 cSt.

SG at 250 °F is 0.860 which is 7.16 lbs/gal.

Rate of flow into E-109 = 191,121/(7.16 × 60) = 445 gpm.

Friction loss in 6″ pipe = 16.1 ft/1,000 ft.

Total line loss:

$$(192 \times 16.1)/1000 = 3.09 \text{ ft or } 1.15 \text{ psi}.$$

Pressure at point "A" therefore is the sum of:

Destination pressure at BL = 50 psig.
Pressure drop for E-109 = 6 psi.
Loss in line from E-109 to battery limits. = 3.86 psi.
Loss in line from point "A" to E-109 = 1.15 psi.
Control valve pressure drop = 5.2 psi.
Flow meter (not shown) say = 0.2 psi.
Total pressure at point "A" = 66.41 psig.

Calculating the Pressure at the Pump Discharge Flange

Total flow from the pump is 519,904 lbs/h.

Oil temperature at outlet of E-110 is 250 °F.

Gpm of flow from E-110 is

$$519,904/(7.16 \times 60) = 1,210 \text{ gpm}.$$

Line size at this point is 8″ Sch. 40.

Head loss in this line is 31.1 ft/1,000 ft.

Equivalent length of line:

Straight line = 82 ft.
1 Tee = 30 ft.
Total equivalent length = 112 ft.
Total head loss in line = $(112 \times 31.1)/1,000 = 3.5$ ft or 1.3 psi.

Pressure at E-110 inlet will be:

Pressure at point "A" = 66.41 psig.
Head loss in line = 1.3 psi.
Pressure drop across 11-E-10 = 8 psi
=75.7 psig.

This pressure is 18 f. above grade as these air coolers are located above the pipe rack. Allowing 1.5 f. from grade to pump center line, the static head at pump discharge flange is 16.5 ft.

Equivalent length of line from pump to E-110 is:

Straight length = 155 ft.
12 elbows = 12 × 20.5 = 246 ft.
3 gate valves = 3 × 4.8 = 14.4 ft.
1 nonreturn valve = 1 × 51 = 51 ft.
Total equivalent length = 466.4 ft.

Head loss in 8″ Sch. 40 pipe at a flow rate of 1,378 gpm:

Pump temperature is 545 °F.
Viscosity at pump temperature is 1.2 cSt.
SG at pump temperature is 0.755.
Head loss = 28.8 ft/1,000 ft.
Total line head loss = (28.8 × 466.4)/1,000 = 13.4 f. or 4.38 psi.

Then the pump discharge pressure is the sum of:

Pressure at E-110 inlet = 75.7 psig.
Line pressure drop = 4.38 psi.
Static head (16.5 ft) = 5.38 psi.
Total discharge pressure = 85.46 psig.

Calculating the Pressures in the Reflux Line from Point "A"

At point "A," the pressure has been calculated as 66.41 psig.

Flow of the reflux stream (from the material balance) is:

519,904 − 191,121 = 328,783 lbs/h.
Temperature of the stream is 250 °F.
Viscosity at 250 °F = 3.5 Cs.
SG at 250 °F = 0.860 and lbs/gal is 7.16
Rate of flow = 328,783/(7.16 × 60) = 765 gpm.

Line to tower from point "A" is a 6″ Sch. 40 and head loss in this line is found to be 40.2 ft/1,000 ft.

Equivalent line lengths:

To the flow controller inlet flange:

Straight line = 16 ft.
2 elbows = 2 × 16 = 32 ft.
1 valve = 1 × 3.5 = 7 ft.
Total equivalent length = 81.5 ft.

From the flow controller to tower:

Straight line = 71ft.
6 elbows = 6 × 16 = 96 ft.
1 valve = 1 × 3.5 = 3.5 ft.
Total equivalent length = 171 ft.

Total line length from point "A" to tower:

81.5 + 171 = 252.5 ft.

Total head loss in line due to friction:

$$(252.5 \times 40.2)/1{,}000 = 10.15 \text{ ft. or } 3.77 \text{ psi.}$$

The pressure required to deliver 765 gpm of reflux to the tower excluding the pressure drop across the control valve at this rate is the sum of the following:

Destination pressure = 0.29 psia.
Static head = 14.11 psi.
Distributor (tower internals) = 2.0 psi (from data sheet).
Flow meter pressure = 0.5 psi (from data sheet).
Head loss in line = 3.77 psi.
Total required = 20.67 psia or 5.97 psig.

Then valve pressure drop at design flow of 765 gpm is:

$$\begin{gathered}\text{Pressure at point ''A''} - \text{required pressure}\\ = 66.41 - 5.97 \text{ psig}\\ = 60.44 \text{ psi.}\end{gathered}$$

Note: Line pressure drops are given in Appendix 9 of this chapter.

References

C. Branan, *The Process Engineer's Pocket Handbook* (Gulf Publishing Company, Houston, 1976) (This book contains a great deal of very useful, practical information on several subjects in addition to pressure drop)

N.P. Cheremisinoff, P.N. Cheremisinoff, *The Hydrodynamics of Gas-Solids Fluidization* (Gulf Publishing Company, Houston, 1984)

A.K. Coker (H&G Engineering, 1990), Article: Understand two-phase flow in process piping. Chem. Eng. Prog. November, pp. 60–65 (1990)

Gas Processors Suppliers Association (GPSA, 1987), Engineering Data Book (2 volumes), GPSA, Tulsa, OK, USA (This is another outstanding reference for many petroleum processing subjects.)

R. Kern (Hoffmann-La Roche Inc., 1969), Article: How to size process piping for two-phase flow. Hydrocarb. Process. October, pp. 105–116 (1969)

Dictionary of Abbreviations, Acronyms, Expressions, and Terms Used in Petroleum Processing and Refining

David S. J. Jones, Peter R. Pujadó, and Steven A. Treese

Abstract

This dictionary provides definitions and background information on hundreds of abbreviations, acronyms, expressions, and terms used in the oil industry. Special emphasis is placed on refining and petroleum processing. References are provided for more detailed discussions of most of these terms elsewhere in this handbook.

Keywords

Petroleum • Refining • Dictionary

Miscellaneous

#2 fuel oil Similar boiling range as diesel. Can be low sulfur or ULS.

#6 fuel oil Heavy residual, high-sulfur fuel oil. AKA bunker fuel oil

3:2:1 crack Generic per barrel crack based on prices of 2 barrels gasoline + 1 barrel diesel minus 3 barrels of WTI crude. This is an indicator of gross refining margin.

David S. J. Jones: deceased.
Peter R. Pujadó has retired.
Steven A. Treese has retired from Phillips 66.

D.S.J. Jones
Calgary, AB, Canada
e-mail: dai.jones.06@shaw.ca

P.R. Pujadó
UOP LLC, A Honeywell Company, Kildeer, IL, USA
e-mail: prpujado@gmail.com

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_31

A

AA (H, HH, L, LL) Analyzer alarm high, high–high, low, or low–low – e.g., AAHH is a high–high analyzer alarm

AACE Association for the Advancement of Cost Engineering

Abel flash points This is a test procedure for determining the flash point of light distillate such as kerosene. The flash points determined by this method will be in the range of 85–120 °C. The apparatus consists of a water bath with a heating source into which is suspended a cup containing the material to be tested. The water bath is heated and retained at a fixed temperature. The temperature of the sample being tested in the cup is measured by a thermometer. The lid of the cup contains a shutter and a small gas burner from which a flame of determined length exits. The rate of temperature rise of the test material is noted, and at predetermined temperatures, the shutter is opened and the burner flame exposed to the space above the test liquid in the cup. The temperature at which a flame is observed crossing the surface of the oil sample when the burner is dipped into the cup is the flash point. The ASTM name and number for this test is D56-01 Standard Test Method for Flash Point by Tag Closed Tester.

Abel tester Apparatus used to determine the Abel flash point of an oil. See “Abel Flash Points”.

ABMA American Boiler Manufacturers Association

ABS (1) Ammonium bisulfide; (2) American Bureau of Shipping; (3) acrylonitrile–butadiene–styrene polymer; (4) absolute (as in absolute pressure)

Absolute pressure Pressure above total vacuum. Normally gauge pressure in psig plus 14.696 psi (result expressed as psia) or as appropriate for the measurement system being used: bar absolute (bara), kg/cm^2 abs, etc.

Absorbent Material capable of removing specific component(s) from a stream by chemical means (absorbing the material) or taking the component(s) into solution

Absorber A type of liquid/vapor or solid/vapor contactor designed to remove or absorb one or more components from the vapor phase into the liquid or solid phase. Liquid/vapor contactors are used to remove H_2S from fuel gas or to remove heavier hydrocarbons from a vapor using a sponge oil, for example. In a solid/vapor absorber example, canisters of activated carbon may be used to remove volatile organic compounds from vapors vented to the atmosphere.

Absorption units Absorption units usually consist of a trayed or packed tower in which a gas stream is contacted with a lean solvent in a countercurrent flow. Usually the gas stream enters below the bottom tray or packed bed and rises up the tower, meeting the solvent liquid stream which enters the tower above the top tray or packed bed flowing down the tower. Undesirable material in the gas stream is selectively absorbed into the liquid stream. This liquid stream then enters a stripping column (usually a Steam Stripper), where the absorbed material is stripped off and leaves as an overhead product. The stripped solvent stream is then rerouted to the absorber tower to complete the cycle. These processes are used in petroleum refining to remove heavy hydrocarbons from a light gas stream. More commonly, this type of unit is used in gas treating for the

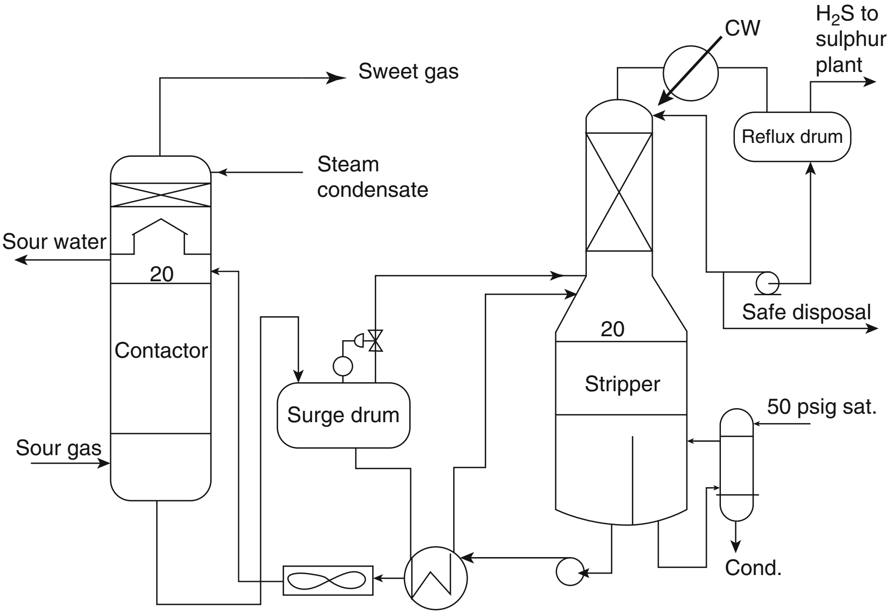


Fig. A.1 A schematic of a typical absorption unit

removal of H_2S from a gas stream (see the topic in chapter "▶ Refinery Gas Treating Processes" of this handbook). Figure A.1 is an example of a typical absorption (gas treating) unit.

ABT Average bed temperature

AC (1) Alternating current; (2) analyzer controller

Accumulation In a relief valve, accumulation is the pressure increase over the maximum allowable working pressure of the vessel during discharge through the pressure relief device expressed as a percent of that pressure, or in psi or bar.

Accumulator A type of surge vessel, normally in distillation or hydraulics. Refer to the equipment chapter.

Acid gas A vapor containing a compound that can form an acidic aqueous solution when dissolved in water. In refining, typical acid gases include vapors containing H_2S or CO_2. The feed gas for a sulfur plant is an "acid gas" because it contains high H_2S concentrations, for instance.

Acid number An ASTM test which determines the organic acidity of a refinery stream. Normally determined by titration and expressed as mg KOH/g oil (or sometimes per 100 g oil - check context).

Acid suit PPE suit intended to prevent acid contact with personnel.

ACFD Actual cubic feet per day

ACFM Actual cubic feet per minute at flowing temperature and pressure

ACGIH American Conference of Governmental Industrial Hygienists

ACS American Chemical Society

Activated sludge unit (ASU) Secondary wastewater treatment unit using aerobic organisms to reduce BOD. See the environmental chapter.

Actuator The device which moves a final control element. Normally a pneumatic diaphragm or a pneumatic or hydraulic piston. See the discussion in the controls chapter.

Adiabatic No external heat input or removal

Adsorbent Material capable of removing specific component(s) from a stream by adsorbing the component(s) onto the surface of the material. For example, the materials used in a PSA are adsorbents. No chemical reaction occurs with adsorbents as compared to absorbents.

Ad valorem tax A tax based on the quantity of an item sold or retained as property. This tax may be levied on inventory in some jurisdictions, for instance. The tax is intended to cover property tax, municipal service costs, etc.

Advanced process control (APC) A control system overlaying the DCS or basic process control system that performs more complex control functions for a process unit. Refer to the chapter on controls.

Aerobic Requiring oxygen – generally refers to organisms.

AFPM American Fuel and Petrochemical Manufacturers – formerly NPRA

AGA American Gas Association

AGO Atmospheric gas oil. Typically boils between about 500 and 850 °F. Sometimes called heavy diesel or heavy D

AHS Albian Heavy Synthetic crude – from Canada

AI (1) Artificial intelligence; (2) analyzer indicator; (3) analog input

AIChE American Institute of Chemical Engineers

AIChE-DIERS AIChE Design Institute for Emergency Relief Systems

AIHA American Industrial Hygiene Association

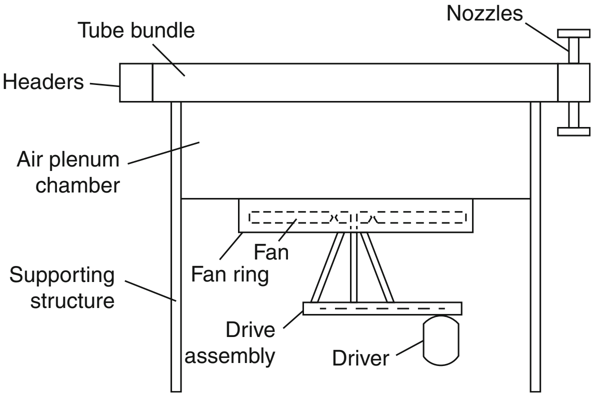
Air condensers and coolers An air cooler or condenser transfers heat from a process stream by passing air over a large, flat tube bundle, similar to an automobile radiator. The tubes may have fins wrapped around them to enhance heat transfer. The use of air cooling saves cooling water. These units are normally elevated above the pipe racks in a refinery. The air is usually blown over the tubes by large fans. Figure A.2 illustrates a typical air cooler or condenser layout. Refer to the chapter "▶ Process Equipment for Petroleum Processing" of this handbook for a detailed discussion under heat exchangers.

Air/fuel ratio The ratio of air weight to fuel weight consumed in an internal combustion engine or a furnace. This ratio is often expressed as a volume or molar ratio for gaseous fuels.

Air-line respirator A type of fresh-air-supply respirator with the air provided through a tube to a full-face mask. The air is generally provided through a regulator from banks of compressed breathing air bottles.

Air systems All chemical and petroleum plants require a supply of compressed air to operate the plant and for plant maintenance. There are usually two separate systems: (1) plant air and (2) instrument air. Plant air is used for general utility services, such as air tools. Instrument air is a clean, dry motive air supply for

Fig. A.2 A forced airflow arrangement



operation of control valves and pneumatic instruments. Refer to the chapter titled "▶ Utilities in Petroleum Processing" of this handbook for a detailed discussion of these critical systems.

AISC American Institute of Steel Construction

AKA Also known as

ALARP As low as reasonably practical

Alcohol An organic chemical compound composed of carbon, hydrogen, and oxygen. Alcohols vary in chain length and are composed of a hydrocarbon plus a hydroxyl group, CH_3-$(CH_2)_n$-OH (e.g., methanol, ethanol, and tertiary butyl alcohol).

Alcohol blend A fuel with alcohol blended into the hydrocarbon base stock. Examples include reformulated gasoline, where ethanol may be blended with conventional hydrocarbon stocks to provide the regulatory required oxygen content.

Algal oil Renewable distillate-range oil derived from processing algae. See the discussion of unconventional stocks and renewables.

Aliphatic Refers to a nonaromatic hydrocarbon. Aliphatic compounds may be saturated (like paraffins and naphthenes) or unsaturated (olefins).

Alkylate The hydrocarbon product from an alkylation unit. Normally used as a gasoline blendstock.

Alkylation Alkylation is a process which reacts a small paraffin molecule (e.g., isobutane) with a small olefin molecule (e.g., 1-butene) to make larger molecules. The normal product of alkylation (alkylate) is a high-octane gasoline blending component with a relatively low vapor pressure (RVP) and almost no sulfur. The reaction is catalyzed by strong liquid and solid acids. The most common catalysts are liquid anhydrous hydrofluoric acid and concentrated sulfuric acid. Figure A.3 illustrates a typical alkylation unit employing anhydrous hydrofluoric acid catalyst in the UOP configuration. Alkylation is provided on a licensed basis by a handful of licensors. Refer to the topic "▶ Alkylation in Petroleum Processing" of this handbook for a detailed discussion of this technology.

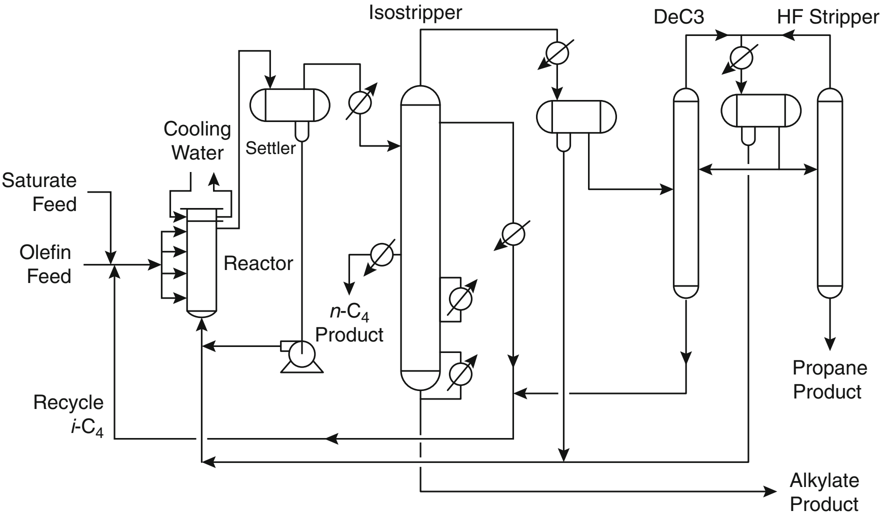


Fig. A.3 AHF alkylation process

Alkylation unit HF An HF alkylation unit uses anhydrous hydrofluoric acid to catalyze the alkylation reaction, which builds smaller paraffins and olefins into larger molecules. The product alkylate is normally a high-octane gasoline blending component with low vapor pressure and sulfur content. Figure A.3 is a simplified process flow diagram for the UOP propylene–butane HF alkylation process. Refer to the topic "▶ Alkylation in Petroleum Processing" of this handbook for a detailed discussion of this technology.

Alkylation unit H_2SO_4 A sulfuric acid alkylation unit uses concentrated sulfuric acid to catalyze the alkylation reaction, which builds smaller paraffins and olefins into larger molecules. The product alkylate is normally a high-octane gasoline blending component with low vapor pressure and sulfur content. There are two primary processes licensed for H_2SO_4 alkylation: (1) the cascade process licensed by ExxonMobil and M.W. Kellogg and (2) the Stratco effluent refrigerated process. Figure A.4 is a simplified process flow diagram for the cascade alkylation process. Refer to the topic "▶ Alkylation in Petroleum Processing" of this handbook for a detailed discussion of this technology.

American National Standards Institute Private, nonprofit organization that develops and administers voluntary consensus standards for products, services, processes, systems, and personnel in the United States. Abbreviated, ANSI

American Petroleum Institute US trade association for the oil and natural gas industry. Abbreviated, API. Develops and administers consensus standards for refining, among other activities. Advocates for the petroleum industry

American Society for Testing and Materials International standards organization. Develops and publishes voluntary, consensus technical standards for a wide

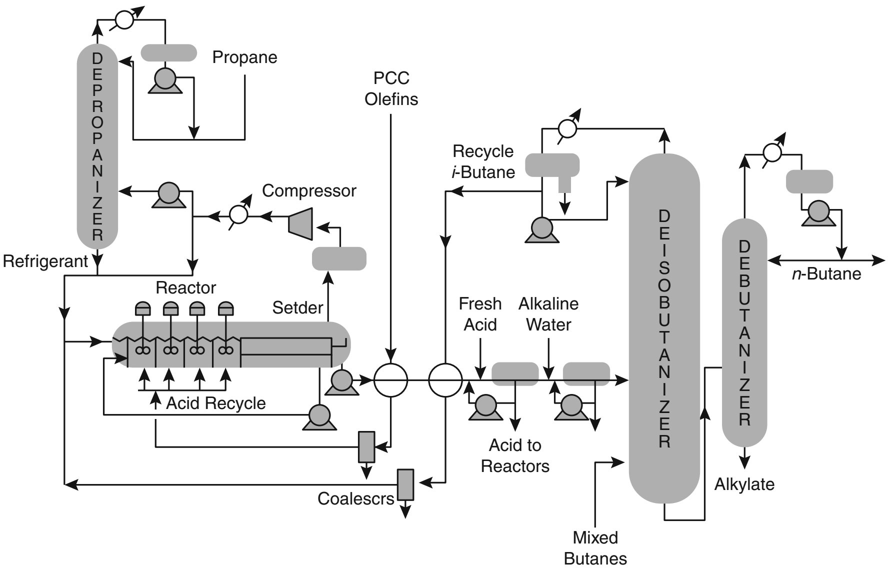


Fig. A.4 H_2SO_4 alkylation process

range of materials, products, systems, and services. Abbreviated, ASTM. Many fuel standards are set based on specific ASTM procedures.

Amine An amine is an organic nitrogen compound based on substitution of one or more organic groups around the nitrogen in ammonia. $NR^1R^2R^3$ where R^1, R^2, and R^3 are either hydrogen or an organic group like methane or ethanol. An example is diethanolamine, $(HOC_2H_4)_2NH$.

Amine solvents Several amines are used, in aqueous solutions, as solvents in the removal of hydrogen sulfide or carbon dioxide from refinery gas streams. There are many amine compounds used for this purpose. The more common of these are monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), methyl diethanolamine (MDEA), and diisopropanol amine (DIPA). Amine mixtures may also be used. The handbook chapter titled "▶ Refinery Gas Treating Processes" provides a detailed discussion of amine applications in refineries. The topic in the handbook on "▶ Hazardous Materials in Petroleum Processing" discusses handling of these chemicals.

Amine units These are process units which use chemically "basic" aqueous amine solutions to remove "acid gases," such as H_2S and CO_2, from refinery streams. The typical amine unit has an absorber tower coupled with a reboiled regenerator tower, with the amine solution circulating between the two towers. The handbook chapter titled "▶ Refinery Gas Treating Processes" details the processes and applications of amine units in refineries. The topic in the handbook on "▶ Hazardous Materials in Petroleum Processing" discusses handling of these chemicals.

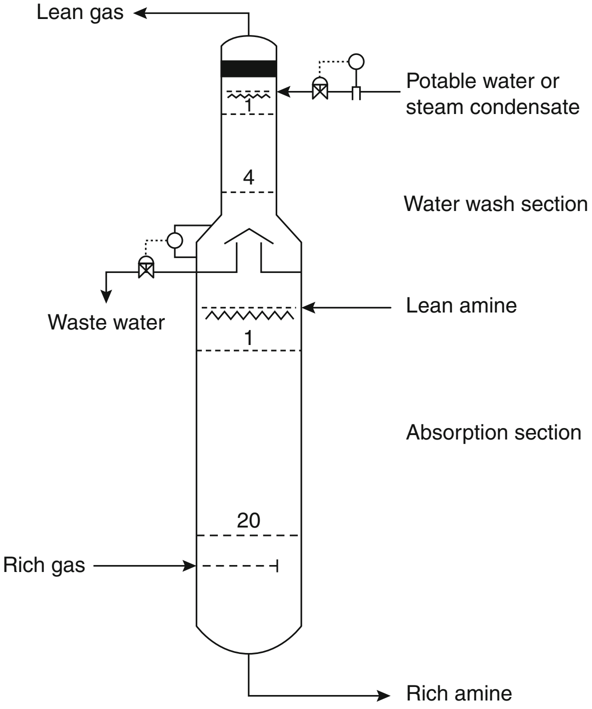


Fig. A.5 A typical amine absorber for MEA or DEA unit

Amine absorber An amine absorber is a tower in which a "lean" amine solution is contacted countercurrently with a stream containing a contaminated gas to scrub an "acid" gas contaminant from the stream. The "rich" solution produced is sent to a regenerator where the "acid" gas is stripped from the amine for further processing. The regenerated "lean" amine is recycled to the absorber. A typical amine absorber tower is illustrated in Fig. A.5.

Ammonia NH_3

Anaerobic Not requiring oxygen – generally refers to specific organisms

Analyzer A device for determining a specific chemical or physical property of a material. The analysis is then used for controlling the process or for ensuring that product specifications are met. Analyzers are found both offline (in the lab) and online. Online analyzers are often connected directly to the process control system.

Ancillary equipment Attachments and support systems required to make a main piece of equipment function properly, such as lubrication system, frame cooling, etc. Refer to the equipment chapter for some examples.

Anhydrous Refers to a chemical that is not in a water solution or a material that contains no water.

Anhydrous ammonia Ammonia is used in the refinery to neutralize vapor containing HCl at the overhead section of the atmospheric crude distillation tower. The ammonia is injected into the vapor spaces above the top four (or five) trays of the tower and into the overhead vapor line. The ammonia may be in the anhydrous form and introduced directly from cylinders or may be in the form of an aqueous solution. The aqueous form is injected from a storage bullet by means of metering pumps. Anhydrous ammonia is also used for NOx control in SCR and SNCR systems on flue gases.

Anhydrous hydrofluoric acid Anhydrous hydrofluoric acid (AHF) is a colorless, mobile liquid that boils at 67 °F at atmospheric pressure. It is used in the HF alkylation process. Refer to the topic "▶ Alkylation in Petroleum Processing" of this handbook for a discussion of its application in a refinery. The acid is hygroscopic, and its vapor combines with the moisture of air to form "fumes." It attacks glass, concrete, and some metals – especially cast iron and alloys that contain silica (e.g., Bessemer steels). The acid also attacks such organic materials such as leather, natural rubber, and wood. The handbook chapter titled "▶ Hazardous Materials in Petroleum Processing" provides a detailed discussion on handling this chemical.

Aniline point Minimum temperature at which equal volumes of aniline ($C_6H_5NH_2$) and the oil are miscible. The oil and aniline are heated until no more solids are present and then cooled until the first indication of cloudiness occurs. This is recorded as the aniline point. A low aniline point is indicative of a stock high in aromatics. A high aniline point indicates a paraffinic stock.

Annular flow A flow regime where a liquid film flows along the wall of the pipe with gas or dispersed flow at a higher velocity in the center core of the pipe. Refer to the chapter on equipment, section on two-phase pressure drop.

ANS Alaskan North Slope crude oil

ANSI American National Standards Institute

Anti-backflow Preventing the flow of fluids backwards through a process system. Backflow may result in overpressure or other undesired consequences. Refer to the discussions in the chapters on utilities and safety.

Anti-cross-contamination Preventing fluids from mixing together and contaminating each other. A major concern with utility systems. Refer to the chapter on utilities.

Anti-surge or antisurge In centrifugal compressors, this is a control system or technique that automatically keeps the compressor away from the unstable surge point, which can damage the machine.

APC Advanced process control

API (1) American Petroleum Institute; (2) application programming interface

API codes The American Petroleum Institute provides the industry with a set of standards which defines the design and measurement parameters that will be used in the petroleum industry. These codes cover such items as vessel design, oily water separators, boiler design, safety items, etc., and a number of laboratory test procedures for feed and petroleum products.

API gravity This item is used in the compilation of most crude assays (see chapter "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook). Although not a laboratory test, as such it is derived from the standard test to determine the specific gravity of a liquid. The correlation between specific gravity and degrees API is as follows:

$\text{Sp. Gr. or SG} = 141.5/(131.5 + {}^{\circ}\text{API})$

The specific gravity and the API are at 60 °F. Note API is always quoted in degrees.

API separator A device for gravity separation of oil and sludge from facility effluent water. Refer to the chapter on offsites.

Aqueous Water based. Normally refers to water solutions

Aqueous or aqua ammonia A water solution of ammonia, available in various concentrations

AR Analyzer recorder

ARAMCO Arabian American Oil Company

Arbitrage In economics, taking advantage of a price difference between two or more markets

Arbor coil A furnace design where the furnace tubes form an arch over the top of the firebox – like a garden arbor

ARC Analyzer recorder and controller

Arch The roof of a fired heater above the firebox in an upflow firebox

Aromatics Aromatics are present throughout the entire boiling range of crude oil above the boiling point of benzene, the compound with the lowest boiling point in the homologue. These compounds consist of one or more closed, conjugated carbon rings with one or more alkyl groups attached. The lighter aromatics such as benzene, toluene, and the xylenes are removed as products in the petroleum chemical plants (see the chapter on "▶ Non-energy Refineries in Petroleum Processing" in this handbook). In the energy petroleum refinery, these lighter aromatics are included in the finished gasoline products to enhance the octane rating of the products, but their maximum content in gasoline is usually limited (especially benzene). Catalytic reforming is aimed at converting the lower-octane compounds (predominately naphthenes) into the high-octane light aromatics. The heavier aromatic compounds are undesirable compounds in many products, such as kerosene, jet fuel, and many lube oils. In these cases, the aromatic compounds are either converted (dearomatizing hydrotreater for kerosenes) or removed by solvent extraction as in the case of lube oils. Figure A.6 illustrates a typical chemical plant configuration for aromatics production.

ARU Amine regeneration unit

As Arsenic

Ash or ash content (petroleum) Petroleum ash content is the noncombustible residue of a lubricating or fuel oil determined in accordance with ASTM D582 – also D874 (sulfated ash).

ASM Abnormal situation management – responding to an emergency

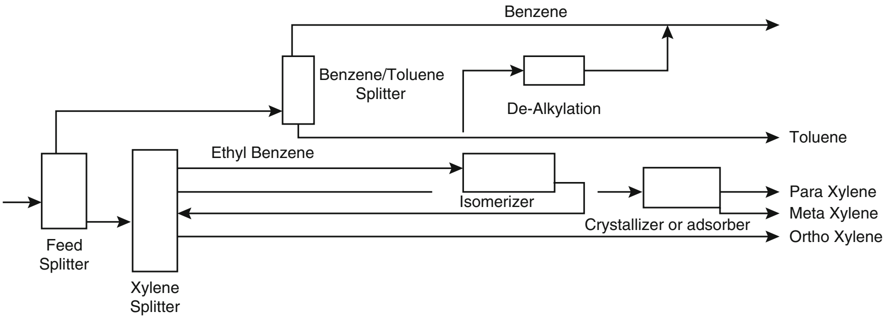


Fig. A.6 A typical aromatic plant configuration

ASME (American Society of Mechanical Engineers) The American Society of Mechanical Engineers has been a world leader in codes, standards, accreditation, and certification for over a century. These programs have now been extended to include the registration (certification) of quality systems in conformance with the standards set by the International Organization of Standardization (ISO). In the petroleum industry, this organization sets the quality requirements for vessel fabrication, piping, and in particular the boiler code among many other standard definitions.

ASO Acid-soluble oil(s) in the alkylation process

Asphalt Asphalt is a group of products produced from the vacuum distillation residue of crude oil. The products that make up this group have distinct properties that must be met by the treating of the vacuum residue. There are two major categories of asphalt products: (1) paving and liquid asphalt and (2) roofing asphalt. Refer to the topic "▶ Upgrading the Bottom of the Barrel" in this handbook for a detailed discussion of asphalt types and production.

Asphaltene Insoluble, semisolid or solid particles which are combustible and are highly aromatic (AKA "polyvinyl chicken wire"). Asphaltenes contain a high carbon/hydrogen ratio and entrap water, fuel ashes, and other impurities. They are primarily characterized by being insoluble in n-heptane and soluble in toluene.

Aspiration Normally refers to inhalation of a substance that is not a gas, such as aspiration of droplets of a chemical. May result in impaired lung function

Assay The crude oil assay is a compilation of laboratory and pilot plant data that defines the properties of a specific crude oil. At a minimum, the assay should contain a distillation curve for the crude and a specific gravity curve. Most assays however contain data on pour point (flowing criteria), sulfur content, viscosity, and many other properties. The assay is usually prepared by the company selling the crude oil. It is used extensively by refiners in their plant operation, development of product schedules, and examination of future processing ventures. Engineering companies use the assay data in preparing the process designs for petroleum plants they are bidding on or, having been awarded the project, they are now building. Refer to the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook for a detailed discussion of crude assays. The Appendix of this handbook titled "▶ Selection of Crude Oil Assays for Petroleum Refining" provides examples of assays for several common crudes. The crude assay should not be confused with the Fischer assay used for characterizing the potential yields from destructive distillation of oil shale and similar solids. Fischer assay is discussed in the topic "▶ Unconventional Crudes and Feedstocks in Petroleum Processing."

ASSE American Society of Safety Engineers

AST Aboveground storage tank

ASTM (American Society for Testing and Materials) ASTM is an organization that standardizes test methods for many types of materials. The ASTM tests and test methods provided by this body define and establish the quality of petroleum products and provide data on petroleum intermediate streams. This latter provision is used as a basis for refinery planning, operation, and engineering work associated with the refinery. Further details are given in the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook. Among the more important tests of interest to us in petroleum processing are:

- D56 – Tag closed flash point (the Abel flash)
- D86 – Standard Test for Distillation of Petroleum Products
- D93 – The Pensky–Martens flash-point, closed-cup test
- D97 – Cloud and pour points
- D129 – Sulfur content (Bomb Method)
- D189 – Conradson carbon content
- D323 – Reid vapor pressure
- D445 – Kinematic viscosity
- D613 – Cetane number
- D908 – Octane Number, Research
- D1160 – Gas oil distillation (subatmospheric)
- D1298 – Specific gravity (by hydrometer)
- D1837 – Weathering test for LPGs
- D2163 – Component analysis of LPGs (by gas chromatography)
- D2887 – Simulated distillation

ASTM distillation Refers normally to a D86 distillation, but may refer to any ASTM method of distillation testing. Be sure you know which distillation test is being used.

ASTM ON Motor octane number of a gasoline determined using the standard ASTM test apparatus. AKA MON and F-1

ASU (1) Air separation unit, separates nitrogen and oxygen out of the air; (2) activated sludge unit, for microbio treatment of wastewater

AT Analyzer transmitter

ATB Atmospheric tower bottoms – see atmospheric resid

Atmospheric crude distillation unit Often referred to simply as the "crude unit," the atmospheric crude distillation unit provides the initial separation of crude oil

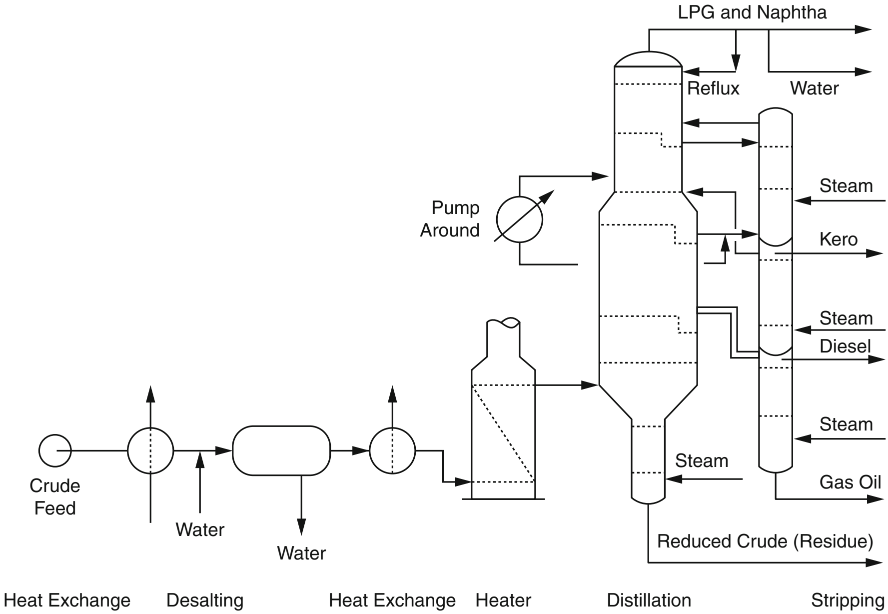


Fig. A.7 A typical atmospheric crude distillation unit

into distinct boiling ranges to be further refined into finished products. It is called "atmospheric" because it operates at a slightly positive gauge pressure, as opposed to the vacuum crude distillation unit that operates at low, negative gauge pressure. In practice, the atmospheric unit will operate at pressures between about 20 and 50 psig. The chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" discusses these units in detail. Figure A.7 illustrates a typical atmospheric crude unit configuration.

Atmospheric discharge In reference to relief systems, release of vapors and gases from pressure relief and depressurizing devices to the atmosphere

ATU Atmospheric tower unit. See "Atmospheric Crude Distillation Unit."

Autoignition and autoignition temperature Autoignition refers to spontaneous ignition of a compound or stock when exposed to air at a specific temperature without the presence of an ignition source. The autoignition temperature is the temperature at which autoignition will occur.

Auxiliary See "Ancillary Equipment." Often this refers to the utilities required to operate a major piece of process equipment.

Aviation gasoline A complex mixture of relatively volatile hydrocarbons with or without small quantities of additives, blended to form a fuel suitable for use in aviation reciprocating engines meeting ASTM or military specifications. The octane requirement for aviation gasoline is very high compared to road gasoline.

Aviation gasoline blending components Naphthas used for blending into finished aviation gasoline. May include straight-run gasoline, alkylate, reformate, benzene, toluene, and xylene

Axial (flow) compressor These compressors consist of bladed wheels that rotate between bladed stators. Gas flow is parallel to the axis of rotation through the compressor. A jet engine air compressor is an axial compressor example. Refer to the equipment chapter discussion of compressors.

AXL Arab extra-light crude oil

B

Back pressure In relief devices, back pressure is the pressure existing at the outlet of the pressure relief device due to pressure in the discharge system at the time the device must be relieved.

BACT Best available control technology – for the environment. Refer to the environmental chapter.

BACT box Operating limits on a heater to stay within emissions and permit limits

Baffle A dividing wall to separate two compartments or regions in equipment. For instance, in a separator, a baffle may be used at one end to keep a collected oil phase separated from an oil/water interface or two-phase zone in the separator. Baffles are also used to direct flow into desired patterns, such as in a heat exchanger. Refer to the chapter on equipment.

Baker correlations Calculation method for two-phase liquid/vapor flow in piping systems. Refer to the equipment chapter discussion of two-phase pressure drop.

Balanced safety relief valves A balanced safety relief valve incorporates means for minimizing the effect of back pressure on the performance characteristics-opening pressure, closing pressure, lift, and relieving capacity.

Barge A large, flat-bottomed boat used to move oil or other materials. A barge is not normally powered but must be pushed or pulled using a tug or towboat.

Barrels In the petroleum industry, the barrel is a standard form of measuring liquid volume. A barrel of oil is defined as 42 US gallons (1 US gallon equals 231 in^3). It is still used extensively in most countries but is being replaced particularly in European countries by the metric measures of cubic meters or liters or by weight measures like kg or tonnes (1,000 kg).

Barrels per calendar day See “BPCD and BPSD.”

Barrels per stream day See “BPCD and BPSD.”

Base lube oils This refers to a lube product that meets all lube specifications and is suitable for blending to meet performance specifications.

Basic process control system (BPCS) Primary control system that takes input from the process variables, compares the input to the setpoints, and outputs the appropriate control moves to the control elements in the field. See the chapter on controls.

BAT Best available technology. Similar to BACT for Europe. Refer to the environmental chapter.

Batch blending Adding components to a blend tank and then mixing the tank contents to achieve the target product properties. Refer to the chapter on offsites.

Battery limit (station) The interface between a process system and the rest of the facility. Often all the piping connecting a unit to external locations passes through a localized battery limit station where it can be isolated when necessary.

Bayonet heater A coil that is inserted into the side of a tank or tower to supply heat. The bayonet can be used for keeping the contents warm or for reboiling. Also called a stab-in heater. See the chapter on offsites.

BB Butane–butylene

Bbl or BBL or bbl Abbreviation for barrel (42 US gallons)

BCF Billion cubic feet

BCFD Billion cubic feet per day

Benfield process A licensed process employing a regenerable hot potassium carbonate solution to remove carbon dioxide from an acid gas stream. This process is used in steam-methane-reforming hydrogen plants and partial oxidation/gasification plants to clean up product gases. Similar to Catacarb process. The process is licensed from UOP.

BenSat Benzene saturation process

Benzene The simplest aromatic compound with a six-member carbon ring: C_6H_6. Benzene is found in many processes and petroleum products within a refinery and related facilities. In some cases, the product may be benzene that is deliberately recovered. In other streams, such as gasoline or reformate, the benzene is present as part of the hydrocarbon mixture.

BEP Best efficiency point (compressor or pump)

Berl saddle A type of mass transfer packing shaped somewhat like a saddle. Refer to the chapter on equipment, discussion of packed towers.

BFD Block flow diagram

BFOE Barrel of fuel oil equivalent – about 6.05 MMBtu, although the number may vary. The US IRS considers it 5.8 MMBtu. Other sources use 6.4 MMBtu.

BFW Boiler feed water

BHP Brake horsepower

Biochemical oxygen demand (BOD) Amount of oxygen required for biological organisms to digest the impurities in an effluent water stream. See the environmental chapter.

Biocide A chemical used to prevent microbiological growth. The most common biocides are chlorine and bleach. Uses in refineries include cooling water, potable water, sour water storage tanks, and certain product storage tanks (e.g., kerosene).

Biocrude Renewable oil made by destructive distillation of biomass – such as wood or corn stover pyrolysis

Biodiesel Applies to long-chain methyl, ethyl, and propyl esters, like FAME. These are made by transesterification of lipids with methanol. Refer to the discussions on renewables and unconventional stocks.

Bioethanol Ethanol made from a renewable source, usually corn or sugar cane.

Biofuel Any fuel derived from recently fixed carbon, usually plant or animal sources; this is in contrast to petroleum or other oils where carbon was fixed in the distant past.

Biooil See "Biocrude."

Bitumen Bitumen is the term often given to a sticky, black, highly viscous liquid or semisolid form of petroleum (essentially tar). It is also applied to untreated asphalt from the vacuum distillation of crude and the extract from the deasphalting unit. This is before the stream has been treated, with cut backs or by air blowing to make the various asphalt product grades. This term is also used for the extra heavy oils produced from tar or oil sands and other, similar deposits.

Blanket or blanket gas Providing a compatible vapor above a storage tank or vessel, normally to prevent contact with air or development of an explosive mixture. See offsites chapter.

Bleach Sodium hypochlorite solution

BLEVE Boiling liquid expanding vapor explosion

Blend component A stock that is to be used for blending a finished product.

Blank A solid metal disk inserted into a pipe (usually between flanges) to isolate equipment or a system and prevent flow. The terms blank and blind are often used interchangeably.

Blind or blind flange Like a blank, this is a solid metal disk inserted between flanges to isolate equipment or a system and prevent flow. The terms blank and blind are often used interchangeably.

BLM Bureau of Land Management

Blocked Preventing flow

Blocked discharge Applies to pumps or compressors when flow is prevented because a discharge valve is still closed or there is some other flow obstruction (like a blind) in the discharge piping. This is a controlling relief scenario in many cases.

Blocked-in Isolated by valve(s) so that flow is prevented.

Blowdown (or blow-down) (1) Purging of part of a process stream to manage buildup of impurities in the stream, e.g., blowdown from a cooling tower or steam generation system. Refer to the discussions in the chapter on utilities. (2) In some plants, this refers to the flare or waste gas system where relief valves and process vents can be safely routed. Refer to the discussion in the chapter on offsites. (3) In relief valves, blow-down is the difference between the set pressure and the resealing pressure of a pressure relief valve, expressed as a percent of the set pressure, or in psi or bar.

BLS Bureau of Labor Statistics

BMS Burner management system

BOD Biochemical oxygen demand – in wastewater. The BOD is a measure of the oxygen depletion due to wastes which are biologically oxidizable. Refer to the environmental chapter section on water.

BOE Barrel of oil equivalent – about 6.05 MMBtu HHV. See also "BFOE."

BOG Boil-off gas

Boiler feed water (BFW) Water that has been treated to make it suitable for use in a boiler to make steam. Refer to the chapter on utilities.

Boiling point analyzer This analyzer can be used to determine the 5 % or 95 % points of products for fractionation control purposes, for instance. Refer to the chapter on controls.

Boiling points and boiling range It is not feasible or necessary to separate the components of crude oil into individual chemical compounds. However, groups of these component mixtures are grouped together and identified by the boiling point at atmospheric pressure of the lightest component in the group and the boiling point of the heaviest component in the group. The group itself is called a cut, and the range of temperatures that identify it is called the boiling range or cut range. These can be related to the crude TBP curve to determine its yield on that particular crude (see the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook).

BOM Bill of materials

BOQ Bill of quantities

Bottoms or botts Refers to the material produced from the bottom of a distillation column. In an atmospheric crude distillation unit, this would be the atmospheric residuum. In a propane–butane splitter, the butane product would be the bottoms or botts.

Bourdon tube A mechanical pressure measuring device used in most local pressure gauges. Refer to the chapter on controls.

Box cooler A type of exchanger with tubes immersed in a water bath. Refer to the equipment chapter discussion of heat exchangers.

BPC (1) Basic process control – normally the DCS system or individual loop controllers that are active all the time as opposed to systems that act only in hazardous situations. (2) Blend property control

BPCD and BPSD BPCD is the measure of throughput or stream flow based on an operation over 1 year of 365 days. BPSD is the rated throughput of a plant or the rate of a stream over the total operating days in the year. BPCD is barrels per calendar day, and BPSD is barrels per stream day. BPSD is defined as BPCD divided by the service factor as a fraction. The service factor is the fraction of time over a calendar year that a unit is operating (see "Service Factor").

BPCS Basic process control system

BPD Barrels per day

BPSD Barrels per stream day. See "BPCD and BPSD."

BRC (1) Basic regulatory control – the normal control system for a unit; (2) blend ratio control

Breakeven The point at which product value = cost of production

Bridgewall In a fired heater – see Arch and the discussion in the equipment chapter section on fired heaters.

Bright stocks (lube oils) These are processed from the raffinate of the vacuum residue deasphalting unit. (See the chapter on non-energy refineries in this handbook.)

Bromine number The bromine number of petroleum distillates is determined by electrometric titration in accordance with ASTM laboratory test D1159. It is a measure of olefins in the sample according to the equation:

$\% \text{ Olefins} = (\text{Bromine number} \times \text{molecular wt. of olefins})/160$

BS&W Bottom sediment and water – settles out of oil during storage. Standard test by centrifuge

BTEX Benzene, toluene, ethylbenzene, and xylene

Btu or BTU British thermal unit – how we measure heat in refineries in the United States

BTX Benzene, toluene, and xylenes

Bubble cap A mass transfer/contacting device consisting of an inverted, slotted cup (or cap) fitted over a riser with an annular gap. Vapor is forced to move through a path that contacts it with a standing liquid level around the cap. Refer to the chapter on equipment, distillation design discussion.

Bubble flow (AKA froth flow) Flow regime in which bubbles of gas are dispersed in a primarily liquid phase with the gas moving about the same velocity as the liquid. Refer to the chapter on equipment, two-phase pressure drop discussion.

Bubble point Bubble point is the temperature and pressure at which a hydrocarbon begins to boil. Refer to the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook for an example of how this definition is used in setting a reflux drum pressure.

Bulk terminal Facility used primarily for the storage and/or marketing of petroleum products with stores of oil in bulk tankage

Bullet or storage bullet A horizontal, cylindrical vessel generally used for storage of high-vapor-pressure materials such as propane or ammonia

Bunker fuel Heavy residual fuel oil used in ships. See "#6 Fuel Oil."

Burner The purpose of a burner is to mix fuel and air to ensure complete combustion in a fired heater. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for a detailed discussion of burner designs and critical factors. Additional discussion on burner design factors affecting emissions are included in the topic "▶ Environmental Control and Engineering in Petroleum Processing" in this handbook.

Burner management system A safety system to avoid conditions that can result in an explosion or other problems in a fired heater or boiler

Burner tip The tube through which fuel is introduced into a burner – normally, it has several small holes in it of specific sizes and orientations

Bernoulli principle The observation that a stream's velocity and pressure are inversely related. High flow velocity results in reduced pressure in the high-velocity streamline.

Burst pressure Burst pressure is the value of inlet static pressure (or the differential pressure, considering backpressure) at which a rupture disk device functions.

BWON Benzene waste operations NESHAP

Bz Shorthand for benzene

C

C/H ratio Carbon/hydrogen molar or weight ratio - be careful of the units used

Ca Calcium

CAA US Federal Clean Air Act. Refer to the environmental chapter.

CAAA US Federal Clean Air Act amendment

CAD Computer-aided design

CADD Computer-aided drafting design

CAE Computer-aided engineering

CAF Vapor capacity factor in a distillation tower. Refer to the equipment chapter, section on distillation.

California Air Resources Board (CARB) State agency in California responsible for regulating motor fuels in that state. Generally, CARB sets the fuel specification trends others follow somewhat later.

Calorie The amount of heat required to raise the temperature of 1 g of water by 1 °C, at or near maximum density.

Calorific value Amount of heat produced by the complete combustion of a unit weight of fuel. Usually expressed in calories per gram or BTUs per pound; the latter being numerically 1.8 times the former

Capacity-factored estimate Capital facility cost estimate method that uses estimated unit capacities and a scaling factor applied to known unit costs to estimate cost for a new facility. This method requires the least information to apply but provides the least accurate estimate. It is normally used very early in screening studies for capital projects.

Car seal A numbered plastic or metal seal that provides a method for tracking proper positioning of a valve or other equipment. The car seal must be broken to operate the sealed device. Normally these are administrative controls.

CARB diesel Term which refers to the diesel standard mandated for sale by the California Air Resources Board. It includes tough standards for sulfur and for very low aromatics.

CARBOB California version of RBOB – meets additional specs

Carbon monoxide CO

Carbon residue Carbon residue is a measure of the coke-forming tendencies of oil. It is determined by destructive distillation in the absence of air of the sample to a coke residue. The coke residue is expressed as weight percent of the original sample. There are two standard ASTM tests, Conradson carbon residue (CCR) and Ramsbottom carbon residue (RCR).

Carbonyl sulfide (COS) Sulfur compound found in cracked products (like FCC or coker) and other sour gases with some oxygen exposure. COS must sometimes be removed from these gases when they are used as fuel.

Carcinogen or carcinogenic Substance (or property of a substance) that can cause cancer

CAS Chemical abstract services

Cascade control A control system with two or more controllers. The "master controller(s)" provides a setpoint to the "slave controller."

Casing The outer shell of a fired heater

Cat cracker See "FCC" or fluid catalytic cracking.

Catacarb A licensed process employing a regenerable hot potassium carbonate solution to remove carbon dioxide from an acid gas stream. This process is used in steam-methane-reforming hydrogen plants and partial oxidation/gasification plants to clean up product gases. Similar to Benfield process. Catacarb is licensed by Eickmeyer & Associates.

Catalyst A substance that speeds up a reaction and directs the course of the reaction, but is not consumed by the reaction.

Catalyst fines Hard, abrasive crystalline particles of alumina, silica, and/or alumina–silica that can be carried over from the fluidic catalytic cracking process of residual fuel stocks. Particle size can range from submicron to greater than 60 microns in size. These particles become more common in the higher-viscosity marine bunker fuels from FCC products.

Catalytic hydrocracking See "Hydrocracking."

Catalytic hydrotreating See "Hydrotreating."

Catalytic reforming unit A refining process that rearranges naphtha-range hydrocarbons to increase octane. Hydrogen is a by-product. The reformate product contains no sulfur and has an increased aromatic content. It is applied to naphtha boiling range stocks to produce gasoline blendstock. There is detailed discussion of this process in the chapter "▶ Catalytic Reforming in Petroleum Processing" of this handbook. Figure C.1 illustrates a typical semi-regenerative catalytic reformer.

Caustic or caustic soda Sodium hydroxide (NaOH) in solution or solid form

CBO Carbon black oil

CBOB Conventional gasoline blendstock intended for blending with oxygenates downstream of the refinery where it was produced. CBOB must become conventional gasoline after blending with oxygenates. Motor gasoline blending components that require blending other than with oxygenates to become finished conventional gasoline are reported as all other motor gasoline blending components. Excludes reformulated blendstock for oxygenate blending (RBOB)

CBS Cost breakdown structure

CBT Computer-based training

CCB Central control building

CCPS Center for Chemical Process Safety – a group under the American Institute of Chemical Engineers that defines process safety practices – sets de facto standards for process safety.

CCR (1) Continuous catalytic reformer; (2) central control room; (3) Conradson carbon residue

CCTV Closed circuit television

CD Consent decree

CDCIR Community Documentation Centre on Industrial Risk

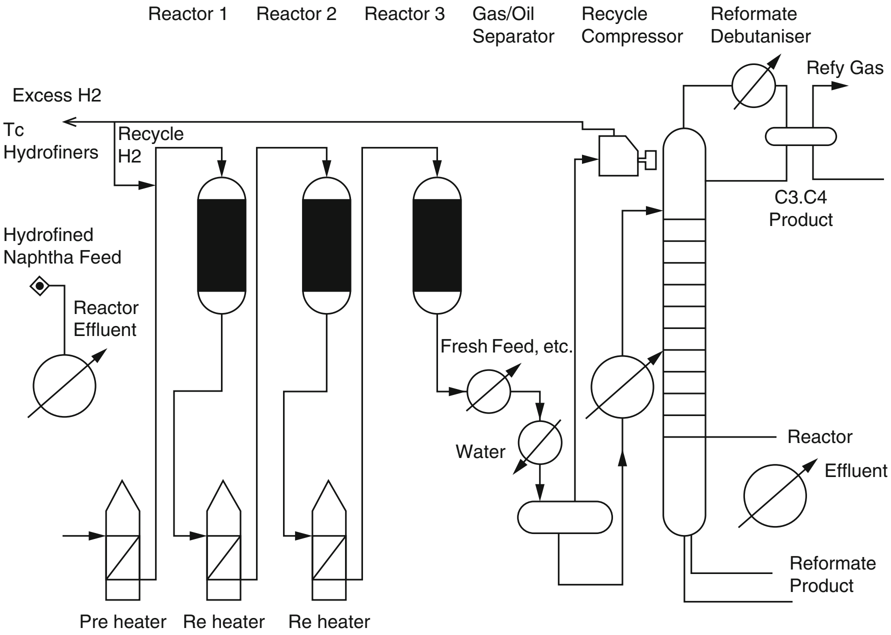


Fig. C.1 A typical catalytic reforming unit

CE Civil engineer or engineering

CELD Cause–effect logic diagram

Celsius Europeans use this term instead of centigrade (see below) to honor physicist Anders Celsius who developed a temperature scale that uses the freezing and boiling points of water as references.

CEM Continuous emission monitor

CEMS Continuous emission monitoring system

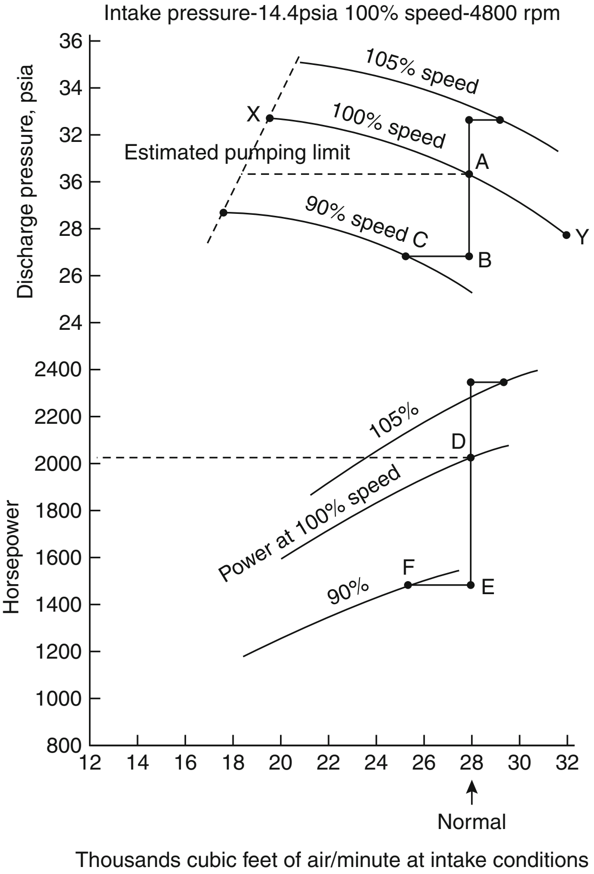
Centigrade Temperature scale based on 0° for the temperature at which water freezes and 100° for the temperature at which water boils. See "Celsius" above. This term is accepted and used in North American chemical textbooks; so which term you use may depend on your location, but both are abbreviated with a degree symbol and capital C (°C).

Centipoise 0.01 poise or centistokes times specific gravity at the test temperature. Abbreviated cP or cPs

Centistoke 0.01 stoke (see "Stoke"). Abbreviated cS or cSt

Centrifugal compressors Compressors which use centrifugal force or action to increase the pressure of a gas. This type of compressor consists of an impeller or impellers rotating at high speed within a casing. Centrifugal compressors are widely used in the petroleum, gas, and chemical industries primarily due to the large volumes of gas that frequently have to be handled. Long continuous

Fig. C.2 Typical performance curves for a centrifugal compressor



operating periods without an overhaul make centrifugal compressors desirable for use in petroleum refining and natural gas applications. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for a detailed discussion of centrifugal compressors. A typical centrifugal compressor performance curve is illustrated in Fig. C.2.

Centrifugal pump A very wide class of pumps in which pumping of liquids or generation of pressure is effected by a rotary motion of one or several impellers. The impeller or impellers force the liquid into a rotary motion by impelling action, and the pump casing directs the liquid to the impeller at low pressure and leads it away under a higher pressure. Refer to the chapter on equipment, discussion of pumps.

Centrifuge A machine using centrifugal force produced by high-speed rotation for separating materials of different densities. Applied to diesel engine fuels and lubricating oils to remove moisture and other extraneous materials, among other uses.

CEO Chief executive officer

CEP Chemical Engineering Progress magazine (from AIChE)

CERCLA US Comprehensive Environmental Response, Compensation, and Liability Act

Cetane A measure of the engine combustion characteristics of a fuel in a diesel engine. Higher cetane is desired. Can be measured in an engine (cetane number) or calculated (cetane index)

Cetane index An empirical measure of ignition quality. Defined as the percentage by volume of cetane in a mixture of cetane and methyl naphthalene which has the same ignition quality when used in an engine as a fuel under test.

Cetane number Normally refers to cetane values measured by a CFR diesel testing engine. See "Cetane."

CFC Chlorofluorocarbons

CFL Compact florescent light

CFPP Cold filter plugging point in diesel fuels. This is a measure of a fuel's cold weather plugging potential, which can cause engine failure from lack of fuel.

CFR US Code of Federal Regulations

CFR diesel testing unit A standard engine employed in making cetane number tests of diesel engine fuels

CFS Cubic feet per second

CH_4 Methane

Channel In a shell-and-tube exchanger, the channel bolts onto the tube side of the tube sheet and provides the route into and/or out of the tubes.

Characteristic curve Graph or curve that relates pump or compressor flow rate to head, discharge pressure, or differential pressure at various speeds or other parameters. Refer to the equipment chapter, sections on pumps and compressors.

Charge Feedstock to a unit

Charge capacity The input (feed) capacity of the refinery processing facilities

ChE Chemical engineer or engineering

Check valve or check A valve that allows fluid flow in only one direction and stops or "checks" any flow in the reverse direction

Chemical sewer Sewer system designed to accept chemical wastes from a facility and convey them to treatment or reuse

Chemiluminescence analyzer This type of analyzer works for compounds like NO, NO_2, NO_x, and O_2. The analyzer makes use of the luminescence when the compounds are reacted with ozone.

Chiksan joint Mechanical swivel joint that seals piping segments, normally used inside a storage tank. FMC brand name

CHOPS Cold heavy oil production with sand. See the chapter on unconventional crudes.

CHPS Cold high-pressure separator

CHPV Cold high-pressure vapor

Chronic Long-term or lingering

CII Construction Industry Institute

CIPS Cold intermediate pressure separator

Cl Chloride

Claus process The most common process for sulfur recovery to reduce air emissions. Uses the reaction between H_2S and SO_2 to produce a pure sulfur product. Refer to the environmental chapter section on air pollution.

Clearance pocket In a reciprocating compressor, a dead-ended, fixed volume that can be opened or closed by a valve to change the equivalent displacement and thus capacity of the compressor. Refer to the chapter on equipment, section on reciprocating compressors.

Cloud point(s) The cloud point of a transparent or semitransparent oil sample is the temperature at which a cloud or mist forms in the sample. The method is ASTM D2500 and is carried out in the laboratory where a sample of the oil is reduced in temperature by submerging the sample in its container first in ice then in iced salt and finally in a solid CO_2 bath. The container is a cylindrical glass vessel about 19 mm in diameter by 100 mm deep. The vessel is filled to a mark about 80 mm deep and a low-range thermometer inserted so the bulb is about 10–12 mm below the sample surface. Temperature readings are taken at every stage. Readings are more frequently taken in the last cooling stage, and that temperature at which the sample becomes misty is taken as its cloud point.

Clarifier A machine used for a liquid-sludge separation in which the particles with a higher specific gravity are separated from the lower specific gravity of the liquid. A clarifier bowl has one outlet for the light phase oil; the heavier phase particles are retained on the bowl wall. Similar to a centrifuge.

CLPS Cold low-pressure separator

CMA Chemical Manufacturers Association

CMS Continuous monitoring system

CO (1) Carbon monoxide; (2) change order

Co Cobalt

Coagulation Process to cause suspended impurities in effluent or wastewater to form larger particles and drop out. Refer to the chapter on offsites.

Coal A readily combustible black or brownish-black rock whose composition, including inherent moisture, consists of more than 50 % by weight and more than 70 % by volume of carbonaceous material. It is formed from plant remains that have been compacted, hardened, chemically altered, and metamorphosed by heat and pressure over geologic time.

COBRA Consolidated Omnibus Budget Reconciliation Act

COD (1) Chemical oxygen demand – in wastewater. The COD is a measure of the oxygen depletion due to organic and inorganic wastes which are chemically oxidizable. (2) Cutoff date

COE (1) Center of excellence; (2) common operating environment

Co-generation (or cogeneration or cogen) Generating both power and steam (normally) in a utility system. Refer to the chapter on utilities.

COGS Cost of goods sold

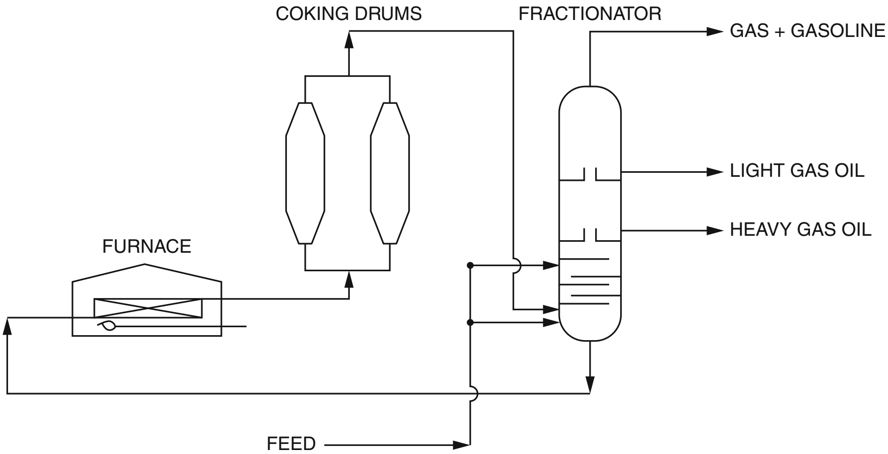


Fig. C.3 A delayed coker

Coke Coke is formed in the processes to convert the residuum fuels to the more desirable distillate products of naphtha and lighter through to the middle distillates. By far, the largest production of coke is the sponge coke from the delayed coking process. Uncalcined sponge coke has a heating value of about 14,000 Btu/lb and is used primarily as a fuel. High-sulfur sponge coke is popular for use in cement plants since the sulfur reacts to form sulfates. Sponge coke is calcined to produce a coke grade suitable for anodes in the aluminum industry.

Coker Resid thermal cracking process. See "Coking Process."

Coking process Coke is formed in the processes to convert the residuum fuels to the more desirable distillate products of naphtha and lighter through to the middle distillates. Coking is essentially destructive distillation of heavy, residual oil (usually vacuum resid) at high temperature and low pressure. The process produces gases, oils, and a residual solid "petroleum coke." There are two coking processes: delayed (Fig. C.3) and fluid coking (Fig. C.4). Delayed coking is the simplest and most common. Refer to the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook for additional details.

Coking or cracking propensity Tendency of an oil to form coke or thermally crack when heated, as in a furnace

Cold flash separator In many high-temperature and high-pressure hydrocracker or hydrotreater units, the reactor effluent is reduced in pressure and temperature in several stages. The last of these stages is the cold flash separation stage. Figure C.5 shows a common cold flash separator arrangement in a hydrotreater.

Cold properties (or cold flow properties) Refer generically to hydrocarbon properties at low temperatures. These are important in middle distillate fuels (jet, diesel) and fuel oils to permit the materials to be handled at low or winter

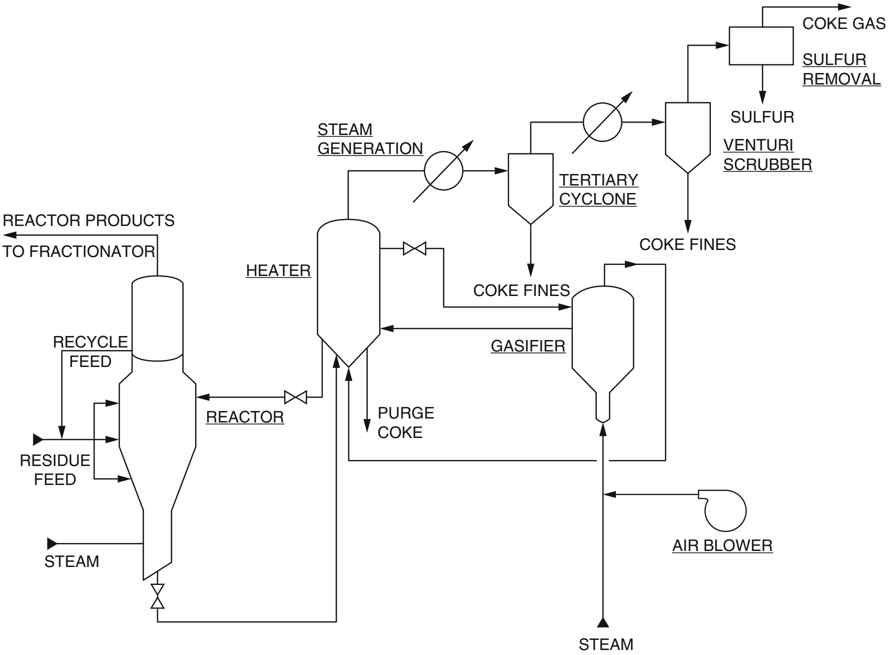


Fig. C.4 A flexi (fluid) coking process

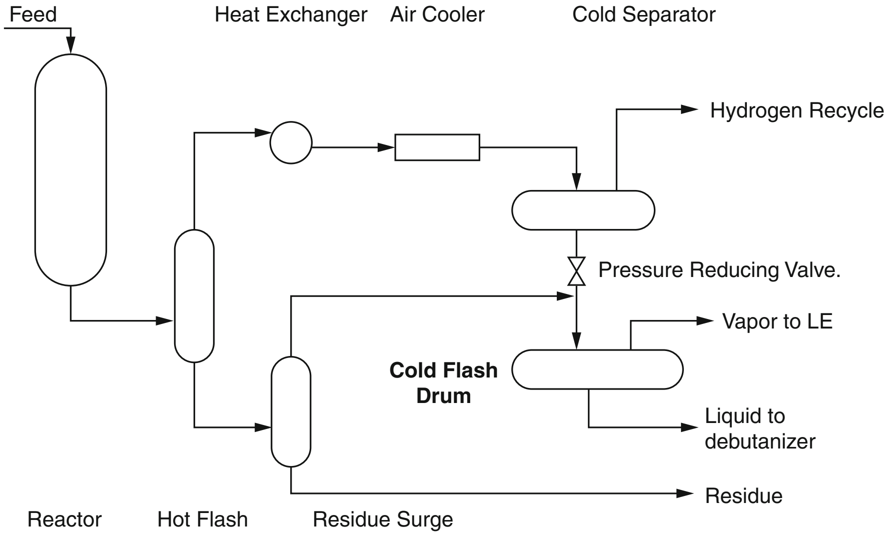


Fig. C.5 Typical residue hydrocracker with cold flash drum temperatures and to avoid engine failure due to lack of fuel flow. Typically, cold properties include pour point, cloud point, freeze point, viscosity, and the cold filter plugging point.

Column Generally refers to a distillation, absorption, or stripping tower/vessel because of the tall cylindrical shape of this equipment (they look like columns). Refer to the equipment chapter, section on tower and distillation design.

Commingling Term which generally applies to the mixing of two petroleum products with similar specifications. Most branded gasoline firms require that their product not be commingled to preserve the integrity of the brand. May also refer to mixing two streams within a unit to achieve specific properties

Commissioning In projects, commissioning describes the activities necessary to prepare a process unit for operation. This includes line cleaning, refractory curing, catalyst/sorbent loading, etc.

Common carrier A pipeline or transport company which has government authority to move product for hire, operating like a public utility with standard rates for various shipments.

Complex refinery Also known as a "full conversion" refinery; this is a type of refinery configuration with process capability for conversion of nearly all crude oils to high-value products. Complex refineries may also make petrochemicals in addition to fuels and other petroleum products. These refineries include crude distillation, hydroprocessing, reforming, cracking, resid conversion, octane/cetane improvement, and other processes.

Component balances Component balances are derived from the TBP of the material requiring the balance. These component balances are derived by splitting the TBP into mid-boiling point pseudo components (see the topic chapter "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook for definition of pseudo components and mid-boiling points). The purpose of component balances is to calculate more accurately fractions of the feed material properties in terms of specific gravity, sulfur content, mole weight, cloud and pour points, and the like. Figure C.6 illustrates a hypothetical TBP curve of a middle distillate fraction. This fraction has been broken up into six pseudo components, with mid-boiling points of 410–591 °F. By referencing the crude feed assay from which this fraction originates, the SG of each component can be read off as °API. If it is a well-produced assay, the component sulfur and cloud and pour points can also be read off for each pseudo component. The volume of each pseudo component forming the fraction is shown as the "x" of the TBP curve.

Condensate (1) Material condensed from vapor anywhere in a process. (2) A naturally occurring gaseous hydrocarbon that liquefies when cooled to surface temperature. Condensate is usually considered to be a part of crude oil production. (3) Frequently refers to steam that has been condensed to liquid water.

Condensers (e.g., shell and tube) In the chemical process, plant vapors are condensed either on the shell side of a shell and tube exchanger, the tube side of an air cooler, or by direct contact with the coolant in a packed tower. By far

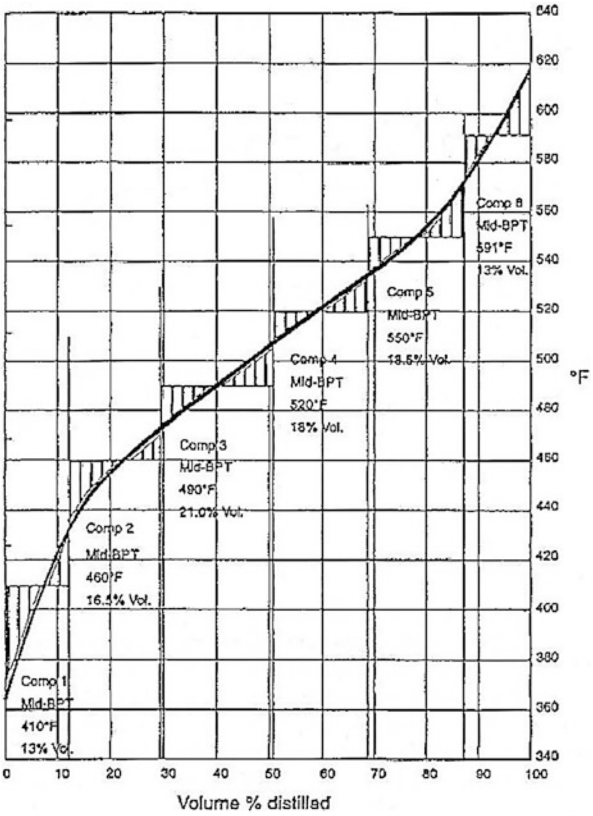


Fig. C.6 A typical component breakdown

the most common of these operations are the first two listed. In the case of the shell and tube condenser, the condensation may be produced by cooling the vapor by heat exchange with a cold process stream or by water. Refer to the handbook topic chapter "▶ Process Equipment for Petroleum Processing" for a detailed discussion of heat exchangers and exchanger design.

Conductivity A measure of the ability of a material to conduct electricity. Measurement units are usually mhos/cm. Conductivity prevents the accumulation of static electric charge during handling, which can lead to explosions with hydrocarbon stocks. Middle distillates, like jet fuel and diesel, often require conductivity additives for handling. Crudes with very high conductivity, like shale oil, are often hard to desalt because the conductivity interferes with the development of electric charges on the suspended water droplets.

Cone-roof tank A storage tank having a fixed, conical-shaped roof. Refer to the chapter on offsites.

Configuration In a refinery, the arrangement of refinery process units to make the desired products from crudes. Configuration establishes the capabilities of the refinery and greatly determines potential profitability.

Confined space A space large enough to enter with limited access and not intended for occupancy. Such spaces also include spaces with configurations that could trap personnel, such as sloping bins. Refer to the chapter on safety.

Conradson carbon (ASTM D189) A measure of the coke generated from an oil when heated at low pressure in the absence of air. This is a rough indication of potential coker yield and the tendency to form coke (carbon deposits) on a catalyst when hydrotreated or cracked. See the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook.

Contactor A generic term normally applied to a mass transfer tower, for intimately mixing and separating two streams to transfer components from one stream to another in an equilibrium stage process. An H_2S absorber for fuel gas is an example of a vapor/liquid contactor. There are liquid–liquid contactors as well, such as those used for removing H_2S with amine solutions from liquefied petroleum gases (propane, butane, etc.).

Control element A device that performs a control function, such as a control valve or variable speed controller.

Control loop The basic device arrangement from process sensing element in the field to the process controller to the final field control element (like a control valve)

Control system architecture Refers to essentially a map of how the process control system is assembled. Architecture would include what devices are tied into the process control system or network.

Control valves Control valves are specially designed valves with actuators which enable automatic, remote control of the valves. They are used throughout the process and oil refining industries to control operating parameters, such as flow, temperature, pressure, level, and composition. Refer to the handbook chapter on "▶ Process Controls in Petroleum Processing" for a detailed discussion of these critical control elements in petroleum processing. Figure C.7 illustrates the key parts of a typical control valve.

Control valve characteristic The relationship between a control valve position (% open) and the amount of flow the control valve can pass (% of maximum). Refer to the chapter on controls.

Control valve response The time required for a control valve to respond to a control system output signal.

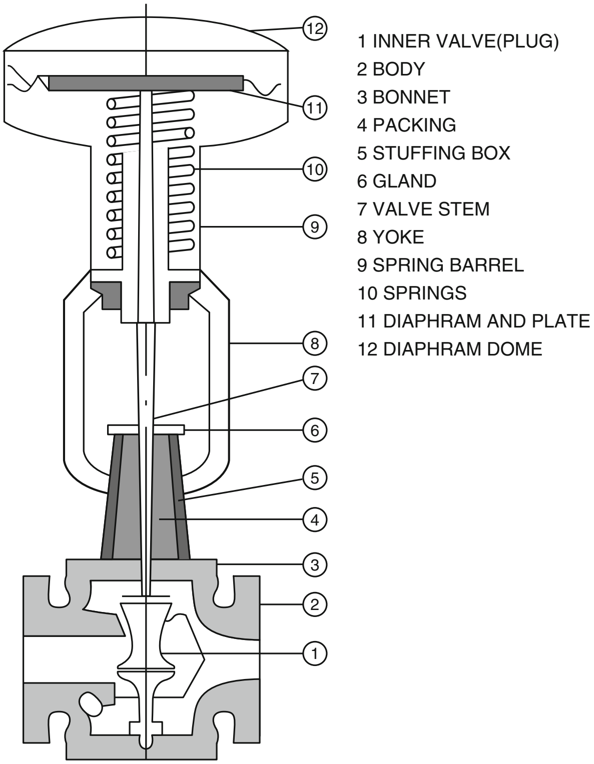
Convection section The portion of a fired heater through which the hot flue gases travel on their way to the stack and exchange heat with other fluids

Convection tube or coil Tubes in the convection section of a fired heater that are heated by exchange with hot flue gases

Conventional crude Crude produced from the types of sources that have been traditionally used where a producer can just drill, pump, and separate the produced fluids

Conventional safety relief valve A conventional safety relief valve is a closed bonnet pressure relief valve that has the bonnet vented to the discharge side of the valve. Refer to the safety chapter.

Fig. C.7 A doubled seated control valve



Coprocessing Processing two or more dissimilar materials together in the same process units. For instance, running conventional diesel and vegetable oil in the same hydrotreater at the same time to produce a green diesel stock is coprocessing.

Cooling water A circulating or once-through water system used for process or equipment cooling. Refer to the discussion in the chapter on utilities.

Cooling tower Equipment that generates cool/cold water for use in process cooling services through evaporation of part of the water. Refer to the chapter on utilities.

Coproduct A by-product or additional product from a process

Correlation coefficient (1) A statistical measure of how well a correlation fits a specific data set. A correlation coefficient of 1 would indicate a perfect 1-to-1 relationship; (2) more specifically, a statistical factor measuring how well any two markets (i.e., a cash market and a futures market) move in unison.

Corrosion Detrimental change in the size or characteristics of material under conditions of exposure or use. It usually results from chemical action either regularly and slowly, as in rusting (oxidation), or rapidly, as in metal pickling.

Corrosivity Hazardous waste characteristic of being corrosive to materials or skin – generally refers to waste caustic or acidic materials. Refer to the environmental chapter section on hazardous wastes.

Corrugated plate interceptor A device for enhancing gravity separation of oil from facility effluent water using multiple, parallel plates. Refer to the chapter on offsites.

Cost estimating Estimating the cost of facilities or services prior to purchase or construction. There are several types of cost estimates used. The scope and accuracy of the different types of estimates depend on the available detail on which to base the estimate. Details about cost estimating as it applies to process plants, including oil refineries, are discussed in the chapter titled "▶ Petroleum Processing Projects" in this handbook.

Cost-plus A pricing mechanism, commonly used by contracting and transportation firms. Creates a buying price for a good or service by starting with actual cost to supply the good or service and adding a markup

COT (1) Coil outlet temperature from a fired heater; (2) critical operating task

Counterflow cooling tower A cooling tower where air flows upward through a downward shower of water to cool the water. Refer to the chapter on utilities.

Coupon A method for monitoring corrosion by subjecting a piece of test metal to the same conditions as the process and testing the metal for properties.

CPE Continuing professional education

CPI (1) Continuous process (or performance) improvement; (2) chemical process industries; (3) cost performance index; Corrugated plate interceptor for oil/water separation

CPM (1) Critical path method; (2) certified purchasing manager

CPQRA Chemical process quantitative risk analysis

CPR Cardiopulmonary resuscitation

CPU Central processing unit

CPVC Chlorinated polyvinyl chloride

CQI Continuous quality improvement

Cr Chrome

Crack Difference between product value and cost in \$/bbl. Gross measure of margin. Tracked generically. (1) Light oil crack/3:2:1 = 2 RU gasoline bbls +1 ULSD bbl – 3 WTI bbls prices converted to per bbl crude; (2) gas crack =1 bbl gasoline – 1 bbl WTI prices; (3) heat crack = ULSD price – WTI crude price per bbl; (4) various other cracks are defined.

Crack spread See "Crack"

Cracked Refers to a petroleum product produced by a secondary refining process such as thermal cracking or visbreaking processes which yield very-low-quality residue and gasoil and lighter stocks

Cracking refinery A refinery configuration which includes gasoil conversion to high-value products in addition to crude distillation, hydrotreating, and reforming. Cracking refineries do not substantially convert any residuum instead produce resid as fuel oil or tar/asphalt.

Cradle A device to support a tube in a fired heater.

CRC Chemical Rubber Company - original publishers of the Handbook of Chemistry and Physics

Crossflow cooling tower A cooling tower where air flows horizontally through a packed section with water flowing downward through the packing. Refer to the chapter on utilities.

Crossover Piping used to connect the radiant with the convection section of a fired heater; usually external to the heater. Refer to the chapter on equipment, section 6.

CRU Catalytic reforming unit

Crude distillation unit Initial separation unit in a refinery where the crude oil is fractionated into components by boiling ranges for further processing

Crude oil or crude Crude oil is a mixture of hydrocarbon compounds produced from underground geological formations by various production methods. These compounds range in boiling points and molecular weights from methane as the lightest compound to those whose molecular weight will be in excess of 500. In addition to the hydrocarbons, there are impurities like sulfur, nitrogen, and metals. Refining and petroleum processing take the raw crude and convert it to useful products. The topic chapter "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook describes crude in some detail. The balance of this book focuses on the processes to convert the wide variety of crudes to products.

Crude unit See "Crude Distillation Unit" and "Atmospheric Crude Distillation Unit."

Cryogenic (AKA cryo) Processing fluids at very low temperatures where things that are normally gases can be liquefied

CS Carbon steel

CSA Canadian Standards Association

CSC (1) Car sealed closed; (2) commercial subcommittee; (3) customer support center

CSCC Caustic stress corrosion cracking

CSO Car sealed open

cSt or CST or CS Centistokes at 50 °C (or other temperatures as defined

CTE Coefficient of thermal expansion

CTL Coal to liquids

CTU Crude topping unit

Cu Copper

CUI Corrosion under insulation

Cumulative cash flow and present worth There are several methods of assessing profitability based on discounted cash flow (DCF), but the most reliable yard stick is a return on investment method using the present worth (or net present value) concept. This concept equates the present value of a future cash flow as a product of the present interest value factor and the future cash flow. Based on

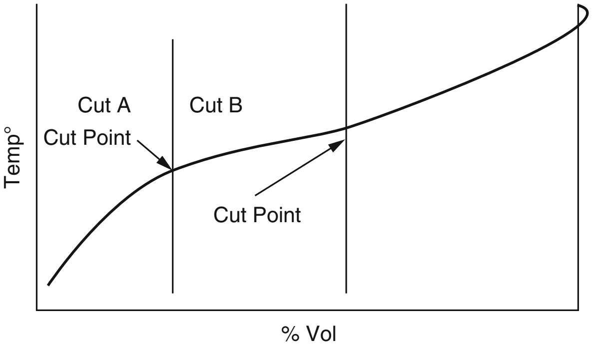


Fig. C.8 Typical cut points on a TBP curve

this concept, the return on investment is that interest value or discount factor which forces the cumulative present worth value to zero over the economic life of the project. Refer to the chapter titled "▶ Petroleum Processing Projects" in this handbook for a detailed discussion of this evaluation.

Curing Preparation of refractory for operation by careful dryout. Refer to the chapter on equipment, section on fired heaters.

Cut Material boiling in a specific temperature range. See also "Cut Point."

Cut point(s) A cut point is defined as that temperature on the whole crude (or any other) TBP curve that represents the limits (upper and lower) of a fraction to be produced. Consider the curve shown in Fig. C.8 of a typical crude oil TBP curve. A fraction with an upper cut point of 100 °F produces a yield of 20 vol% of the whole crude as that fraction. The next adjacent fraction has a lower cut point of 100 °F and an upper one of 200 °F; this represents a yield of $50-20\ \% = 30$ vol% on crude.

Cutter stock or flux stock A petroleum stock which is used to reduce the viscosity of a heavier residual stock by dilution.

CUWI Corrosion under wet insulation

CV (1) A measure of valve size/capacity [C_v], valve flow coefficient (see the chapter on controls and the appendix to that chapter); (2) control valve abbreviation; (3) control volume in fluid calculations; (4) controlled variable in control systems

CVU Crude vacuum unit

CWA US Federal Clean Water Act

CWMS Crinkled wire mesh screen – for liquid demisting in vapor phase or water coalescing in liquid phase. Refer to the chapter on equipment, section on vessels and drums.

CWO Chain wheel operated

CWR Cooling water return

CWS Cooling water supply

Cycloparaffin A paraffin molecule with a ring structure. A naphthene

D

DBA or dBA A-weighted decibels – sound pressure level measurement. Refer to the section on noise control in the environmental chapter.

DT or dT (1) Differential temperature (rise or drop, also ΔT); (2) design temperature

D1160 Distillation curve (vol% distilled vs temperature) using a specific ASTM method. This method is for hydrocarbons boiling up to about 1,150 °F and employs vacuum.

D2887 See “SimDist”

D86 Distillation curve (vol% distilled vs temperature) using a specific ASTM method. This method is for hydrocarbons boiling up to about 700–750 °F.

DAF Dissolved air flotation – for wastewater treatment

Damper A large, loose-fitting butterfly valve or set of louvers that control draft in a fired heater firebox by creating a small back pressure – usually at the base of the stack or ahead of an induced draft fan.

Darcy equation Equation used to estimate pressure drop in piping due to single-phase flow. Refer to the equipment chapter, section on pressure drop.

Dashboard Collection of key variables for display

Data historian The computer system and files used to collect and access historical operating and lab data in a refinery

DC (1) Direct current; (2) delivery capacity; (3) document control

DCAT Drug, chemical, and allied trades

DCS Distributed control system – computer-based control system for a process unit

DCSC Distributed control system controller

DCU Delayed coking unit – resid conversion process. See “Coking Process.”

DDC Direct digital control

DEA See Diethanolamine

Dead time (or dead band) The amount of time before a process starts changing after a disturbance or control action in the system

Deaerator A type of process equipment used to eliminate or strip air from boiler feed water. Refer to the chapter on utilities.

Dearomatization process The dearomatization process is a hydrotreating process that converts aromatic compounds to naphthenes and paraffins. Its most common use is to raise the smoke point of kerosene, particularly if the product is to be blended to make aviation turbine gasoline. Initially, the increase of kerosene smoke point was effected by the removal of aromatic compounds by extraction using liquid SO_2 (Edeleanu process). A typical kerosene dearomatizing unit is shown in Fig. D.1. Pressure at the separator is 350–450 psig, and kerosene recovery is 85–90 % of feed. The feed must be nearly sulfur-free. Catalyst options include nickel and precious metals.

Deasphalting and deasphalting process Deasphalting is an extraction process used in petroleum refining to remove the asphaltene portions of residue to prepare a suitable feedstock for catalytic conversion units. This eliminates the

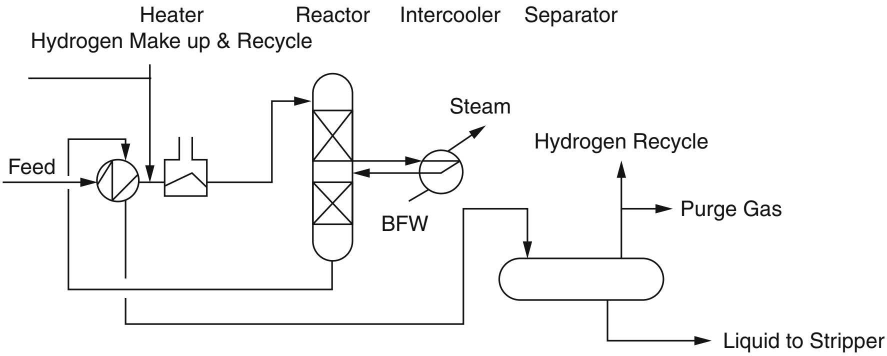


Fig. D.1 Typical hydro-dearomatizer process

heavy metals and the high Conradson carbon content of the residue feed that affect the catalytic units. In lube oil production, the light liquid phase resulting from the extraction of the asphalt makes excellent lube base oil. Details of the deasphalting process are in the chapter "▶ Non-energy Refineries in Petroleum Processing" of this handbook.

Debottlenecking Increasing the capacity of a process unit by removing or modifying parts of the system that limit feed or production rates

Debutanizer (or de-butanizer) Debutanizers are used in refineries to remove butanes and lighter compounds from product streams. The most notable of the feed streams is the overhead distillate from the atmospheric crude distillation tower. Other uses of this process are in the removal of these light ends from hydrotreaters (kero and heavier products) and the reactor effluent liquids from catalytic reforming and hydrocracking. The overhead from the fluid catalytic cracker main tower is also debutanized, but the butane compounds from this process will also contain the olefinic compounds from the cracking process. A typical process configuration for a debutanizer is shown in Fig. D.2. Refer to the topic "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook for details on debutanizers and debutanizer design.

Decarboxylation Eliminating oxygen from an organic molecule via partial hydrotreating with CO/CO_2 by-products

Decarburization Damage to steel caused by removal of carbon from grain boundaries

Decoking Removal of accumulated coke deposits, normally from heater tubes, by burning the coke off using air and a moderator, such as steam. May also be done mechanically without burning

Deethanizer (or de-ethanizer) The purpose of the deethanizer is to remove ethane from the product stream of LPG. Normally, it will be the last tower in a light ends distillation configuration. Refer to the topic "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook for a discussion of where the deethanizer fits into light ends fractionation.

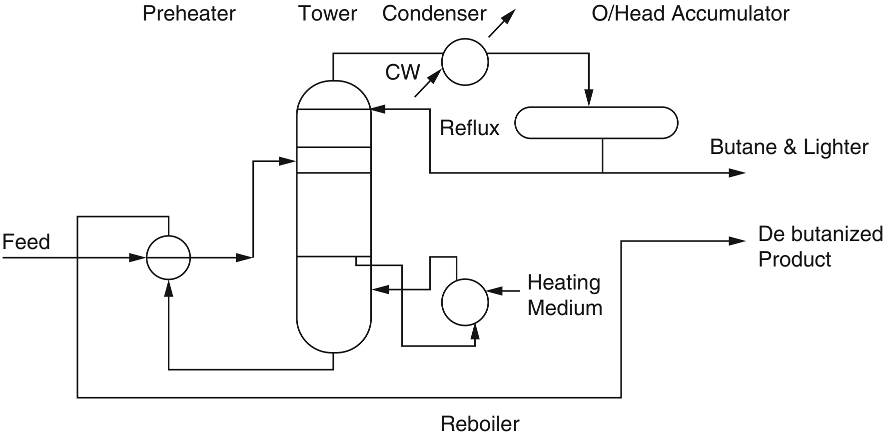


Fig. D.2 A typical debutanizer configuration

A deethanizer tower operates at an overhead accumulator pressure below 450 psia at 100 °F. This ensures that the operating pressure at the bottom of the tower, which is propane LPG, will be below its critical pressure. In the design example given in the topic "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook, the pressure in the accumulator was calculated to be 350 psia at 100 °F, and this was the dew point of the overhead vapor product. Deethanizers operating without overhead refrigeration facilities have partial condensers, and in this case, only sufficient overheads from the tower are condensed to meet the reflux required in the tower. Thus, the accumulator becomes a theoretical tray itself and there will be no liquid distillate product as such.

Definitive estimate A capital cost estimate-based quoted equipment prices and completion of most engineering work. The accuracy is around +/−5–10 %.

Degasifier Similar to a deaerator, a degasifier is used to strip out CO_2 or other gases from an aqueous stream. Commonly found in hydrogen plants. Refer to the chapters on utilities and hydrogen production (SMR section).

Degree days Temperature times number of days at temperature used for tracking aging in catalysts or materials

Degrees API or °API A measure of hydrocarbon density. 10 °API = 1.000 specific gravity or 349.776 lb/bbl. Normally measured at 60 °F. Specific gravity = 141.5/(131.5 +°API).

Delayed coking See "Coking Process."

Deluge system A permanently installed firefighting system which sprays copious amounts of water on specific equipment to help manage a fire. Deluge systems are sometimes found around pump seals, for instance. A sprinkler system in a building is another example of a deluge system. They can be automatically or manually actuated. Refer to the chapter on firefighting.

Demethanizer Distillation tower for stripping methane from a stream. Normally cryogenic.

Demethylation Thermal decomposition of a hydrocarbon to methane.

Demulsibility The resistance of an oil to emulsification or the ability of an oil to separate from any water with which it is mixed. The better the demulsibility rating, the more quickly the oil separates from water.

Demurrage Charge for or cost of holding a bulk carrier (ship, truck, or iso-container) for an extended period of time beyond a normally expected period

Denitrogenation Removing nitrogen from an oil. See also "Hydrodenitrogenation."

Density Mass of a material per unit volume at specified conditions. Be very careful of the actual conditions (pressure and temperature) used for the basis.

Department of Energy The US government, cabinet-level agency concerned with energy development, policies, and safety. Includes responsibility for hydrocarbon and alternative energy sources plus nuclear energy

Department of Transportation The US government, cabinet-level agency concerned with transportation policies and safety. Promulgates regulations for fuels, as well as movement of fuels

Depropanizer In the refinery configuration of light ends distillation, this unit is usually located between the debutanizer and the deethanizer. The process flow is similar to the debutanizer, with total overhead product and reflux being condensed. The tower operates at a reflux drum pressure of between 200 and 250 psia at 100 °F. The tower contains 35–40 actual trays, and the bottom product will be butane LPG. The overhead distillate will be fed to the deethanizer whose bottom product will be propane LPG.

Derivative control A control mode where the controller output is determined by the rate of change of the deviation from the setpoint. Acts like a dampening term. Normally used as a fine-tuning parameter in a proportional control mode

Desalter The desalter extracts salts from a hydrocarbon stream by mixing the stream with a small amount of fresh water (e.g., 10 % by volume) forming a water-in-oil emulsion. The resulting emulsion is subjected to an electric field wherein the water is coalesced as an underflow from the upper flow of a relatively water-free, continuous hydrocarbon phase. The desalted hydrocarbon stream is produced at relatively low cost and has a very small residual salt content.

Design basis The operating conditions, yields, etc., upon which a process unit is designed

Design pressure Pressure used in the design of equipment to determine the minimum permissible thickness or physical characteristics of the different parts of the equipment. Works with the design temperature

Design temperature Temperature used in the design of equipment to determine the minimum permissible thickness or physical characteristics of the different parts of the equipment. Sets the stress limits for the materials of construction. Works with the design pressure

Desulfurization Removing sulfur from an oil. See also "Hydrodesulfurization."

Desuperheater A device for reducing the temperature of superheated steam by injecting a controlled amount of boiler feed water into the stream

Detonation An explosion that generates an expanding, supersonic shock wave from the point of initiation. An unconfined vapor cloud explosion is an example. A controlled detonation also occurs in internal combustion engines when the fuel–air mixture in the cylinders is ignited by a spark or heat of compression.

Dew point(s) Is the temperature and pressure condition at which a hydrocarbon vapor begins to condense. In a calculation, the sum of the mole fraction composition of the vapor divided by the equilibrium constant of each compound must equal the sum of the sum of the mole fraction of the liquid phase at the dew point condition of temperature and pressure. Table D.1 is a dew point calculation example based on a tower top condition for an atmospheric crude distillation unit. The dew point calculation here is carried out at 8.3 psia, which is the partial pressure of the hydrocarbons in the overhead vapor.

Dewaxing Removal of wax from a hydrocarbon stock. May refer to solvent processes or specific types of hydroprocessing. Used extensively in lube oil production

DGA See diglycolamine

DHA Detailed hydrocarbon analysis

Diaphragm A relatively thin metal or elastomer disk that is moved by differential pressure between the two sides of the membrane. These are used extensively in control valve actuators and certain types of pump. One side of the membrane normally has an actuating fluid whose pressure and/or frequency is varied as needed. The other side of the membrane may be connected mechanically to the device to be moved or may have a fluid to be pumped.

Diaphragm pump A type of pump used for moving thick pulps, sludge, acid or alkaline solutions, and fluids containing gritty solid suspensions. The pump can use a diaphragm material compatible with the pumpage.

DIB De-isobutanizer

Diesel index Product of the API gravity and the aniline point (in degrees Fahrenheit) of a diesel fuel divided by 100; an indication of the ignition quality of the fuel

Diesel oil or diesel Diesel oil (sometimes called automotive gas oil) is used as fuel for heavy internal combustion engines such as heavy trucks (lorries) and rail locomotives, as well as automobiles. Its main components are light gas oils from the atmospheric crude distillation unit and hydrotreated light gas oils. In some cases, light FCC cycle oil may be included. This product has a nominal ASTM boiling range of around 480–610 °F but may boil over a 350–700 °F range. Hydrocarbon cuts in this boiling range are hydrotreated to remove sulfur (and the process does change pour and cloud points to some extent) and blended with kerosene and some heavier middle distillate stocks to meet the diesel oil specification. Sulfur in diesel ranges from less than 10 ppm for diesel used in vehicles on the road in the United States and Europe up to 500 ppm for some

Table D.1 Example dew point calculation

		1st trial @ 220		2nd trial @ 225 °F						
COMP	Mole frac Y	K	$X = Y/K$	K	$X = Y/K$	MOL wt	Weight factor	SG	vol factor	Liquid prop
C_2	0.008	–	NEG		NEG					
C_3	0.054	84.3	0.001	93.9	0.001	44	0.044	0.508	0.009	
iC_4	0.021	38.6	0.001	39.8	0.001	58	0.053	0.563	0.010	Mol wt = 130.7
nC_4	0.084	29.52	0.003	30.1	0.003	58	0.174	0.584	0.030	
C_5	0.143	12.53	0.011	12.65	0.011	72	0.792	0.629	0.126	SG = 0.766
C_6	0.155	4.70	0.033	4.94	0.031	85	2.635	0.675	0.390	
C_7	0.175	2.17	0.081	2.19	0.080	100	8.00	0.721	1.110	°API = 53
Mid-BP 260	0.124	1.00	0.124	1.16	0.107	114	12.193	0.743	1.642	
Mid-BP 300	0.124	0.506	0.245	0.518	0.239	126	30.114	0.765	3.936	K = 12
Mid-ESP 340	0.075	0.229	0.328	0.253	0.293	136	39.848	0.776	5.135	
Mid-BP 382	0.037	0.108	0.343	0.126	0.294	152	44.688	0.788	5.671	
Totals	1.000		1.170		1.06	130.7	138.551	0.767	18.059	

$$K = \frac{\text{Vapor press at selected temperature}}{\text{Total system pressure}}$$

2nd trial = 0.108 × 1.170 (K for mid – BP 362 component)

New K = 0.126 then VP = 8.3 psia × 0.126 = 1.05 psia = 225°F

The 2nd trial is close enough to $\sum x_i = 1.00$

Notes:

a. In estimating for the 2nd trial and final temperature, the "K" of the highest X component is multiplied by the total value of X function. Then vapor pressure curves are used to give the component temperature corresponding to this new vapor pressure.

b. The molar composition of the final "X" is the composition of the liquid in equilibrium with the product vapor.

The tower top conditions are 229 °F at 15 psig (this is the total pressure and includes the steam effect).

off-road uses and higher for marine diesel. Directionally, sulfur levels in all grades of diesel are being driven lower in most major markets. At the same time, cetane requirements for diesels are being pushed higher. For more information, see the chapters "▶ Petroleum Products and a Refinery Configuration" and "▶ Quality Control of Products in Petroleum Refining" of this handbook and consult the current diesel specifications for the product grade of interest.

Diethanolamine (DEA, $(HOC_2H_4)_2NH$) One of the common, regenerable amine solvents used for acid gas removal (H_2S or CO_2) from vapor streams

Differential pressure (dP) The actual pressure difference between two points. This pressure is not referenced to atmospheric pressure.

Diglycolamine (DGA, $HOCH_2CH_2OCH_2C_2H_4NH_2$) A regenerable amine acid gas solvent normally used to remove H_2S or CO_2 from gases. Developed by Fluor Corporation

DIH Deisohexanizer. A DIH fractionation column is commonly installed in light naphtha isomerization process units on the stabilized reactor product to separate a side-cut stream rich in lower octane C_6 compounds for recycle to the reactor from an overhead product stream containing C_5 compounds and the higher octane isohexane isomers. A small drag stream of heavy compounds is taken from the bottom.

Diisopropanol amine (DIPA, $(HOC_3H_6)_2NH$) One of the regenerable amine solvents used for acid gas removal (H_2S or CO_2) from vapor streams

Dilbit A blend of some diluent (normally naphtha) and bitumen. Many Canadian tar/oil sands "crudes" are dilbits.

DIN Deutsches Institut für Normung e.V. (The Standards Institute of Germany)

DIP Deisopentanizer. A DIP fractionation column separates isopentane from heavier compounds and is usually fed a light naphtha stream containing C_5 and C_6 compounds.

DIPA See diisopropanol amine.

Direct contact condenser A condenser where the cooling medium is mixed directly into the process stream being cooled. Sometimes used in small towers. Refer to the equipment chapter section on heat exchangers.

Discounted cash flow (DCF) A method for analyzing potential projects by examining the expected cash flow for the project over several years and "discounting" future cash value based on an assumed inflation rate or time value of money back to a present value for the investment. The DCF rate of return for a project is the interest rate that forces the cumulative present net worth of the project to zero over its economic life. See the chapter on economics for additional detail.

Dispersed flow In this flow regime, nearly all the liquid is entrained as a spray in a bulk gas phase. This regime may also be referred to as mist flow. Refer to the equipment chapter section on two-phase pressure drop.

Distillate Kerosene or diesel boiling range materials. Generically, something distilled out of another material, usually crude oil

Distillate hydrocracking Hydrocracking is a versatile catalytic refining process that upgrades petroleum feedstocks by adding hydrogen, removing impurities,

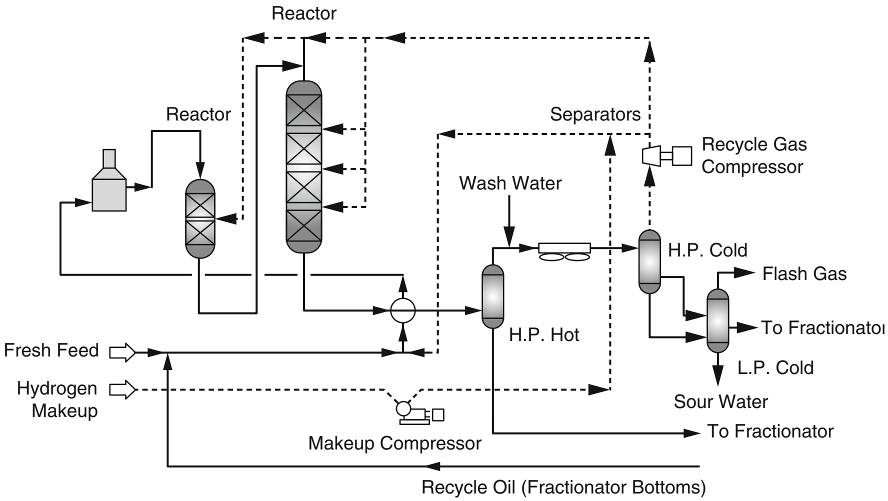


Fig. D.3 A distillate hydrocracker reactor section

and cracking to a desired boiling range. Hydrocracking requires the conversion of a variety of types of molecules and is characterized by products that are of significantly lower molecular weight than the feed. The process is carried out at elevated temperatures (550–825 °F) and hydrogen partial pressures from 1,000 to 2,500 psig using a variety of catalysts suitable for the feedstock and desired selectivity. Hydrocracking feeds can range from heavy vacuum gas oils and coker gas oils to atmospheric gas oils. Products usually range from heavy diesel to light naphtha. Figure D.3 illustrates one hydrocracker flow sheet. The chapter on "▶ Hydrocracking in Petroleum Processing" in this handbook reviews the hydrocracking process in detail.

Distillation Also known as fractionation, there are numerous applications of distillation in petroleum processing. After heat transfer, distillation is the most common unit operation in a refinery. Considered generically, distillation is simply a process that separates materials by boiling range. Examples of distillation applications are discussed in detail in multiple sections of this handbook. For perspective here, the following are offered:

Types of distillation curves:

ASTM distillation curve

While the TBP curve is not produced on a routine basis, the ASTM distillation curves are. Rarely, however, is an ASTM curve conducted on the whole crude. This type of distillation curve is used on a routine basis for plant and product quality control. This test is carried out on crude oil fractions using a simple apparatus designed to boil the test liquid and to condense the vapors as they are produced. Vapor temperatures are noted as the distillation proceeds and are plotted against the distillate recovered. Because only one equilibrium stage is used and no reflux is returned, the separation of components is poor and mixtures are distilled. Thus, the initial boiling point for ASTM is higher than the corresponding TBP point, and the final boiling point of the ASTM is lower than that for the TBP curve. There is a correlation between the ASTM and the TBP curve, and this is dealt with in the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook.

True boiling point curve (*TBP*)

This is a plot of the boiling points of almost pure components, contained in the crude oil or fractions of the crude oil. In earlier times, this curve was produced in the laboratory using complex batch distillation apparatus of a hundred or more equilibrium stages and a very high reflux ratio. Nowadays, this curve is produced by mass spectrometry or gas chromatography techniques much more quickly and accurately than by batch distillation.

Equilibrium flash vaporization curve (*EFV*)

The EFV curve of an oil is determined in a laboratory using an apparatus that confines liquid and vapor together until the required degree of vaporization is achieved. The percentage vaporized is plotted against temperature for several runs to produce the EFV curve. Separation is poorer for this type of distillation than for an ASTM or TBP. Therefore, the initial boiling point will be higher for the EFV than for the ASTM. The final boiling point of the EFV will be lower than that for the ASTM. This test is rarely done, but the EFV curve is calculated either from a TBP curve or an ASTM curve. These methods are given in the introductory and atmospheric and vacuum crude distillation topics of this handbook.

Types of distillation processes:

The separation of products by distillation falls into three general categories:

- Total vapor condensation such as the atmospheric crude distillation
- Vacuum distillation processes, such as the vacuum distillation of atmospheric residue
- Light ends distillation

Total vapor condensation processes

The best example of this type of distillation unit in modern refining is the atmospheric crude distillation unit. In these types of units, the feed is heated and vaporized to a temperature above the total product cut point. This mixed vapor/liquid is produced by an external heater (and heat exchanger system) and the mixed stream flashed in the lower section of a tower. The vapor rises in the tower and is condensed by a cooled reflux stream at various stages up the tower according to the various distillate boiling points. Full details of this type of distillation are given in the chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook. Similar distillation systems are also used in the primary separation of fluid catalytic cracking unit effluent and the reactor effluent from a hydrocracker.

Vacuum distillation processes

These processes are designed to operate as total vapor condensation similar to the atmospheric units. However, the feed to these units is usually heavy residual oils, which if heated to vaporize the product distillate required at atmospheric pressure (or near-atmospheric pressure), would cause the feed to crack and coke. The system is therefore set at low vacuum pressure so that the vaporizing temperature is well below the feed's cracking properties. The distillates are produced in the same way as that for the atmospheric units, that is, by selective cooled reflux streams. Full details of a crude oil vacuum process are also given in the chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook. Vacuum distillation is also used for the distillation of light residues from hydrocrackers to produce light vacuum distillates and heavy residuum for further thermal cracking or lube oil production.

Light ends distillation

The most common of this type of distillation is the crude unit light ends process. The feed to this unit is the overhead distillate from the atmospheric crude unit. This feed may also include overhead distillate from other processes (such as the catalytic reformer). The products from the light ends process are light and heavy naphtha, butane LPG, propane LPG, and refinery gas. These processes are discussed more fully in the topic "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook.

Distributed control system (DCS) This is a computer-based control system used for basic process control. The basic control loops are in the background. The DCS displays the process and control-loop information for the operator. It also records the information and communicates with any advanced control systems. The operator and APC change the settings in the DCS, which then sends the moves on to the process loops. DCS is the most common type of control system today in refineries.

Distributor (1) A device for even distribution of fluids in process equipment, such as at the top of a reactor or inside a distillation column. (2) An organization which disburses products to retail or wholesale locations for sale

dll Dynamic-link library

DMDS Dimethyl disulfide

DME Dimethyl ether

DMS (1) Document management system; (2) dimethyl sulfide

DMSO Dimethyl sulfoxide

DNAPL Dense nonaqueous phase liquid

Doctor test A qualitative method for detecting undesirable sulfur compounds in petroleum distillates using a lead/caustic solution to determine whether an oil is "sour" or "sweet" (positive or negative, respectively)

DOE (1) US Federal Department of Energy; (2) design of experiment – technique for optimizing a unit; (3) direct operating efficiency

DOT US Federal Department of Transportation

Double-pipe exchanger A double-pipe exchanger consists of a pipe within a pipe. One of the fluid streams flows through the inner pipe, while the other flows through the annular space between the pipes. There are also multiple tube versions of these exchangers. Refer to the equipment chapter section on heat exchangers.

Downcomer In a distillation tower or stage contactor, this is a free-flow path for liquid from one tray to the tray below. Normally, the downcomer is a curtained-off area next to the column wall where liquid can fall from one tray to the next without resistance from vapor flowing upward. The downcomer is separated from the active tray areas by overflow weirs. Refer to the equipment chapter section on towers and columns.

Downstream (1) In the petroleum industry, refers to refining and marketing activities and may also include transportation or anything else not associated with exploration and production; (2) refers to processes or activities that occur subsequent to a specific process in refining – e.g., the blender is downstream of hydrotreating, cat cracking, and cat reforming

DP Design pressure

DP or dP or ΔP Differential pressure or pressure drop

dP cell A diaphragm device for measuring small differences in pressure with the higher pressure on one side of the diaphragm and the lower pressure on the other side. The difference may be directly indicated or may be transmitted.

Draft Movement of air or flue gases based on density differences, normally caused by temperature differences, but may be mechanically forced or induced

Drawoff In a distillation tower, refers to pulling a stream from the side of the tower (not the overhead or bottom). Also referred to as a sidestream draw. Within a tower, there is normally an internal sump from which the stream can be drawn.

Drums Drums are horizontal or vertical vessels used to separate gas and liquid phases. Generally drums do not contain complex internals like fractionating trays or packing as in the case of towers. They are used however for removing material from a bulk material stream and often use simple baffle plates or wire mesh to maximize efficiency in achieving this. Drums are used in a process principally for (1) removing liquid droplets from a gas stream (knockout pot) or separating vapor and liquid streams, (2) separating a light from a heavy liquid stream (separators), (3) surge drums to provide suitable liquid holdup time within a process, and (4) reduction of pulsation in the case of reciprocating compressors. A detailed discussion of the design of drums is included in the handbook topic "▶ Process Equipment for Petroleum Processing" with discussion of surge times in drums in the handbook section "▶ Process Controls in Petroleum Processing."

DSO Disulfide oil from caustic treating of oils (e.g., or Merichem processes)

Dumbbell distillation Refers to a stock, normally a blend, with high proportions of light material and heavy material, but little material in the boiling range between the two extremes. An example of such a stock is a dilbit, which consists of a bitumen (tar) that is mixed with a naphtha to facilitate transportation.

E

E&C Engineering and construction

E&I Electrical and instrumentation

E&P Exploration and production

EAM Ergonomic accident model

EBIT Earnings before interest and taxes

EBITDA Earnings before interest, taxes, depreciation, and amortization

Economic evaluation Economic evaluation is used for most aspects of the refinery planning and its operation. The methods used in these evaluations may differ from company to company, but the end product must reflect the profitability of the present and often the future profitability of a proposed venture or operation. This measure is reflected in terms of the return on investment of the item. This is described and discussed in the chapter titled "▶ Petroleum Refinery Planning and Economics" in this handbook.

Economic life Number of years a project is expected to yield the projected profit and pay for its installation

Edmister correlations A series of correlations which relates an ASTM distillation test to the TBP of a petroleum cut is presented in W. Edmister's publication titled: "*Applied Thermodynamics*." The correlations relating to the ASTM and TBP curves from this book are used in this handbook and are given in the topic "▶ Introduction to Crude Oil and Petroleum Processing". Similar correlations have also been prepared by Edmister for the relationship between TBP and the equilibrium flash vapor curve (EFV).

EDS Emergency depressuring system – for dumping a high-pressure unit quickly in an emergency to prevent damage

Eductor A vacuum-producing device; also referred to as an ejector. It uses a high-velocity motive stream, such as steam or compressed air, to create a vacuum applying the Bernoulli effect.

EE Electrical engineer or engineering

EEBSS Emergency escape breathing support system

EEP Enabling event probability – in LOPA

Effluent Refers to materials leaving a process system or facility

Effluent water Effluent water is the wastewater that comes from the petroleum processing units. The effluent water may be contaminated with oil and grease, solids, metals, sulfur compounds, nitrogen compounds, and other undesirable materials. Effluent water must generally be processed to remove the contaminants before it can be discharged into a waterway or an external, finishing treatment plant. Treatment of effluent water is discussed in more detail in the topic "▶ Environmental Control and Engineering in Petroleum Processing" in this handbook. The refinery sources and contaminants that are normally of concern are listed in Table E.1.

EFT Electronic funds transfer

EFV Equilibrium flash vaporization

Table E.1 Effluent water sources and contaminants

Process	Wastewater	Air
Atmospheric and vacuum distillation	Sour water (NH_3 and H_2S)	Furnace
	Desalter water spent caustic	Flue gases – SO_2
	Process area wastewater (pump glands, area drains, etc.)	
Thermal cracking	Sour water	Furnace
Delayed coking	Decking water (oil)	Flue gases
	Process area wastewater	
Fluid cat cracking	Sour water (NH_3, H_2S, phenols)	Furnace
Unsat gas plant	Spent caustic	Flue gases SO_2, CO, particulates
	Process area wastewater	
Hydrocracker	Sour water (inc Phenols)	Furnace
Hydrogen plant	Process area wastewater	Flue gases SO_2
Sat gas plant alkylation	Spent caustic	Nil
	Process area wastewater	
Naphtha hydrotreater	Sour water	Furnace
Cat reformer	Process area wastewater	Flue gases
Sulfur plant	Nil	Incinerator flue gas – SO_2 hydrocarbons – flare
Tankage area	Tank dike area drains, noncontaminated rain runoff	Tank vents, hydrocarbons

EHSRMA Extremely Hazardous Substances Risk Management Act

EI Energy Institute of Petroleum (UK)

EIA Environmental impact assessment

EII Energy Intensity Index as defined by Solomon Associates

EIS (1) Environmental impact study or statement; (2) executive information system

EIT Engineer in training

Ejector A vacuum-producing device; also referred to as an educator or steam-jet ejector. It uses a high-velocity motive stream, normally steam, to create a vacuum applying the Bernoulli effect.

Electrolytic process A process using electrical energy to cause a chemical reaction. An example is electrolysis of water to generate hydrogen. Note that desalting would *not* be considered electrolytic.

Electrostatic precipitator or separator A pollution control or solids removal system which uses an electrically induced charge on suspended particles or droplets to remove the suspended material from a stream. Examples would include removal of catalyst fines from FCC flue gas and removal of acid droplets from alkylation plant hydrocarbon streams. Desalters also apply a form of electrostatic separation.

Element The sensor for a process variable or condition

ELSA Emergency life-saving apparatus

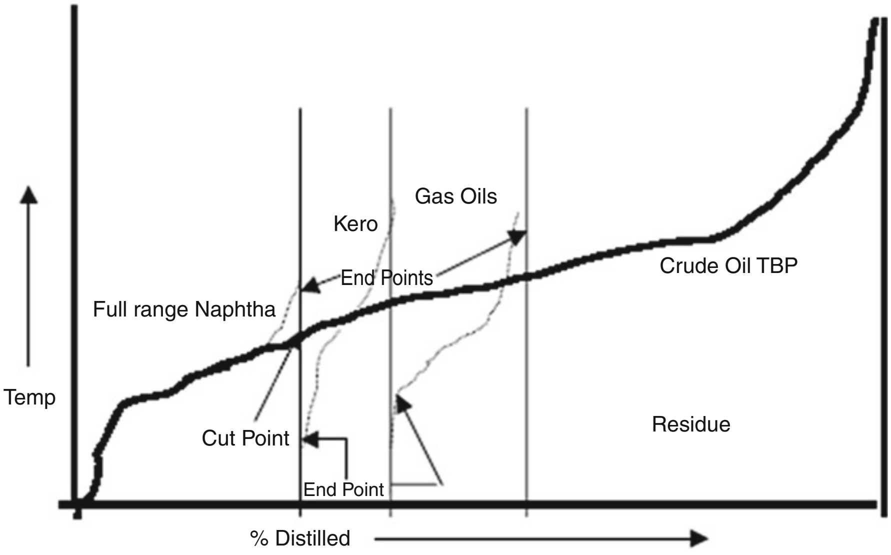


Fig. E.1 Definition of end points

ELV In the EU, emissions limit value for air pollutants. Refer to the environmental chapter.

Embrittlement Loss of metal toughness or ductility due to low temperatures or process exposure

EMI Electromagnetic interference

Emission(s) Generally refers to gases (including pollutants) sent into the atmosphere. Refer to the environmental chapter.

EMS (1) Emergency medical services; (2) environmental management system

EMT Emergency medical technician

Emulsion A liquid mixture of two or more substances not normally dissolved in one another, one liquid held in suspension in the other. Water-in-oil emulsions have water as the internal phase and oil as the external, while oil-in-water have oil as the internal phase and water as the external.

End point(s) Whereas a cut point is an ideal temperature on a TBP curve to define the yield of a fraction, the end points define the shape of the fraction distillation curve when produced commercially. In actual processes, the initial boiling point of a fraction will be much lower than its front end cut point. The final fraction boiling point will be higher than the corresponding cut point. This is demonstrated by Fig. E.1.

There is a correlation between the TBP cut point and the ASTM end point. This is described in the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook. A relationship also exists for the 90 % ASTM point and the TBP 90 % cut point. With these two ASTM data and using an ASTM probability graph (see the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook), a full ASTM curve with its end points can be drawn. This, converted to a TBP curve, is used to define the cut's properties.

Endothermic reaction Reaction that absorbs heat.

Energy Information Administration (EIA) The US federal agency responsible for collecting, analyzing, and providing information about energy. The goals of the agency are to promote sound policies, efficient markets, and public understanding of energy use and impacts.

Energy Intensity Index (EII) From Solomon Associates. Generally expressed as the Actual Btus of energy used per barrel of feedstock in a specific process divided by the standard Btu/bbl for that process developed by Solomon based on their worldwide survey of refineries. The ratio is multiplied by 100 for the final EII number.

Engineering flow diagrams Diagrams that are used extensively by all disciplines of engineers to convey ideas and data. These include: process flow diagram (PFD), mechanical flow diagram (MFD, sometimes called the piping and instrumentation diagram (P&ID)), auxiliary flow diagram (AFD), and utilities diagram. Refer to the chapter titled "▶ Petroleum Processing Projects" in this handbook for further discussion. Examples of sections of these engineering drawings are given in the appendix titled "▶ Examples of Working Flow Sheets in Petroleum Refining" of this handbook as illustration.

Engler viscosity A viscosity obtained by dividing the outflow time in seconds for 200 ml of the material being tested by the time in seconds for 200 ml of water at 68 °F (20 °C) to flow out of an Engler viscosimeter

Enterprise control An overall control system that factors in economics, market, and other factors to optimize and coordinate several refinery units simultaneously

Entrainment Refers to physical carryover of solid particles or liquid droplets in a vapor or liquid stream, respectively, due to velocity

Environmental Protection Agency (EPA) US government agency that promulgates and enforces environmental regulations at a federal level. See the chapter on environment.

EOL (1) Environmental operating limit; (2) end of life (equipment)

EOP Emergency operating procedure

EOR End of run

EP End point

EPA US Federal Environmental Protection Agency. Refer to the environmental chapter of this handbook.

EPBC Ethane, propane, butane, and condensate

EPC (1) In projects – engineer, procure, and construct; (2) event-driven process chain

EPCI Engineering, procurement, construction, and installation

EPCM Engineering, procurement, and construction management

EPCRA US Emergency Planning and Community Right-to-Know Act

EPF Engineering, procurement, and fabrication

EPR Ethylene–propylene chloride

E-PRTR European Pollutant Release and Transfer Register

EQE Earthquake engineering

EQSD EU Environmental Quality Standards Directive

Equilibrium flash vaporization (EFV) When a mixture of compounds vaporizes or condenses, there is a unique relationship between the composition of the mixture in the liquid phase and that in the corresponding phase at any condition of temperature and pressure. This relationship is termed the equilibrium flash vaporization for the mixture or simply the "flash." The topic is detailed under the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook. Refer to Appendix 1 of that chapter for an example calculation procedure.

Equipment-factored estimate A method for estimating capital cost for new facilities that uses known equipment costs scaled to new applications. This method requires rough equipment sizing and completion of significant process engineering. Accuracy is ~ +/−20 %.

ER Emergency response. Refer to the chapter on "▶ Safety Systems for Petroleum Processing" in this handbook.

ER probe Electrical resistance corrosion probe – basically a corroding wire where resistance changes are monitored to indicate corrosion.

Ergun equation Primary equation to calculate single-phase pressure drop through beds of discrete solid materials. Refer to the equipment chapter section on pressure drop.

Error This is usually defined in process control as the difference between the setpoint and the process variable or measurement.

ERP (1) Emergency response plan or program – refer also to the chapter on "▶ Safety Systems for Petroleum Processing" in this handbook; (2) enterprise resource planning

ERT Emergency response team – refer also to the chapter on "▶ Safety Systems for Petroleum Processing" in this handbook.

ES Expert system

ESD (1) Emergency shutdown system – may apply to a piece of equipment or a unit to prevent damage; (2) emergency shutdown

ESP (1) Electrostatic precipitator; (2) emergency shutdown procedure

ETA (1) Estimated time of arrival; (2) event tree analysis

ETBE Ethyl tertiary-butyl ether

ETD In the EU, energy taxation directive. Refer to the environmental chapter topic on air emissions.

Ethane (C_2H_6) A normally gaseous straight-chain hydrocarbon. It is a colorless paraffinic gas that boils at a temperature of –127.48 °F. It is extracted from natural gas and refinery gas streams.

Ethanol Ethyl alcohol, which is most often derived from corn or other renewable organic sources. Ethanol is blended with gasoline to produce a cleaner burning fuel and is an accepted oxygenate component for the oxygenated seasons mandated by the EPA.

Ether A generic term applied to a group of organic chemical compounds composed of carbon, hydrogen, and oxygen, characterized by an oxygen atom attached to two carbon atoms (e.g., methyl tertiary-butyl ether).

Etherification Conversion of a compound into an ether by reaction. An example of etherification is the reaction of methanol and butene to make methyl tertiary-butyl ether (MTBE).

Ethyl tertiary-butyl ether [$(CH_3)_3COC_2H_5$] An oxygenate blendstock formed by the catalytic etherification of isobutylene with ethanol

Ethylene (C_2H_4) An olefinic hydrocarbon recovered from refinery processes or petrochemical processes. Ethylene is used as a petrochemical feedstock for numerous chemical applications and the production of consumer goods.

EU European Union

EuReDatA European Reliability Data Association

EV Earned value

EVP Executive vice president

EWP Environmental work practice – requirements to control pollution

Ex situ Refers to action or processes that are performed on materials that have been removed from their original location. In common use, this term refers to oil shale retorting processes that process rock which has been removed from the shale formation to a surface retort.

Excess O_2 or air In a fired heater, this is the surplus air supplied to the firebox (or leaking in) that is un-combusted. An indication of heater combustion efficiency. Low excess O_2 is more efficient than high O_2 because the furnace has to heat up less air.

Exothermic reaction Reaction that releases heat

Exploration Organization focused on finding crude oil and gas

Exports Normally refer to materials shipped out from a country commercially, but may also refer to materials sent out of an individual unit or refinery, e.g., a hydrogen plant may export surplus steam to a refinery

Extra-heavy oil (EHO) Term used for naturally occurring hydrocarbon deposits where the oil is present as a tar-like substance that must be heated or dissolved with a flux in order to be produced. Tar sands would be considered an EHO.

Extrudate In refineries, this generally refers to a particle produced by extrusion of a mud or clay-like material through a die. The extruded material is then chopped or broken into shorter particles. Used extensively for catalyst and absorbent production

Eyewash A deluge system designed for flushing the eyes, usually located near a potential chemical exposure area, where personnel can flush their eyes with copious amounts of clean water to eliminate or control damage from chemical exposure. Refer to the safety chapter.

F

F1 Research octane number

F2 Motor octane number

FA (H, HH, L, LL) Flow alarm high, high–high, low, or low–low, e.g., FAHH is a high–high flow alarm

FAA US Federal Aviation Authority

Fahrenheit Temperature scale based on 32 °F for the temperature at which water freezes and 212 °F for the temperature at which water boils (180 °F difference). Conversion to Fahrenheit from Celsius (centigrade) temperature scale is by the following formula: $F = 1.8C + 32$, where C is the temperature in Celsius degrees.

Fail-safe Failure of a device toward the safest position. Refer to the chapter on controls.

Failure position For a control device, this is the position the device moves to if the control signal or motive means is compromised. For instance, control valves will normally fail closed, open, or in last position. The failure position is selected based on what position is most safe for the process. Refer to the chapter on controls.

Falldown Unplanned shutdown caused by a failure

FAQ Frequently asked question

FAS Federal accounting standards

FASB Financial and Accounting Standards Board

FAME Fatty acid methyl ester

FAT Factory acceptance test

Fatigue Loss of metal strength due to repetitive strain cycles

Fatty acid methyl ester (FAME) Renewable diesel fuel derived from fats by conversion to an ester in the diesel boiling range. Refer to the chapters on unconventional stocks and renewables.

FBP Final boiling point or end point

FC (1) Flow controller; (2) fail closed valve designation

FCC Fluid catalytic cracker – heavy oil conversion process

FCE Final control element – normally a control valve but can be other devices

FCPA US federal Foreign Corrupt Practices Act

FD (1) Forced draft – in a firebox, a fan that blows air into the firebox; (2) filter drum; (3) fire detection

FE (1) Flow element – like an orifice plate; (2) fundamentals of engineering exam in professional engineer licensing; (3) facilities engineer

Fe Iron

Feed-forward control A control scheme where changes in an upstream variable initiate changes in downstream controls in anticipation of upcoming deviations. For example, if the feed rate to a unit changes, the appropriate controllers can also be changed downstream so they are set correctly for the new feed rate.

Feedstock Any of the raw or semifinished materials which move to the various units of a refinery or petrochemical plant. Crude is a feedstock, but the term is mainly used to describe raw materials after the distillation process which in turn go on to more sophisticated units at the refinery. VGO, cat feed, naphtha, condensate, and straight-run residual fuel are commonly referred to as feedstocks.

FEL Front-end loading in project execution. See the chapter on projects.

Fenceline Refers to the very outer property limits of a processing facility – generally where there is a fence that encompasses the whole facility

FEP Fluorinated ethylene–propylene

FERC US Federal Energy Regulatory Commission

FeS Iron sulfide, frequent corrosion product, may be pyrophoric

FFC Feed-forward controller

FGT Fuel gas treating

FHR Flame and heat resistant

FIFO First in–first out (inventory control)

Filming amine Any of several amines that prevent corrosion by coating the surface of metal equipment – e.g., distillation tower overhead corrosion inhibitors

Filtration A mechanical process for removing solids from a liquid or vapor stream by passing the stream through a fine media to collect the solids. Filtration and ultrafiltration can be used to fractional micron sizes.

Final boiling point, FBP The highest temperature indicated on the thermometer inserted in the flask during a standard laboratory distillation. This is generally the temperature at which no more vapor can be driven over into the condensing apparatus. Usually the end point

Final control element The device which actually controls the desired operating condition in a control loop. Refer to the chapter on controls.

Finned tube A fired heater or air cooler tube that has fins protruding from the surface to enhance heat transfer

Fines Refers to small particles and dust

Fire brick Refractory used in furnaces and other high-temperature equipment that is in the form of a brick. Refer to the chapter on equipment, section on fired heaters.

Fire extinguisher A relatively small, normally hand-operated device for putting out smaller fires quickly at the incipient stage. There are multiple types of fire extinguishers for different services. Refer to the chapter on firefighting.

Fire foam A chemical mixed with water and air to create foam for firefighting. Refer to the chapter on firefighting.

Fire main The main pressurized firefighting water supply piping system in a facility. Branches, laterals, or submains/sublaterals come off the fire main to the various firefighting equipment. Refer to the firefighting chapter.

Fire point The lowest temperature at which an oil vaporizes rapidly enough to burn for at least 5 s after ignition, under standard conditions

Fire relief Relief scenario or relief valve intended to prevent overpressure of a vessel or other equipment when exposed to an external fire. Refer to the safety chapter.

Firebox The chamber in a fired heater where fuel and air are burned to release useful heat. The firebox contains the coils where fluids are heated.

Fired heater Device for providing process heat by burning a fuel in a firebox and transferring the heat generated to a process fluid contained in tubes within the heater. Generally fired heaters fall into two major categories: horizontal and vertical. There is a detailed discussion of fired heaters or furnaces and their design in the handbook topic "▶ Process Equipment for Petroleum Processing." Emissions and emission controls for fired heaters are covered in the topic "▶ Environmental Control and Engineering in Petroleum Processing" of this handbook.

Fireproofing Application of fire-resistant materials, such as insulating concrete, to structures or vessel skirts to help prevent collapse in the event of fire.

Firewater (or firefighting water) Water used for extinguishing or cooling service in a fire. Normally supplied by a secure, dedicated system. Refer to the chapters on utilities and firefighting.

Fischer assay A more-or-less standard test to determine the potential products from retorting or destructive distillation of a solid material. The test involves heating a known amount of solid to high temperature (800 °F plus) at atmospheric pressure and collecting all the products. Yields are determined by material balance. This test is used for shale oil yield comparisons. See the chapter on unconventional crudes.

Fischer–Tropsch process Process for conversion of a synthesis gas (CO + H2) to hydrocarbon products. Refer to the chapters on unconventional crudes, lube oil, and coal or gas to petrochemicals.

Fixed cost A cost that does not depend significantly on rate. For example, the cost of a turnaround does not depend very much on how many barrels were run.

Fixed equipment Vessels, reactors, separators, exchangers, etc. Process equipment that does not move to do its job – hopefully.

FL Fail last (or locked) position – control valve

Flammability Refers to the ease of combustion or ignition of a material

Flammability limits The range of concentrations of a material in air that can support ignition of the material, possibly explosively. The flammability limits are usually expressed as upper and lower explosive or flammability limits as volume % in air at atmospheric pressure.

Flame impingement Flames in a firebox burning directly on a tube's surface – often leads to tube failure

Flame retardant (or fire retardant) Material that does not continue to burn when an ignition source is removed (self-extinguishing). Usually refers to types of clothing, like Nomex, used in refineries to help protect workers in the event of fires or flash fires

Flameout Loss of flame in a fired heater

Flare System for collecting and safely disposing of combustible vapors by burning them. Refer to the offsites chapter.

Flare tip The device at the end of the flare where fluids to be burned are vented. The tip contains multiple ignition sources and usually steam to promote mixing with air. Many flare tips also contain molecular seals to prevent intrusion into the flare system by air. Refer to the offsites chapter.

Flash point(s) The temperature to which a product must be heated under prescribed conditions to release sufficient vapor to form a mixture with air that can be readily ignited. Flash point is used generally as an indication of the fire and explosion potential of a product. For a rough estimate of flash point, the equation below is useful. Refer to the handbook chapters on "▶ Introduction to Crude Oil and Petroleum Processing," "▶ Petroleum Products and a Refinery Configuration," and "▶ Quality Control of Products in Petroleum Refining" for more details on flash point.

$$\text{Flash Point } ^\circ\text{F} =\sim 0.77(\text{ASTM } 5\ \% - 150^\circ\text{F}).$$

Flash zone A flash zone is associated with the distillation of crude oil, both atmospheric and vacuum, and the main fractionating towers of the fluid catalytic cracking unit, visbreaker unit, or thermal cracking unit. The flash zone is the area in these distillation towers where the distillate vapors are allowed to separate from the unvaporized liquid. The transfer line from the heater enters the flash zone. The vapors rise up through the tower to be condensed by cold reflux streams coming down. Steam and some hot vapors enter the flash zone from the bottom product stripper section located below the flash zone. The chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook deals with a calculation procedure to establish these flash zone conditions for atmospheric and vacuum distillation crude distillation towers. The handbook topic "▶ Process Equipment for Petroleum Processing" provides further information.

Flashing A condition where liquid is vaporizing to reach a vapor/liquid equilibrium

Flexicoking Proprietary fluid coking process. A thermal cracking process which converts heavy hydrocarbons such as crude oil, tar sands bitumen, and distillation residues into light hydrocarbons. Feedstocks can be any pumpable hydrocarbons including those containing high concentrations of sulfur and metals.

Flight scraper In an API separator, flight scrapers are used to sweep or scrape the sludge into the sludge pit and along the top of the separator level to move the accumulated oil toward the oil skim pipe.

Floating-roof tank (or floater) A storage tank in which the surface of the fluid is covered by a roughly flat roof that floats on top of the commodity in the tank to prevent vapor losses and contamination. Refer to the chapter on offsites.

Flocculation Process for removal of suspended solids or other undesirable materials from effluent water using chemicals to cause the particles of material to

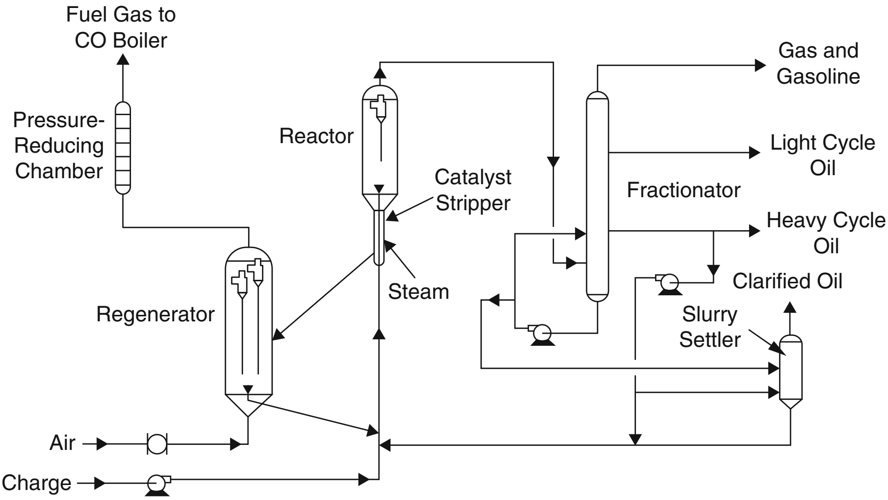


Fig. F.1 A typical "side-by-side" fluid catalytic cracking unit

stick together until they become too heavy to stay suspended. Refer to the chapter on offsites.

Flooding In a distillation tower or absorber, buildup of liquid in the tower producing high-pressure drop and loss of efficiency. Flooding may also mechanically damage the tower internals. Flooding is normally caused by excessive liquid or vapor rates.

Flow meter A device to measure fluid or solid flow rates. Refer to the discussion in the chapter on process controls.

Flow regime Category for the type of flow occurring inside a pipe or other piece of flowing equipment. Refer to the equipment chapter section on two-phase flow.

Flue gas tunnel(s) In a fired heater where the burners are on the roof of the firebox and flow is downward (downfired), these are the refractory tunnels that collect the flue gases evenly and convey them out of the firebox.

Fluid catalytic cracking unit (FCCU or FCC) The fluid catalytic cracking unit (FCCU) is a process for converting middle and heavy distillates to high-octane gasoline and olefin-rich light gases. It is one of the most important conversion processes in a refining. There are several licensed and proprietary versions of this technology and the equipment involved. Generally, the process contacts hot fluidized solid catalyst of very small size with preheated heavy oil. The oil is thermally and catalytically cracked in a very short contact time. The product vapors are separated from the catalyst. Products are fractionated from the vapors, and the catalyst, coated with coke formed in the process, is regenerated with air by burning off the coke. The regeneration process reheats the catalyst for its next trip through the reactor. Figure F.1 shows a simplified flow sheet for an FCC. The process is detailed in the chapter "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining" of this handbook.

Fluid coking A thermal cracking process utilizing the fluidized-solids technique to remove carbon (coke) for continuous conversion of heavy, low-grade oils into lighter products. Flexicoking is an example.

Flushing Using a liquid, such as water or a solvent, to wash out equipment or a system

Flushing oil A low pour point oil used to wash out or "flush" a heavy oil process system or equipment. See the chapter on utilities.

Flux A rate of exposure divided by the area exposed. For instance, a flow rate of 20 lb/h over a 3 square-foot area results in a mass flux of $20\ \text{lb/h} \div 3\ \text{ft}^2 = 6.7\ \text{lb/ft}^2 - \text{h}$. Flux can be applied to rate of heat transfer, rate of mass or volume movement, and so on.

FM Factory Mutual, Inc.

FMEA Failure modes and effects analysis

FMECA Failure modes, effects, and criticality analysis

FO (1) Fail open – control valve; (2) framework order (purchase order type)

Foam generator In firefighting, a device to mix air into a flowing foam chemical stream to create a foam stream to be directed onto a fire. Foam generators may be permanently installed (as on tanks) or portable with a fire truck. Refer to the chapter on firefighting.

Foaming In a tower or separator, foaming is the generation of a stable layer of vapor trapped in liquid film bubbles on top of liquid which can interfere with equipment operation or result in poor performance. Foam can be created by a number of factors, including presence of fine solids or surfactant contaminants in the streams.

FOB Free on board. Terms of a transaction where the seller agrees to make the product available within an agreed-upon time period at a given location. Any subsequent costs are the responsibility of the buyer.

FOE or FOEB Fuel oil equivalent or fuel oil equivalent barrels. A way of accounting for light hydrocarbons by converting their heating value to the equivalent barrels of fuel oil. Normal basis is about 6.05 MMBtu/bbl equivalent, but the basis sometimes varies by user. Used primarily in planning and optimization

Force majeure The legal cancellation of a delivery obligation due to the occurrence of natural acts beyond the direct control of the seller (i.e., operating problems with tankers or refineries or weather disruptions)

Forced draft In a firebox, a fan that blows air into the firebox

Foul (1) See "Fouling." (2) Refers to streams that contain H_2S and other "foul"-smelling compounds

Fouling Deposition of undesirable materials on the surface of equipment or interstitial spaces of packed beds that inhibits operations

FP (1) Flash point; (2) fire protection; (3) freeze point

FPS Feet per second

FQD In the EU, fuel quality directive. Refer to the environmental chapter section on air emissions.

FR Flow recorder

Fracking Crude oil and gas production process used extensively for tight shale formations where a mixture of sand, water, and chemicals is pumped into a well at high pressures to hydraulically fracture the rock formation and prop the fractures apart with sand. On reversing the well flow, oil and gas can go back to the well and be produced.

Fraction A separate identifiable part of crude oil; the product of a refining operation. The different cuts of petroleum products that come off a distillation column contingent on their volatility or boiling range

Fractionation This is a unit operation in chemical engineering which separates components from mixtures in which they are contained by boiling points (AKA distillation). In petroleum refining, this process is a major means of separating precise groups of petroleum components from the crude oil feed and other intermediate refining processes. Separation by fractionation is accomplished by heat and mass transfer on successive stages represented by carefully designed trays. These trays are designed to enhance the heat and mass transfer by good mixing of hot vapors rising through the trays with colder liquid entering the tray. The mixing tends to achieve a phase equilibrium between the liquid and vapor traffic. Refer to the handbook topics "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries," ▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing," and "▶ Process Equipment for Petroleum Processing" for details about some of the applications and design calculations for fractionation units.

FRC (1) Fire (or flame)-resistant (or retardant) clothing (e.g., Nomex); (2) flow recorder and controller

Fresh feed input Represents input of material (crude oil, unfinished oils, natural gas liquids, other hydrocarbons and oxygenates, or finished products) to processing units at a refinery that is being processed (input) into a particular unit for the first time. Examples:

- Unfinished oils coming out of a crude oil distillation unit which are input into a catalytic cracking unit are considered fresh feed to the catalytic cracking unit.
- Unfinished oils coming out of a catalytic cracking unit being looped back into the same catalytic cracking unit to be reprocessed are not considered fresh feed.

Front-end loading (FEL) An approach to project execution that uses more detailed engineering during the early phases of the project evaluation to provide a more accurate project cost and better economic evaluation. This approach is discussed in the chapter on projects.

Froth flow (AKA bubble flow) Flow regime in which bubbles of gas are dispersed in a primarily liquid phase with the gas moving about the same velocity as the liquid. Refer to the chapter on equipment, two-phase pressure drop section.

FSA (1) Flexible spending account; (2) food services administration; (3) formal safety assessment

FSSL Fail-safe solid-state logic

FT (1) Flow transmitter; (2) flash trend

FTA Fault-tree analysis

FTE (1) Full-time equivalent person in hours; (2) in controls = fault-tolerant Ethernet

FTIR Fourier transform infrared analysis method

FTZ Foreign trade zone

Fuel coke Grade of petroleum coke used in fired heaters in place of coal

Fuel ethanol An anhydrous denatured aliphatic alcohol intended for gasoline blending as described in oxygenates definition

Fuel gas Any gas used as fuel in a facility

Fuel oil The heavy distillates from the oil refining process; used as fuel for power stations and marine boilers. Heavy fuel oils produced from the nonvolatile residue from the fractional distillation process. Heavy oils that are "leftovers" from various refining processes. Heavy black oils used in marine boilers and in heating plants

Fuel oil equivalent (FOE) A measure of heat content of a fuel by comparison with a standard barrel of fuel oil, nominally containing 6.05 MMBtu of energy. The basis can vary by user, however.

Fuel oil equivalent barrels (FOEB) See fuel oil equivalent.

Fuel tip See "Burner Tip."

Fuel rich A firebox condition where there is more fuel than combustion air – very dangerous – potential for explosion

Fuel solvent deasphalting A refining process for removing asphalt compounds from petroleum fractions, such as reduced crude oil. The recovered stream from this process is used to produce fuel products.

Fugitive Generally refers to air emissions of pollutants, such as "fugitive" dust generated by material-handling activities

Fungible Term which refers to the likeness or at least "interchangeability of a petroleum product." Material shipped on a pipeline must be "fungible," i.e., meets a common set of specifications acceptable to various shippers, and the same holds true for future contracts. The less fungible the product, the less likely it is to succeed in the futures arena and the more problem it is likely to create in the distribution process. Various elements of the Clean Air Act have made several petroleum products less fungible.

Full-conversion refinery Also known as a "complex" refinery; this is the type of refinery configuration with process capability for conversion of nearly all of a crude oil to high-value products. These refineries may also make petrochemicals in addition to fuels and other petroleum products. Such refineries include crude distillation, hydroprocessing, reforming, cracking, resid conversion, octane/cetane improvement, and other processes.

Fungible crude See "Fungible."

Furfural or furfuraldehyde Furfural is a heterocyclic aldehyde, with a ring structure containing four carbons and an oxygen atom. The chemical formula is OC_4H_3CHO. Used for solvent refining of lube oils. Refer to the chapters on nonfuel refineries and hazardous materials.

Furnace oil Canadian term used to describe high-sulfur No. 2 oil. So, furnace oil in Canada is the equivalent of our high-sulfur, off-road, fuel or home heating oil.

FV Full vacuum

FZGO Flash zone gas oil or "fuzzy gas oil"

G

GAAP Generally accepted accounting principles

Gallon Measurement of volume in the oil industry (42 gal = 1 barrel)

Galvanic corrosion Corrosion of metal caused by electrochemical interaction of incompatible materials

Gap control A process control mode where the controller takes action if the process variable moves outside a specified rage, but takes no action as long as the variable is within the allowable range.

Gaps and overlaps In distillation, gaps and overlaps normally refer to the differences between the temperatures at 95 vol% recovery in a lighter cut and 5 vol% recovery of the adjacent heavier cut based on their ASTM distillation. Figure G.1 illustrates this concept.

The ASTM gap shown in Fig. G.1 would be typical in the separation between naphtha and kero in the atmospheric distillation unit. The 5 % temperature of the kero (cut 2) is higher than the naphtha (cut 1) 95 % temperature. This is a good separation because there are few kero components in the heavy end of the naphtha. The overlap illustration is typical of the separation between the heavier products of the atmospheric distillation of crude oil such as between light gas oil cut and the heavy gas oil cut. A gap then is when the numeric difference between the 5 % of the heavier cut and the 95 % of the lighter cut is positive. An overlap is when this difference is negative.

Gas chromatograph An analyzer type that uses differential diffusion rates of compounds through a tiny packed column to determine a material's composition. Refer to the chapter on controls.

Gas – refinery fuel The gas fractions in petroleum refining may be taken as that fraction of crude or produced in a process that boils below propane. This vapor fraction is usually used as a fuel to the refinery's fired heaters. The fuel gas is normally treated to remove sulfur compounds to control SOx emissions and any

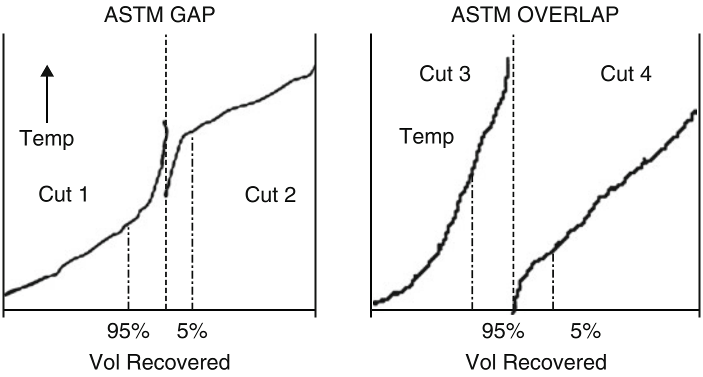


Fig. G.1 Defining gaps and overlaps in fractionation liquids are knocked out ahead of the heaters. Gas treating is discussed in the chapter "▶ Refinery Gas Treating Processes," and fuel gas utility handling is in the handbook chapter "▶ Utilities in Petroleum Processing."

Gas oil (gasoil) A medium-heavy hydrocarbon boiling typically between about 500 and 1,200 °F. Gasoil is normally cracked to lighter products or used as fuel. There are multiple grades: AGO (atmospheric gas oil), VGO (vacuum gas oil), SRVGO (straight-run VGO), LGO (light gas oil), etc. Usually, there will be two gas oil sidestreams, a light gas oil sidestream and, below this take-off, a heavy gas oil sidestream. Both these sidestreams are normally stripped using steam or reboiling to meet their respective flash point specifications (usually 150 °F minimum). The lighter sidestream cut of about 480–610 °F on crude is the principal precursor for the automotive diesel-grade finished product; this sidestream is desulfurized to meet the diesel sulfur specification in a hydrotreater (see the chapter "▶ Hydrotreating in Petroleum Processing" in this handbook). The lower gas oil stream can be a guard stream to correct the diesel distillation end point. This heavy gas oil may also be hydrodesulfurized and routed to either the fuel oil pool (e.g., as a precursor for marine diesel), a finished heating oil product from the gas oil pool, or cracked and lighter products. See also the topic "▶ Petroleum Products and a Refinery Configuration" in this handbook.

Gas to liquids (GTL) A process that converts hydrocarbon gas to liquid hydrocarbon products. See the discussion of "xTL" in the chapters on unconventional crudes and feedstocks and chemicals from natural gas and coal.

Gas treating processes Refinery gas treating usually refers to the process used to remove the so-called acid gases (hydrogen sulfide and carbon dioxide) from the refinery gas streams. These acid gas removal processes used in the refinery are required either to purify a gas stream for further use in a process or for environmental reasons associated with the use of the gas for fuel. Clean air regulations now being practiced in most industrial countries require the removal of these acid gases to very low concentrations. The treating generally involves scrubbing the gas with a chemically "basic" solution to remove the acidic gases. The solution is then regenerated to release the acid gases for further processing, and the lean solution is recycled. See the chapter "▶ Refinery Gas Treating Processes" and the definition for amine absorption processes.

Gas blanketed Using an inert or relatively inert gas to prevent air contact with a petroleum stock during storage or in surge drums. Common blanket gases include natural gas and nitrogen. In ships, frequently engine exhaust is used for blanketing; although it still contains some oxygen, it will not easily support combustion.

Gasification Generic term for conversion of heavy liquids or solids to gaseous products. Gasification includes partial oxidation of solids or tars to form synthesis gas. Examples of gasification include the initial steps of the coal-to-liquids or resid-to-liquids processes.

Gasohol A blend of finished motor gasoline containing alcohol (generally ethanol but sometimes methanol) at a concentration of 10 % or less by volume. Data on gasohol that has at least 2.7 % oxygen, by weight, and is intended for sale inside carbon monoxide nonattainment areas are included in data on oxygenated gasoline. See oxygenates.

Gasoline(s) Fuel generally boiling in the 50–400 °F range used for automotive transportation. Several subgrades exist. They are readily and widely used by the general public. The current trend in gasoline specifications is toward lower sulfur (<10 ppm), lower vapor pressure (RVP <7), and fewer aromatics and air toxics. These enable cleaner engines.

Two major gasoline products are produced in most petroleum refineries. Their specifications and standard quality are discussed in multiple chapters of this handbook. The two finished grades shipped from final blending facilities are usually (1) a regular grade with an octane number of 87 and (2) a premium grade with an octane number of 93. Because of oxygenate blending requirements, the blended gasoline actually leaving a refinery will have a lower octane value because the final grade, with the oxygenate addition, is made at a product terminal. These octane levels may differ slightly from country to country, but these are the key quality for North America, with octane numbers defined as (RON + MON)/2.

Gasoline blending components Naphthas which will be used for blending or compounding into finished aviation or motor gasoline (e.g., straight-run gasoline, alkylate, reformate, benzene, toluene, and xylenes). Excludes oxygenates (alcohols, ethers), butane, and natural gasoline

Gauge (or gage) pressure Pressure referenced to atmospheric pressure. Atmospheric pressure is taken as 0 psig.

GC (1) Gas chromatograph or chromatography – analytical method; (2) Gulf Coast

GC/MS Combined analytical technique using both GC and MS to characterize a hydrocarbon stock

GFCI Ground fault circuit interrupter

GHG Greenhouse gas – refers to CO_2, methane, NO_x, etc., in the atmosphere that can affect global warming

GHV Gross heating value. Essentially the same as higher heating value (HHV)

Gilliland correlations An empirical correlation between the number of stages in a distillation or contacting column at finite reflux ratio and the minimum number of stages required at the minimum reflux ratio. Refer to the handbook chapter on light ends.

GOHDS Gas oil hydrodesulfurization unit

GOPA Gas oil pump around in a fractionator

GOR Gas-to-oil ratio

GPD or gpd Gallons per day

GPM or gpm Gallons per minute

GPSA Gas Processors Suppliers Association. Produce a very good technical data book

Green diesel Renewable diesel stock produced by hydrotreating animal fats or vegetable oils. The category includes stand-alone processing as well as coprocessing. Refer to the discussions on unconventional stocks and renewables.

Green gasoline Renewable gasoline stock produced by coprocessing vegetable oils and animal fats with gas oils in an FCC unit. See the chapters on renewables and unconventional stocks.

Green olefins Renewable petrochemical feedstock produced from an FCC unit by coprocessing vegetable oils and animal fats with gas oils. See the chapters on renewables and unconventional stocks.

Grid (1) Grids are used as low-pressure drop packing in certain fractionation towers. They came into prominence with the development of the crude oil "dry vacuum" units. See the chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook and the relevant section of the chapter on "▶ Process Equipment for Petroleum Processing" for details of this type of packing and its use. (2) The electrical anodes in a desalter, electrostatic precipitator, or other electrostatic separation processes

Gross Apparent overall difference. For example, "Gross Margin."

GRP Gas recovery plant

GTL Gas-to-liquids abbreviation

Gulf Coast spot market Large-volume transactions (from 25,000 barrels to full tankers of petroleum products) bought or sold for a stipulated delivery in the near future. Although this market might entail several pipeline or waterborne transaction points in the Texas and Louisiana area, unless specified otherwise, it reflects the delivery of the product the same month at a Pasadena, Texas, origin on Colonial Pipeline.

GUI Graphical user interface

Gum A heavy polymer that forms in a hydrocarbon stock from polymerization of olefinic components in the stock. It may form in storage, during transit, or when a stock is heated in a refining process. Gums are a significant source of fouling resulting in loss of heat transfer and increased pressure drop/energy consumption in refining units.

GWD EU Ground Water Directive

H

H&MB Heat and material balance

H_2 or H2 (1) Hydrogen; (2) how to

H_2S Hydrogen sulfide

HAZ waste or Haz Waste Hazardous waste

Hazardous waste A waste that is either defined as a hazardous waste by regulation or possesses certain hazardous characteristics. Refer to the environmental chapter.

HAZCOM Hazard communication

HAZID Hazard identification

HAZMAT Hazardous materials

HazOp or HAZOP Hazard and operability review – one of the process hazards analysis methods most commonly used

HAZSUB Hazardous substance

HAZWOPER Hazardous Waste Operations and Emergency Response

HC Hydrocarbon – generic

HCGO Heavy coker gas oil

HCK Sometimes used as abbreviation for hydrocracker

HCO Heavy cycle oil – from an FCC

HCR Human cognitive reliability model

HCU Hydrocracking unit

HDC Hydrocracker

HDF Hydrofinisher

HDN Hydrodenitrification or hydrodenitrogenation

HDPE High-density polyethylene

HDS (1) Hydrodesulfurization; (2) hydrodesulfurization unit – a hydrotreater

HDT Hydrotreater

HDW Hydrodewaxer

Header A piping system used for collection/distribution of a process fluid from/to multiple points. For example, a steam header is used to distribute steam to various steam users within an area.

Heat and material balance A material balance with all the heat inputs, outputs, chemical releases, and other thermodynamic factors included

Heat of combustion, gross Total heat evolved during complete combustion of unit weight of a substance with water vapor condensed, usually expressed in Btu per pound

Heat of combustion, net Gross heat of combustion minus the latent heat of condensation of any water produced

Heat pump A system for moving heat from a lower temperature to a higher temperature using a working fluid

Heater(s) Heaters are used extensively in petroleum refining to provide heat energy to the process plants utilizing an independent energy source, namely, fuel oil or fuel gas. A heater or fired heater provides process heat by burning a fuel in a firebox and transferring the heat generated to a process fluid contained in tubes within the heater. Generally, fired heaters fall into two major categories: horizontal and vertical. There is a detailed discussion of fired heaters or furnaces and their design in the handbook topic "▶ Process Equipment for Petroleum Processing." Emissions and emission controls for fired heaters are covered in the topic "▶ Environmental Control and Engineering in Petroleum Processing" of this handbook.

Heater burners (or burners) The purpose of a heater burner is to mix fuel and oxidizer (normally air) to ensure complete combustion in a fired heater. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for a detailed discussion of burner designs and critical factors. Additional discussion on burner design factors affecting emissions is included in the topic "▶ Environmental Control and Engineering in Petroleum Processing" of this handbook.

Heater coil The tubes in a fired heater through which the process fluid flows as it is being heated

Heating oil A distillate used for home or commercial heating. Widely used as a synonym for No. 2 fuel oil or diesel

Heavy crude Crude with a high specific gravity, i.e., high density (low API gravity, e.g., <15 °API); due to the presence of a high proportion of heavy hydrocarbon fractions and metallic content

Heater efficiency The efficiency of a fired heater is the ratio of the heat absorbed by the process fluid to the heat released by combustion of the fuel expressed as a percentage. Heat release may be based on the LHV (lower heating value) of the fuel or HHV (higher heating value). Process heaters are usually based on LHV and boilers on HHV. The HHV efficiency is lower than the LHV efficiency by the ratio of the two heating values. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing."

Heat exchangers Devices for transferring heat from a hot fluid to a cooler fluid. Heat exchange is the science that deals with the rate of heat transfer between hot and cold bodies, in this case, different flowing streams. There are three modes of heat transfer typically encountered in petroleum processes: conduction, convection, and radiation. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for a detailed treatment of heat exchange and heat exchangers.

Heavy oil cracking (HOC) This is a process similar to a fluid catalytic cracker (FCC) that is designed to crack residual oils that were beyond the heat balance capability of FCCs. The primary difference in the process compared to an FCC is the introduction of steam generation coils into the regenerator vessel to enable control of the regeneration temperature. Please refer to the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook for more details on this process.

HEP (1) Height equivalent to a theoretical tray for packing in a mass transfer or fractionation tower. Refer to the equipment chapter, section on distillation and packed towers. (2) Human error probability

HETP Height equivalent to a theoretical tray (or "plate") for packing in a mass transfer or fractionation tower. Refer to the equipment chapter section on distillation and packed towers.

HF Hydrofluoric Acid

Hg Mercury

HGO Heavy gas oil – normally refers to vacuum gas oil material (650 °F and heavier) but may also refer to heavy diesel (normally 500–650 °F). Refiner (and sometimes refinery) specific.

HHC Highly hazardous chemical

HHPS Hot high-pressure separator

HHPV Hot high-pressure vapor

HHV Higher heating value – assumes all combustion products are cooled back to 25 °C

HID Hot inlet temperature, design

High-TAN crude Crude with total acid number (TAN) >1.0

HIPPS (1) High-integrity pressure protection system; (2) high-integrity pipeline protection system

HIPS Hot-intermediate-pressure separator

HIT Hot inlet temperature, normal

HK Hydrocracker or hydrocracking

HKO Hydrocracked oil

HLL High liquid level

HLSD High-level shutdown

HMI Human–machine interface – the way we interact with a control system

HOD (1) Heating oil distillate; (2) hot outlet temperature, design

Homogenizer A mechanical device which is used to create a stable, uniform dispersion of an insoluble phase (asphaltenes) within a liquid phase (fuel oil)

Horton sphere A type of spheroidal pressure storage tank designed for products having vapor pressures higher than atmospheric pressure but relatively limited vapor pressure – such as pentanes.

Hose reel or hose station Firefighting equipment consisting of a coiled reel of hose with a fire nozzle. In the event of a fire, the hose can be unrolled and generally operated by one person. Refer to the chapter on firefighting.

HOT (1) Hot outlet temperature, normal; (2) head of terms – agreement in principle for a business arrangement

Hot and cold flash separators Hot and cold flash separators are used in high-pressure, high-temperature hydrocracking, gasoil hydrotreating, and similar applications where heavy oils are present along with lighter oils. Purposes of the hot/cold separations include (1) avoiding heavy oils setting up at the low temperatures in the cold separator, (2) recovering high purity hydrogen for recycle in as economically as possible, (3) increasing energy efficiency by reducing heat rejected to air, and (4) reducing the size of the effluent train exchangers and cold separator. The hot separator is normally located in the process effluent at a temperature of ~400–600 °F. Liquid from the hot flash is dry and can go directly to fractionation or another unit. The hot flash vapor is cooled further and sent to the cold-high-pressure separator where the recycle hydrogen gas and lighter oils are drawn and sour effluent wash water is removed. See the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook for an example of a hot/cold separator system in a resid hydrotreater. Some units also have warm separators at ~300–400 °F interposed between the hot and cold separators, but these are not common.

Hot lime process Method for purifying water using lime to remove hardness components. Used for boiler feed water. Refer to the chapter on utilities.

Hot work Work in a facility that produces sparks or sufficient heat to ignite flammable materials

HP (1) Horsepower; (2) high pressure; (2) human performance
HRA Human reliability analysis
HRF Hazard reduction factor
HRSG Heat recovery steam generator – waste heat boiler
HSE (1) Health, safety, and environmental; (2) Health and Safety Executive (UK)
HSM Horizontal support members
HSR (1) Heavy straight run; (2) high-sulfur recarburizer (coke)
HSS Heat stable salt
HSSR Heat stable salt removal
HSWA Hazardous and solid waste amendments to the US RCRA
HT Hydrotreater or hydrotreating
HTHA High-temperature hydrogen attack
HTML HyperText Markup Language
HTRI Heat Transfer Research, Inc.
HTSD High-temperature simulated distillation
HTTP Hypertext Transfer Protocol
Huff and puff Production method for heavy oils that involves heating a formation with superheated steam or other means followed by a soak period. The heated hydrocarbon in the formation is then produced as crude oil. See the discussion of bitumens and extra heavy oils in the chapter on unconventional crudes and feedstocks.
HVAC Heating, ventilation, and air conditioning
HVGO Heavy vacuum gas oil
HX Heat exchanger
Hydrant Firefighting water connection point for hoses and for direct use on a fire or for pumper truck suction. Hydrants are usually located at defined intervals along the mains and in the loops. See the chapter on firefighting.
Hydraulic analysis of process systems Hydraulic analysis is used to calculate a pressure profile of a process system. Such a calculation is used to size pipelines and to determine the pumping requirements for the system, as well as setting operating and design pressures for equipment within the system. Refer to Appendix 14 of the chapter entitled "▶ Process Equipment for Petroleum Processing" for an example of how a hydraulic analysis can be performed. That chapter contains a significant discussion of pressure drop calculations for various scenarios.
Hydraulic fracturing An oil field production process which creates fractures or cracks in the rock formation to allow oil and gas to flow out of the formation. See "Fracking" and the discussion of shale crudes in the chapter on unconventional crudes.
Hydraulic horsepower Power required for pumping liquid to the required pressure at the specified flow rate. Neglects efficiency and other losses. Only the amount of power that must be put into the fluid. Refer to the equipment chapter section on pumps.
Hydroclone An in-line device for separating solids from a liquid using centrifugal force and density differences. This is a liquid version of a gas cyclone.

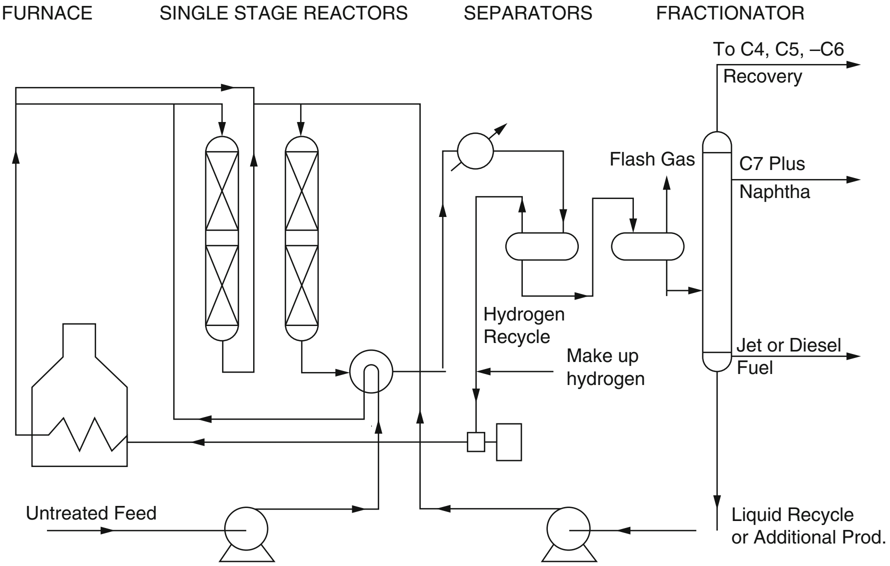


Fig. H.1 A distillate hydrocracker configuration

An example application would be removal of fine particulates from a flushing oil stream going to a centrifugal pump seal.

Hydrocracker Process using high-pressure hydrogen at high temperatures with acidic catalyst to reduce the size of various hydrocarbon feed molecules to smaller, more valuable products. Products typically include diesel, kerosene, and naphtha with nearly zero sulfur and nitrogen. The unconverted oil can be reduced to a very small stream in a hydrocracker. See the chapter on "▶ Hydrocracking in Petroleum Processing" in this handbook for additional details. Also, see Fig. H.1.

Hydrocracking (distillate) See "Hydrocracker" above. Details of this process are given in the chapter on "▶ Hydrocracking in Petroleum Processing" in this handbook. Figure H.1 shows the reaction section for a typical hydrocracking unit for distillates. Figure H.2 is a typical block flow diagram for recovery of distillate hydrocracker products.

Hydrodenitrogenation Removing nitrogen from an oil by hydrotreating it to ammonia

Hydrodesulfurization Removing sulfur from an oil by hydrotreating it to hydrogen sulfide

Hydrofluoric acid HF. Refer to "Anhydrous hydrofluoric acid."

Hydrogen Hydrogen gas is used in several petroleum processes. The primary users in a refinery are the hydrotreater and hydrocracker processes. It also finds smaller uses in reformers for startup and in some sulfur plants. Hydrogen is produced by catalytic naphtha reformers as a by-product of the reforming reactions and by steam-methane-reforming hydrogen plants. Many refineries

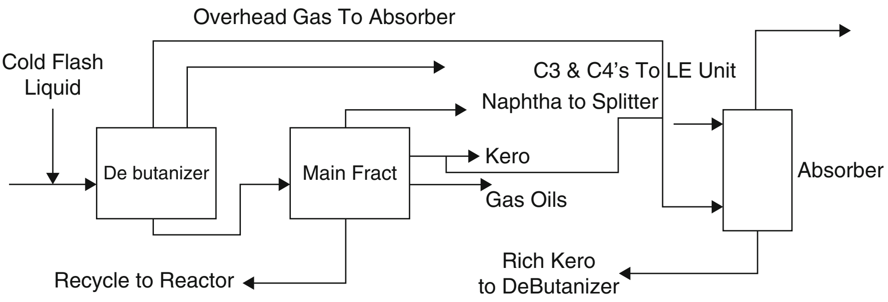


Fig. H.2 Block flow diagram of a typical hydrocracker recovery side

buy hydrogen externally, often delivered by pipeline from a producer. Unused hydrogen finds its way into the fuel gas system. Many facilities recover and recycle hydrogen from the fuel gases. Refer to the chapter "▶ Hydrogen Production and Management for Petroleum Processing" in this handbook for a more detailed discussion of hydrogen in a refinery.

Hydrogenation Adding hydrogen to an unsaturated organic molecule

Hydrogen sulfide (H_2S) Hydrogen sulfide is a colorless, extremely poisonous gas that has a very disagreeable odor, much like that of rotten eggs, in low concentrations. In high concentrations that are IDLH, it deadens the sense of smell. In a refinery, it is usually formed during the desulfurizing processes used to sweeten product streams as well as other processes. In practice, H_2S can be assumed to be present throughout a refinery in most processing streams at varying concentrations.

Hydrolysis Breaking down a substance by addition of water

Hydrometer An instrument (float) for determining the gravity of a liquid

Hydroprocessing The generic term for refining processes employing hydrogen in reactions. They operate at elevated temperatures and pressures using a selective catalyst. The term includes hydrotreating, hydrocracking, isomerization, reforming, hydrodewaxing, and other processes that use recycle or once-through hydrogen-containing streams.

Hydroskimming refinery A simple refinery configuration in which straight-run atmospheric crude distillation products are processed to meet product specifications. Atmospheric resid is normally sold as fuel oil. Processing may include reforming, hydrotreating, isomerization, and other product property improvement processes in addition to crude distillation. There is no cracking or resid conversion in hydroskimming facilities.

Hydrotreater Process using hydrogen at high temperatures and elevated pressures with catalyst to remove sulfur, nitrogen, and other contaminants from hydrocarbon stocks. See "Hydrotreating."

Hydrotreating The hydrotreating family of processes removes sulfur, nitrogen, oxygen, and other impurities from petroleum stocks to yield clean, finished

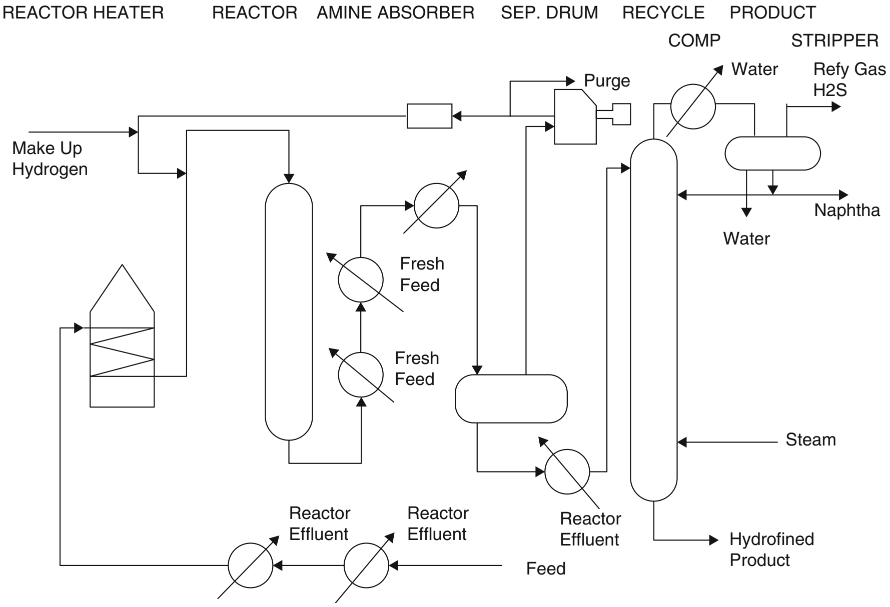


Fig. H.3 A simple gas oil hydrodesulfurizer

blendstocks or feeds for other processes. Hydrotreating can also improve distillate product yield properties. The flavors of hydrotreating are based on the boiling range of the feedstock and the product objectives. Hydrotreating applications include naphtha, kerosene, diesel, gas oil, and residuum. Refer to the chapter "▶ Hydrotreating in Petroleum Processing" in this handbook for a discussion of hydrotreating for most of these stocks. Figure H.3 illustrates a simple gasoil hydrotreater flow.

I

I/O Input/output for a control system

I/P Current to pneumatic transducer or converter

IA Instrument air

IAP (1) Incident action plan; (2) integrated asset planning

IBP Initial boiling point. In a standard laboratory distillation, the temperature on the distillation thermometer at the moment the first drop of distillate falls from the condenser

i-component The "i" as a prefix to a chemical component indicates that the compound is an isomer. There are several isomers in petroleum refining, and the most common relate to the light components of the structure. Notably these are:

- Isobutane: *i* C_4 or *i*-butane
- Isopentane: *i* C_5 or *i*-pentane
- Isohexane: *i*C_6 or *i*-hexane

and so on through the homologues. When isomers exist and are quoted together with the normal compound, this normal compound will be identified by a prefix *n*.

IC Initiating cause

ICC (1) International Chamber of Commerce; (2) US Interstate Commerce Commission (eliminated by legislation in 1995 and replaced with the DOT)

ICFM Inlet cubic feet per minute

IChE Institute of Chemical Engineers (UK)

ICL Independent control layer

ICS Incident command system. See the chapter on firefighting in this handbook.

ID (1) Inside diameter; (2) induced draft (in a firebox – a fan that sucks out the flue gases)

IDLH Immediately dangerous to life and health

IDW Isodewaxer

IEA International Energy Agency (Paris)

IEC International Electrotechnical Commission (Switzerland)

IED Industrial Emissions Directive – in the EU. Refer to the environmental chapter.

IEEE Institute of Electrical and Electronics Engineers

IFP (1) Institute Francais do Petrole (France); (2) invitation for prequalification or proposal

IG Index of gravity

IGCC Integrated gasification combined cycle

Ignitability Hazardous waste characteristic of being pyrophoric or self-heating on exposure to air. Refer to the environmental chapter section on hazardous wastes.

IHS (1) Industrial health and safety; (2) a company providing database services in the IHS areas; (3) industrial hygiene standard; (4) information handling services

Immediately Dangerous to Life and Health (IDLH) Concentration or exposure to a substance which can result in immediate or imminent death. For example, exposure to 1,200 ppm of CO is likely to result in death unless the person receives medical attention immediately.

IMO International Maritime Organization. Refer to the environmental chapter section on air emissions.

Impeller speeds (pumps) This term refers to the revolutions per minute (rpm) at which a centrifugal pump impeller spins. Higher-speed centrifugal pumps normally operate at impeller speeds of ~3,550 rpm (60 cycles/s power) or ~2,950 rpm (50 cycles/s power). Lower-speed pumps operate at ~1,750 or ~1,450 rpm on 60 and 50 cycles/s power, respectively. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for a more detailed discussion.

Impingement Refers to direct contact or impact of one material on another, for example, flame impingement on heater tubes when the flame "licks" the tube.

In another example, fluid entering the shell side of a heat exchanger may impinge on the tubes.

Imports Receipts of crude oil and petroleum products into a country or other region. May also refer to imports into a refinery or process units

IMT Incident Management Team (for emergency responses)

In. W.C. Inches of water column (pressure measure)

Incident command system (ICS) A standardized organization and responsibilities structure for responding to emergencies that represents best practices. It is a key feature of the US National Incident Management System (NIMS). This system can be used for fires, releases, medical emergencies, or any other type of situation where fast response is required. Refer to the chapter on firefighting for a detailed discussion.

Incompatible Refers to materials or stocks that have adverse results when mixed together. For instance, mixing a very aromatic crude and a very paraffinic crude together will usually result in precipitation of asphaltene compounds from the aromatic crude or paraffin wax from the paraffinic crude. May also refer to tolerance of construction materials in contact with stocks. For instance, a high-TAN crude is not compatible with carbon steel at elevated temperatures.

Indices Indices are used extensively in petroleum refining technology to correlate one set of data with another. The handbook discussions under the topics "▶ Introduction to Crude Oil and Petroleum Processing" and "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" provide indices that relate the properties of various components to temperature, viscosities, flash point blending, and the like. A number of these indices are used in the blending of petroleum fractions to give the properties of the blended product. For example, the components listed in Table I.1 are to be blended in the proportions given and the viscosity of the blended product determined.

Induced draft In a firebox, a fan that sucks out the flue gases

Inert Incapable of reacting

Table I.1 An example of viscosity blending using viscosity blending indices

Component	Vol %	Mid BPt °F	Viscosity cSt 100 °F	Blending index	Viscosity factor
	(A)			(B)	(A × B)
1	13.0	410	1.49	63.5	825.5
2	16.5	460	2.0	58.0	957
3	21.0	489	2.4	55.0	1,155
4	18.0	520	2.9	52.5	945
5	18.5	550	3.7	49.0	906.5
6	13.0	592	4.8	46.0	598
Total	100.0				5,387.0

Overall viscosity index $= \frac{5.387}{100} = 53.87$

An index of 53.87 corresponds to 2.65 cSt (actual plant test data was 2.7 cST). Indices are covered in the introductory chapter of this handbook

Inert entry Personnel entry into equipment that is full of inert gas (normally nitrogen) used to prevent undesirable reactions. Inert entry requires an air supply for those entering and strict, extensive procedures to protect the entrant. Refer to the chapter on safety.

Inferred properties In control systems, physical and chemical properties in a stream can be estimated fairly accurately over a limited range using the plant operating conditions. This approach is used extensively in advanced control, especially around fractionation systems. Development of the inferred property correlations requires an initial set of controlled conditions and analyses. See the chapter on controls.

Infrared analyzer An analyzer (online or offline) which determines composition of a sample by measuring absorption or transmittance of infrared light through the sample. Refer to the chapter on controls.

Initial boiling points Initial boiling points or IBPs refer to the temperature at which a petroleum cut begins to boil. Usually, this temperature is taken as that at atmospheric pressure. These are determined in the refinery's laboratory from the ASTM distillation carried out as a routine test. Details of these tests are given in the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook.

Inlet diffuser A device at the inlet to a reactor or other equipment to dissipate the incoming fluid momentum and provide a rough distribution of the incoming fluid over the equipment cross section

Inlet guide vane In a compressor, a set of vanes that control the velocity of incoming gas to affect the compressor equivalent capacity. Refer to the equipment chapter section on centrifugal compressors.

In-line blending System which produces a blended product by continuously mixing controlled proportions of the blend components in a common line going to a finished blend tank. Refer to the chapter on offsites.

Innage Space occupied in a product container

INPNA Analytical method that determines iso and normal paraffins, naphthenes, and aromatics in a hydrocarbon stock

INPO Institute of Nuclear Power Operations

Input (1) Total of all streams entering a refinery or process unit. (2) The measured parameter or parameters provided to a controller. These may be direct readings, 3–15 psi pneumatic signals, 4–20 ma electrical signals, or digital.

In situ Refers to processes that are performed with raw materials still in place, for example, processes that retort oil shale while it is still in place in the ground

Instrument air Compressed, dried air supplied by a secure system that is used for motive force in pneumatic instruments. Refer to the chapter on utilities.

Instrumentation This term refers generically to the control systems used in managing the petroleum refining processes. These systems are used to sense and maintain the correct, stable operating conditions (such as flow, temperature, pressure, level, and composition) in process equipment and piping.

These are described and discussed in detail in the chapter "▶ Process Controls in Petroleum Processing."

Insulation Material to prevent heat loss

Intalox saddle A mass transfer packing shaped somewhat like a saddle with additional structure to increase surface area and contacting. Refer to the chapter on equipment, section on packed towers.

Integral control A control mode where the controller output is determined by the deviation from the setpoint and how long that deviation has existed. Acts like an amplification term. Normally used as a fine-tuning parameter in a proportional control mode

Integrated oil company A company involved in all aspects of the petroleum business from exploration to retail sales of refined petroleum products

Intercooling Cooling between stages of a reciprocating compressor to improve compression efficiency. Refer to the chapter on equipment, section on reciprocating compressors. More generically, refers to cooling between two stages of any stage-wise process system

Interface A mixture of petroleum products occurring when batches of different products are shipped consecutively through a pipeline

Intermediate Partially refined product between process units. Intermediates may also be traded between refineries to manage short-term needs or bought and sold

Intermediate law A mathematical relationship that describes the rate of movement of a particle or droplet through another continuous phase in the transition flow regime between laminar and turbulent conditions. Refer to the environmental chapter section on water and the process equipment chapter discussion of separators and drums.

Internals (vessels) This is a generic term used to designate the parts of process equipment that are inside vessels, towers, drums, and other equipment. These internals are primarily aimed at (1) enhancing heat and mass transfer (e.g., fractionating towers), (2) maintaining proper conditions for settling (e.g., condensate drums), (3) promoting good distribution of fluids (vessel or reactor inlet distributors), and (4) preventing vortexing of fluids leaving vessels to pump suction. Vessel internals are discussed in several chapters of this handbook, but a detailed discussion is in the handbook topic "▶ Process Equipment for Petroleum Processing."

International Energy Agency (IEA) An agency in Paris, France, which tracks energy statistics and information on an international level

International Petroleum Exchange Now "ICE Futures"; formerly one of the world's largest energy futures and options exchanges (London). Brent crude pricing

Interstate Commerce Commission (ICC) Former US federal authority regulating interstate commerce that was eliminated by legislation in 1995 and replaced with the Department of Transportation (DOT).

Investment analysis See earlier term: "Economic analysis." Refer to the chapter titled "▶ Petroleum Processing Projects" in this handbook.

IOD Immediate oxygen demand. Oxygen consumption by reducing chemicals, such as sulfides and nitrates where oxidation occurs rapidly. Refer to the environmental chapter section on water.

Ion exchange A process using specifically designed polymer resins which can react with ions in aqueous solution. The resins are preloaded with a desirable ion, like H^+ or OH^- using a strong acid or base, respectively. When a solution is passed through beds of the resin, the more desirable ions in the resin displace the original undesirable ions (ion exchange), improving the solution purity. Refer to the chapter on utilities.

Ionization The process of adding electrons to, or removing electrons from, atoms or molecules, thereby creating ions. High temperatures, electrical discharges, and nuclear radiation can cause ionization.

IP (1) Intellectual Property – company confidential information; (2) British Institute of Petroleum

IPE International Petroleum Exchange, now "ICE Futures" (London)

IPL Independent protection layer – part of LOPA method

IR (1) Infrared; (2) integrated review in projects; (3) individual risk

IRR Internal rate of return

IS (1) Information systems; (2) inherently safer or safe

ISA Instrument Society of America

ISO (1) International Organization for Standardization (Switzerland); (2) short for isometric drawing – a 3-D representation of equipment or piping

Isobutane ($i\text{-}C_4H_{10}$) A normally gaseous branch-chain hydrocarbon. It is a colorless paraffinic gas that boils at a temperature of 10.9 °F. It is extracted from natural gas or refinery gas streams. AKA 2-methyl propane

Isobutylene ($i\text{-}C_4H_8$) An olefinic hydrocarbon recovered from refinery processes or petrochemical processes. AKA 2-methyl propene

Iso-container A special tank used for bulk shipment of chemicals. An iso-container can be connected to a truck bed or be moved on its own. Iso-containers can withstand moderate pressures and are used for shipping many hazardous materials.

Isohexane (C_6H_{14}) A saturated branch-chain hydrocarbon. It is a colorless liquid that boils at a temperature of 156.2 °F.

Isomerization The rearrangement of straight-chain hydrocarbon molecules to form branched-chain products

ISS Instrumented safety system

Isomerization The isomerization process forms branched hydrocarbons from paraffins or less-branched hydrocarbons. The branching increases the octane value of the product. Isomerization can also be used to improve cold-flow properties of distillates. This is a type of hydroprocessing operated at mildly elevated temperature and pressure using a selective catalyst. A simplified isomerization flow diagram is shown in Fig. I.1. Refer to the chapter titled "▶ Isomerization in Petroleum Processing" in this handbook for a detailed discussion of the process.

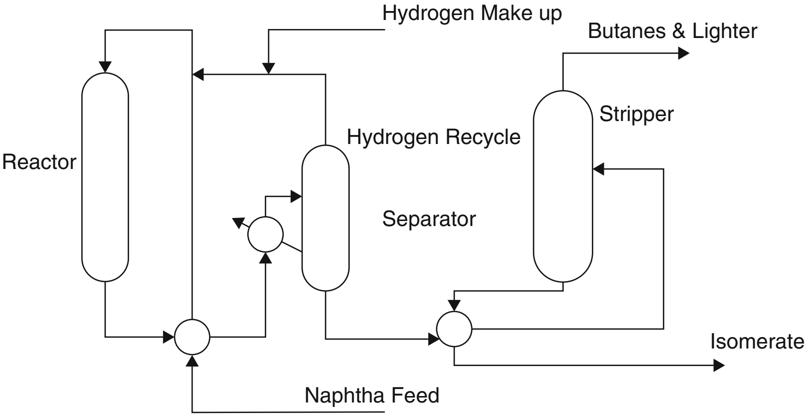


Fig. I.1 A process diagram of a typical isomerization unit

Table J.1 Comparison of some jet fuels

Specification	ASTM D1655	Def Std 91–91
Aromatics vol% max	25	25
Distillation °C		
10 % recovered max	205	205
50 % recovered max	Report	Report
90 % recovered max	Report	Report
End point	300	300
Flash point °C min	38	38
Density at 15 °C kg/m_3	775–840	775–840
Freezing point °C max	−40	−47

IT Information technology – the computer group
ITS (1) Incident tracking system; (2) installation of template
IUPAC International Union of Pure and Applied Chemistry

J

Jet See “Jet Fuels” and “Kerosene.”

Jet fuel Jet fuel refers to products meeting the specifications for civilian or military jet aircraft fuel. A simplified comparison of these two types of fuel is in Table J.1. Jet fuel is discussed in detail in the chapter on “▶ Quality Control of Products in Petroleum Refining” in this handbook.

Jet mixer A device, normally inside a storage tank, which promotes mixing of two fluids using a high-velocity stream. Refer to the chapter on offsites.

Jetties Tankers and barges are loaded and unloaded at jetties or docks. In almost all circumstances, these facilities for handling petroleum products are separate from those used for general cargo. Very often, tankers, particularly modern "super" tankers are loaded and unloaded by submarine pipelines at deepwater anchorage. Only the "onshore" jetty facility is discussed in this handbook. See the chapter on "▶ Off-Site Facilities for Petroleum Processing."

JIT Just in time

Jobber Someone who purchases refined products at the wholesale level and then transfers or resells the product at the retail level. The retail level sale/transfer can occur at facilities owned by the jobber, independent dealers, or commercial accounts.

Joint venture A facility that is operated by two or more companies in partnership. The companies share in the JV profits.

Joule–Thomson effect The observed phenomenon of heating or cooling of a compressed gas if it is allowed to expand adiabatically. Most gases cool on pressure reduction. Hydrogen gas actually heats up when its pressure is reduced ("reverse Joule–Thomson effect"). Hydrogen can even ignite in air when pressure is reduced sufficiently.

JRC Joint Research Centre

JSA Job safety analysis – pre-walk of a job to ensure it can be done safely

JV Abbreviation for joint venture

K

K Watson characterization factor. A factor introduced by Watson and Nelson in 1933 to "quantify" the paraffinicity of petroleum hydrocarbon fractions. It is defined as

$$K = \frac{\left(T_b^{1/3}\right)}{S}$$

where T_b is the mid-boiling point in degrees Rankine and S is the specific gravity at 60 °F. It is also sometimes referred to as the UOP K (please refer to "UOP K" for details).

KB (1) Thousand barrels; (2) kilobyte

KBPD Thousand barrels per day

Kerosene Fuel boiling in the 350–550 °F range normally used for jet aircraft fuel blending but also used for heating and lamps in some areas. The term kerosene generally refers to the blendstocks within the boiling range required for jet and related uses. Table K.1 gives the general spec for some of the kerosene products. Refer to the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook for additional discussion of the product quality tests.

Kerosene-type jet fuel A kerosene-based product having a maximum distillation temperature of 400 °F at the 10 % recovery point and a final maximum boiling point of 572 °F and meeting ASTM specification D1655 and military specifications MIL-T-5624P and MIL-T-83133D (grades JP-5 and JP-8). It is used for

Table K.1 Specifications for some kerosene finished products

Parameters	Reg kero	ATG	TVO	Test
Flash point °F	100	<66	100	D-56
Aromatics vol%	–	20	–	D-1319
Temperature at 20 % max		293°	–	D-86
Temperature at 50 % max		374°	–	D-86
Temperature at 90 % max		473°	540	D-86
Final boiling point	572 °F	572°	–	D-86
Sulfur max wt%	0.04	0.04	0.3	D-1266
Smoke point min	–	25 mm	25 mm	D-1322
Freeze point °C	–	−47	–	D-2386

commercial and military turbojet and turboprop aircraft engines:

- Commercial – kerosene-type jet fuel intended for use in commercial aircraft
- Military – kerosene-type jet fuel intended for use in military aircraft

Kettle A type of heat exchanger used for tower reboilers and steam generation. Refer to the chapters on equipment and utilities.

KEV (1) Key energy variable – for a specific unit or process; (2) thousand electron volts

Kinematic viscosity The ratio of the absolute viscosity of a liquid to its specific gravity at the temperature at which the viscosity is measured. Expressed in stokes or centistokes. Example: viscosity, kinematic, cSt at 100 °F. The Darcy–Weisbach and Colebrook relationships are based on using a Reynolds number which varies inversely with the *kinematic* viscosity. This kinematic viscosity is defined as the dynamic (or absolute) viscosity divided by its density, where dynamic or absolute viscosity is force x (time/length squared) and the unit for this is the poise. The unit most frequently used for the kinematic viscosity is the metric unit: the stoke. Both viscosities are usually quoted in the hundredth unit. Thus, absolute viscosity would be the centipoise, while the kinematic viscosity would be centistokes.

Knockout or knock-out Separating entrained solids or liquid droplets from a gas stream, normally ahead of a compressor or analyzer

Knockout drum or pot Vessel with the primary purpose of preventing undesired or potentially harmful materials from carrying over to downstream equipment. Refer to the chapter on equipment, section on drum design.

KO Knockout, normally in reference to liquid removal from a gas stream in a "knockout drum"

KOH Potassium hydroxide

KPI Key performance indicator

KPM Key performance measure

KS Knowledge sharing

KVA Thousand volt-amps – a way of expressing electrical load or power. Approximately kw

KW or kw Kilowatts – power

L

LA (H, HH, L, LL) Level alarm high, high–high, low, or low–low, e.g., LAHH is a high–high-level alarm

LAB Liquid alive bacteria – a proprietary odor suppressant for sulfur-containing chemicals

LAER Lowest achievable emissions rate

LAH Level alarm high

LAL Level alarm low

Laminar Smooth, nonturbulent flow regime

LAN Local area network

Langelier Saturation Index (LSI) Measure of water fouling potential equal to the difference between the actual pH and the pH at saturation of calcium carbonate. Refer to the chapter on utilities.

Larkins, White, and Jeffery method Technique for estimating two-phase liquid/vapor pressure drop through a bed of discrete solids. Refer to the description in the equipment chapter section on two-phase pressure drop.

Latent heat Heat required to change the state of a unit weight of a substance from solid to liquid or from liquid to vapor without change of temperature

Lateral In sewer systems, refers to a branch. Refer to the chapter on utilities.

Layering This occurs in tanks when a high-density fuel is mixed with a low-density fuel. AKA stratification

Layers of protection analysis (LOPA) Technique for evaluating process hazards protection that considers the number of protective layers of instruments or systems and the relative reliability of each compared to the hazard presented.

LC (1) Level controller; (2) local content

LC50 Lethal concentration of a chemical in air that results in 50 % mortality

LCC Life cycle cost

LCCA Lifecycle cost analysis

LCGO Light coker gas oil

LCL (1) Less-than car load; (2) lower control limit in statistical controls

LCO Light cycle oil (from an FCC). Typically boils between 350 and 700 °F

LD50 Lethal amount of a chemical ingested that results in 50 % mortality

LDAR Leak detection and repair – environmental

Leaded gasolines Until the restrictions on lead compounds imposed by the “Clean Air” Act of the 1960s, tetraethyl lead was used extensively as a gasoline additive to improve octane number.

Tetraethyl lead is a liquid with a gravity of 1.66 and a formula $Pb(C_2H_5)_4$. It is extremely toxic. The restriction of “no lead” in gasolines promoted further development of the catalytic reformer process to obtain higher conversion. It also influenced the use of the alkylation process and the development of isomerization and the oxygenated compounds as octane enhancers in gasoline. Coupled with this, motor manufacturers improved their respective auto engine design to operate efficiently on lower octane number fuel. Tetraethyl lead has all but disappeared from the petroleum industry. See the chapter titled "▶ Petroleum Products and a Refinery Configuration" in this handbook. Details of octane enhancing processes are given in the handbook chapters on alkylation, olefin condensation, and isomerization.

Legionella bacteria Bacteria that grow in moist environments, like cooling towers, and produce potentially life-threatening respiratory illness. Refer to the utilities chapter.

LEL Lower explosive limit

Letdown Reducing pressure of a fluid – sometimes recovering work as the pressure is reduced

Level control range This is the distance between the high liquid level (HLL) and the low liquid level (LLL) in the vessel. When using a level controller, the signal to the control valve at HLL will be to fully open the valve. At LLL, the signal will be to fully close the valve.

LFL Lower flammable limit

LHSV Liquid hourly space velocity

LHV Lower heating value – assumes all combustion products are vapor. Close to actual heat available from a fuel

LIFO Last in–first out in inventory management

Lift In relief valves, lift is the actual travel of the disk away from closed position when the valve is relieving.

Lifting Refers to tankers and barges taking on cargoes of oil or refined product at the terminal or transshipment point

Light crude Crude oil with a low specific gravity and high API gravity due to the presence of a high proportion of light hydrocarbon fractions and low content of metallic compounds.

Light ends Light hydrocarbons and other gases. Normally refers to methane, ethane, propane, and butane produced as by-products of refining. May also include other associated gases, like hydrogen, H_2S, and ammonia

Light ends unit The light ends unit in a refinery produces the light and heavy naphtha cuts, the butane LPG, and the propane LPG products, respectively. The straight-run light ends units take the atmospheric overhead distillate, the overhead distillate from the catalytic reformer stabilizer, the overhead distillate from a thermal cracker fractionator (if there is one in the configuration), and light ends from any other units. Often, a facility has more than one light ends unit, with each unit handling different feedstocks and possibly producing different products. A typical process flow schematic showing a typical process flow for a light ends unit is given in Fig. L.1. Refer to the topic "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook for a thorough discussion of light ends processing.

Light gas oil Normally refers to a straight-run diesel boiling range material (~300–700 °F). In some facilities, it may also refer to similar boiling range materials in other process units.

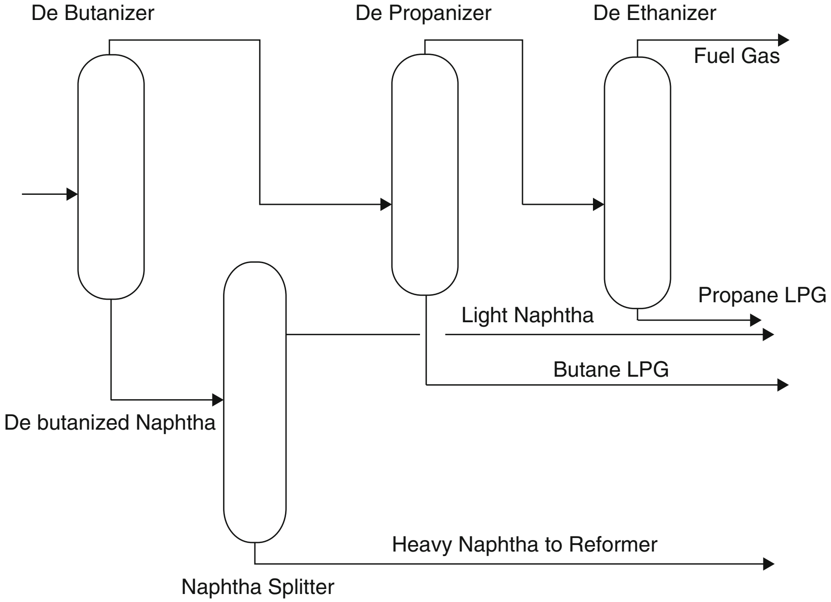


Fig. L.1 Process flow schematic for light ends plant

LIMS Laboratory information system – where a lab collects and disperses lab analyses. Many software options are available.

Linear program(ming) This is a computerized technique that came into prominence during the late 1960s and early 1970s. It is used extensively now by most refiners to (1) optimize new process configurations, (2) plan the refinery operation, and (3) select crude oil feed slate and product slate. The technique uses equations (linear) that represent the properties of the crude feed and the resulting products. These equations also describe the blending characteristics of the components making up the finished product slate. Included also are the cost parameters such as the price of crude feed, the refinery fence selling price of products, operating cost, and any other relevant cost centers (such as licensing fees, interest on loans, etc.). These equations form a mathematical model, and a suitable programmed computer is used to solve these equations simultaneously to meet the objective function subject to the constraints of the analysis. Further details describing linear programs are in the handbook topic "▶ Petroleum Refinery Planning and Economics."

Liquid ring Rotating type of compressor with vanes sealed at the outer ends by a fluid or liquid ring

Liquefied petroleum gas(es) (LPG) A group of hydrocarbon-based gases derived from crude oil refining or natural gas fractionation that are often liquefied, through pressurization, for ease of transport. They include: ethane, propane, normal butane, and isobutane and natural gasoline. Uses of these fuels include: home heating, industrial, automotive fuel, petrochemical feedstocks, and drying purposes in farming. Refineries produce two types of LPG (liquefied petroleum gas) products: butane LPG and propane LPG. LPGs are used widely in industry and domestically as portable fuel source.

Liquefied refinery gas(es) (LRG) Liquefied petroleum gases fractionated from refinery or still gases. Through compression and/or refrigeration, they are retained in the liquid state. The reported categories are ethane/ethylene, propane/propylene, normal butane/butylenes, and isobutane/isobutylene. Excludes still gas

Liter A measure of capacity in the metric system equal to 61,022 cubic inches, 0.908 US quarts dry and 1.0567 US quarts wet

LLL Low liquid level

LME Liquid metal embrittlement

LN2 or LN$_2$ Liquid nitrogen

LNAPL Light nonaqueous-phase liquid

LNG Liquefied natural gas

Loader or lifter In a reciprocating compressor, a device to open or close the compressor cylinder valves to control compressor capacity. Refer to the equipment chapter section on reciprocating compressors.

LOC (1) Loss of containment – can describe a small leak to a major explosion; (2) letter of commitment

Lockhart–Martinelli modulus Dimensionless number used to relate vapor and liquid rates in two-phase pressure drop calculations in piping. Refer to the equipment chapter section on two-phase pressure drop.

Logarithmic mean temperature difference (Δt_m or ΔT_{LM}) For heat transfer in exchangers, this is defined as

$$\Delta \mathrm{t_m} = (\Delta \mathrm{t_1} - \Delta \mathrm{t_2})/\ln(\Delta \mathrm{t_1}/\Delta \mathrm{t_2})$$

The Δts are the temperature differences at each end of the exchanger and Δt_1 is the larger of the two.

LOHC Lube oil hydrocracker

LOI (1) Loss on ignition; (2) letter of indemnity; (3) letter of intent

Long ton An avoirdupois weight measure equaling 2,240 lb

LOPA Layer(s) of protection analysis in process safety

LOS Light oil spread – see “Crack.” Same as 3:2:1 crack

LOTO Lockout–tagout – part of making equipment safe to work on

LOX Liquid oxygen

LP (1) Linear program. Used for planning refinery operations. (2) Lost production; (3) liquid product

LPG Liquefied petroleum gas(es)

LR Level recorder

LRC Level recorder and controller

LRG Liquefied refinery gas(es)

LSD Low-sulfur diesel – usually refers to diesel with less than 500 wppm sulfur

LSG Low-sulfur gasoline – usually refers to gasoline with less than 30 wppm sulfur

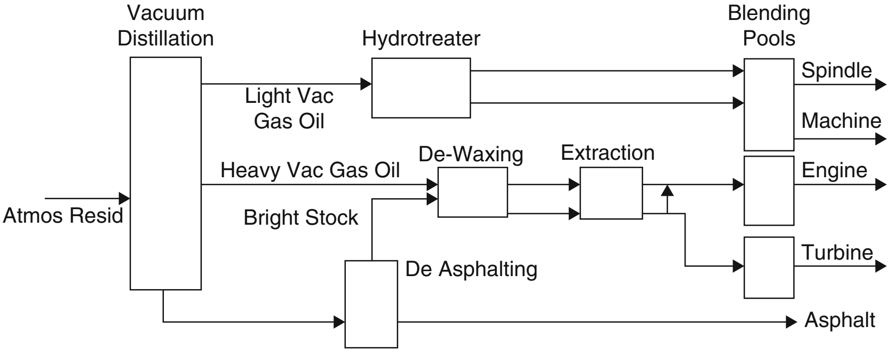


Fig. L.2 A schematic of one lube oil processing configuration

LSR (1) Light straight-run naphtha; (2) low-sulfur recarburizer (coke)
LT (1) Level transmitter; (2) long ton – 2,240 lb
LTL Less-than truck load
LTPD Long tons per day
Lube oils Lube oils are specialized, refined products intended for machinery lubrication. They include automotive oils, greases, and other lubricants derived from petroleum or synthetic products. Not all refineries produce lubricating oils. When they are produced, about three to ten grades of basic lube oil components are made and then blended to meet the many grades of light lube oils, engine lubes, and heavy turbine lube oils. A simple block flow diagram for lube oil production using the solvent approach is shown in Fig. L.2. More recently, high-quality lube oil stocks are being produced by heavy vacuum gas oil hydrocracking followed by hydrodewaxing and hydrofinishing at pressures over 2,000 psig. Some plants are also producing lube stocks via gas-to-liquids processes. The chapter "▶ Non-energy Refineries in Petroleum Processing" in this handbook discusses lube oils in more detail.
Lubricants Substances used to reduce friction between bearing surfaces or as process materials either incorporated into other materials used as processing aids in the manufacture of other products or used as carriers of other materials. Petroleum lubricants may be produced either from distillates or residues. Lubricants include all grades of lubricating oils from spindle oil to cylinder oil and those used in greases.
Lubricity The ability of a material to maintain a lubricating film. There are ASTM tests for lubricity. Hydrocarbon products, such as jet fuel, have lubricity specifications and often require additives.
LVGO Light vacuum gas oil

M

M (1) Maintenance; (2) thousand; (3) million – watch out for context
M&EB Material and energy balance

M&S Materials and supplies or services

MACT Maximum achievable control technology – refer to the environmental chapter.

MAE Major accident event

Manifold Term used to describe a system for connecting multiple sources or destinations. Manifolds are used for sending products to different destinations, for collecting feedstocks entering a unit, for connecting heater passes to the process piping, and so on.

MAOP Maximum allowable operating pressure

Margin Difference between two numbers. (1) Gross margin = gross revenues minus raw material costs – does not include operating or capital costs. (2) Variable margin = gross margin minus variable costs. (3) Net margin = variable margin minus fixed costs.

Marine diesel oil Marine diesel oil is a middle distillate fuel oil which can contain traces, often 10 % or more, residual fuel oil from transportation contamination and/or heavy fuel oil blending. The MDO does not require heated storage.

Marketing Organization that promotes sales of products to the public, the government, or other businesses

MARPOL International convention on the prevention of pollution from ships. Refer to the environmental chapter on air emissions.

Mass spectrometry Mass spectrometry is concerned with the separation of matter according to atomic and molecular mass. It is most often used in the analysis of organic compounds of molecular mass up to as high as 200,000 Daltons and until recent years, was largely restricted to relatively volatile compounds. Continuous development and improvement of instrumentation and techniques have made mass spectrometry one of the most versatile, sensitive, and widely used analytical method available today. One of its major uses in the petroleum refining industry is for the production of distillation curves such as TBP and EFV. This technique does away with the cumbersome distillation apparatus previously used for this purpose. It is also by far the more accurate method.

MAST Maximum allowable skin temperature in a furnace tube

Material balance The weight balance of all inputs to and outputs from a process unit or refinery. Material balances form the basis for plant design and are essential in refinery operation to account for gains and/or losses in the refinery's daily production. They are also essential in process plant audits and troubleshooting. The material balance in all cases is complete and correct when the quantities into the process equal the total quantities out when expressed in mass (weight) units. Volumes and moles in and out may differ because of chemical changes and/or thermal and pressure effects.

Material safety data sheet (MSDS) An information sheet for each substance, including internal refinery streams, that is handled which provides workers and emergency personnel with procedures for handling that substance in a safe manner. These sheets include information such as physical data, fire hazards and control measures, toxicity, health effects, first aid, reactivity, storage, disposal, protective equipment, and spill-handling procedures. AKA safety data sheet (SDS) or product safety data sheet (PSDS)

MAWP Maximum allowable working pressure

MBO (1) Management by objectives – technique of setting goals and tracking against goals; (2) multiblend optimizer

MC (1) Mechanical completion; (2) management committee

MCP (1) Methylcyclopentane; (2) major capital project

MCR Maximum continuous rating

MCSF (1) Thousand standard cubic feet; (2) minimum continuous stable flow; for a pump, the minimum flow limit

MDEA Methyl diethanolamine

MDMT Minimum (or maximum) design metal temperature – watch out for context

MDO Marine diesel oil

MEA Monoethanolamine

Mechanical flow diagram This type of flow diagram is sometimes referred to as a P&ID or the Engineering Flow Diagram. Details of this type of drawing are given under the item flow sheets.

Mechanical integrity Physical condition of equipment to contain materials and perform its required function

MEK Methyl ethyl ketone

Membrane unit A type of process equipment that uses a membrane barrier that allows diffusion of specific gas compounds through the membrane while excluding others. Membrane units are often used to purify hydrogen streams, separating the streams into high purity hydrogen (that diffuses through the membrane) and waste gas containing the impurities. Membrane separations are controlled by diffusion rates and limited by equilibrium so products are generally not chemically pure. Membranes are also applied to liquids in the form of reverse osmosis, dialysis, or electrodialysis to remove impurities.

Merichem Licensor of proprietary hydrocarbon treating and sweetening processes, such as Merifining. Refer to the environmental chapter section on air emissions.

Merox A proprietary UOP process for caustic treating of petroleum stocks to remove mercaptans. Refer to the environmental chapter section on air emissions.

Metals in crude oil Metallic organic compounds have a deleterious effect on some products and are also usually poisonous to catalysts in some processes. The most common metals met with are sodium, nickel, and vanadium. Sometimes other metals are encountered, such as mercury or selenium, in the associated gas streams or arsenic in some crudes. Many of these metallic compounds are found in the asphalt portion of the crude oil and are usually deeply imbedded in the asphaltene molecules. In the production of fuel oil, the metal content of the fuel makes the product problematic to the steel production companies who use fuel oil in their processes. Secondly, in the upgrading of the "bottom of the barrel" using a catalytic process (such as hydrocracking or fluid catalytic cracking), these metallic compounds deteriorate the catalyst life and performance of the processes. Much has been done to improve the catalysts to withstand metals. Today, the metals may be removed by either (1) the coking processes or (2) deasphalting. These processes are described in the handbook topics "▶ Upgrading the Bottom of the Barrel" and "▶ Non-energy Refineries in Petroleum Processing."

Metering pump A positive displacement pump which can be adjusted to deliver a precise amount of flow

Methanation Highly exothermic reaction of carbon oxides with hydrogen to form methane

Methanol (CH_3OH) A light, volatile alcohol intended for gasoline blending as described in oxygenate definition.

Methyl diethanolamine (MDEA, $(HOC_2H_4)_2NCH_3$) One of the common, regenerable amine solvents used for acid gas removal (H_2S or CO_2) from vapor streams

Methyl ethyl ketone (MEK) $CH_3C(O)CH_2CH_3$ colorless liquid with a sweet/sharp, fragrant, acetone-like odor. It is extremely flammable in both the liquid and vapor phase. Used in oil refining for the removal of wax from lube oil stock

Methyl tertiary-butyl ether (MTBE) An ether used at one time in the blending of reformulated gasolines, affecting vapor pressure and octane level. Unlike ethanol, MTBE is fungible and will not separate out during shipment. There is no US market for MTBE due to experience with groundwater contamination; so any production is exported.

Metric ton A weight measure equal to 1,000 kg, 2,204.62 lb, and 0.9842 long tons

Metric(s) (1) Measurement system; (2) a performance measure

MFD (1) Mechanical flow diagram; (2) multifunctional device (a printer/copier/scanner/fax)

MFG Manufacturing

mg/l Milligrams per liter (= ~ppm (parts per million) in water) – expresses a measure of the concentration by weight of a substance per unit volume

MI Mechanical integrity – keeping fluids in the equipment and pipes

MIC Microbiologically influenced corrosion

Micron A unit of length. One millionth of a meter or one thousandth of a millimeter. One micron equals 0.00004 of an inch.

Mid-barrel A term sometimes used to refer to middle distillates, the "middle" of a crude barrel.

Mid-boiling point and mid-volume point components These have been defined and described earlier under "Component balances" and in the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook.

Middle distillate Term applied to hydrocarbons in the so-called middle range of refinery distillation. Examples: heating oil, diesel fuels, and kerosene

Midstream The portion of the value chain concerned with the marketing and transportation of hydrocarbons.

MII Maximum intended inventory

MIS Management information system

MM (1) Materials management; (2) materials manager

mm Millimeter

MMBOE Million barrels of oil equivalent

MMBOPD Million barrels of oil per day

MMBtu Million British thermal units

MMI Man–machine interface. See "HMI."

MMS (1) Maintenance management system; (2) US Minerals Management Service

MMscf/d Million standard cubic feet per day

MMxxx Used in refineries to indicate 1,000,000. For example, 1 MMbbls = one million barrels. Latin derivation

MOC Management of change in Process Safety Management requirements

Molecular sieve (or mol sieve) Material with very small holes of precise and uniform size (Angstrom sizes) which is small enough to block large molecules but allows small molecules to enter. Mol sieves uses in a refinery include drying instrument air, pressure swing adsorption, and paraffin separations.

Molecule The smallest division of a compound that still retains or exhibits all the properties of the substance

Mollier diagram A chart that relates the enthalpy and entropy of steam to its conditions (pressure/temperature)

MON Motor octane number

Monitor (1) In process operations, refers to continuously or regularly reviewing operating data to enable the plant to make appropriate changes or plans for operating/maintaining the facility based on the observed data. (2) A piece of firefighting equipment capable of spraying or streaming water continuously onto a fire or adjacent equipment. A monitor does not require continuous presence of someone to operate it. Refer to the chapter on firefighting.

Monoethanolamine (MEA, $HOC_2H_4NH_2$) One of the common, regenerable amine solvents used for acid gas removal (H_2S or CO_2) from vapor streams

MOR Middle of run

Motor gasoline (AKA mogas) A complex mixture of relatively volatile hydrocarbons, with or without small quantities of additives, which have been blended to form a fuel suitable for use in spark-ignition engines

Motor gasoline blending Mechanical mixing of motor gasoline blending components, and oxygenates when required, to produce finished motor gasoline. Finished motor gasoline may be further mixed with other motor gasoline blending components or oxygenates, resulting in increased volumes of finished motor gasoline and/or changes in the formulation of finished motor gasoline (e.g., conventional motor gasoline mixed with fuel ethanol to produce oxygenated motor gasoline).

Motor gasoline blending components Naphthas (e.g., straight-run gasoline, alkylate, reformate, benzene, toluene, xylenes) used for blending or compounding into finished motor gasoline. These components include reformulated gasoline blendstock for oxygenate blending (RBOB) but exclude oxygenates (alcohols, ethers), butanes, and pentanes. Note: Oxygenates are reported as individual components and are included in the total for other hydrocarbons and oxygenates.

Motor octane number (MON, ASTM ON, F-1) A measure of resistance to self-ignition (knocking) of a gasoline under laboratory conditions which correlates with road performance during highway driving conditions. The percentage by volume of isooctane in a mixture of isooctane and n-heptane that knocks with the same intensity as the fuel being tested. A standardized test engine operating under standardized conditions (900 rpm) is used. This test approximates cruising conditions of an automobile, ASTM D2723.

MPC Model predictive control – a type of advanced control

MPT Minimum pressurization temperature

mpy Mils per year corrosion rate

MRU Methanol recovery unit

MS (1) Mass spectrometer – analytical method; (2) marketing services

MSA (1) Master service agreement; (2) Mine Safety Appliances

MSDS Material safety data sheet

MSFD EU marine strategy framework directive (water pollution)

MSP Monosodium phosphate

MSW Mixed sweet crude – from Canada

MT (1) Thousand tons; (2) metric ton (2,205 lb) in environmental reporting – be careful of context; (3) magnetic testing; (4) management team

MTBE (1) Methyl tertiary-butyl ether (octane booster); (2) mean time between events – electrical

MTBF Mean time between failures

MTDF Mean time to detect failures

MTO (1) Material take-off; (2) Methanol to olefins

MTP Methanol to propylene

MTPA Million tonnes per annum

MTTF Mean time to failure

MTTR Mean time to repair

Multipass tray In distillation, a tray with multiple liquid flow paths and more than one downcomer and overflow weir. Used in large towers. Refer to the chapter on equipment, section on tower design.

MV (1) Millivolts; (2) motor valve – a control valve

MVA Million volt-amps – a way of expressing connected electrical load. Approximately MW

MW Megawatts – power

Mxxx Used in refineries to indicate 1,000. For example, 1 Mbbls = one thousand barrels. Latin derivation

N

Na Sodium

NAAQS National ambient air quality standards

NAC Naphthenic acid corrosion

NACE National Association of Corrosion Engineers

NAICS North American Industry Classification System

Naphtha A volatile, colorless product of petroleum distillation. Used primarily as paint solvent, cleaning fluid, and blendstock in gasoline production to produce motor gasoline by blending with straight-run gasoline. Typically boils at 50 to ~400 °F. There are usually two straight-run naphtha cuts produced from crude: (1) light naphtha (sometimes called light gasoline) and (2) heavy naphtha.

Naphtha-type jet fuel A fuel in the heavy naphtha boiling range having an average gravity of 52.8° API, 20–90 % distillation temperatures of 290–470 °F, and meeting military specification MIL-T-5,624 L (Grade JP-4). It is used primarily for military turbojet and turboprop aircraft engines because it has a lower freeze point than other aviation fuels and meets engine requirements at high altitudes and speeds.

Naphthalene ($C_{10}H_{10}$) An aromatic compound with two adjacent aromatic rings. The simplest polynuclear aromatic compound

Naphthene A cyclic, non-aromatic hydrocarbon. One of the three basic hydrocarbon classifications found naturally in crude oil. Naphthenes are widely used as petrochemical feedstock. Examples are cyclopentane, methyl, ethyl, and propylcyclopentane.

National Pollutant Discharge Elimination System (NPDES) NPDES is the regulatory authority which issues permits to control all discharges of pollutants from point sources into US waterways. NPDES permits regulate discharges into navigable waters from all point sources of pollution, including industries, municipal wastewater treatment plants, sanitary landfills, large agricultural feed lots, and return irrigation flows.

Natural draft In a furnace, flue gas and airflow induced by natural convective circulation

Natural gas A naturally occurring raw material often produced in conjunction with crude oil that is processed through a variety of facilities to yield NGLs. It is a commercially acceptable product for industrial and residential consumption and is shipped via pipeline.

Natural gas liquids Those hydrocarbons in natural gas that are separated from the gas as liquids through the process of absorption, condensation, adsorption, or other methods in gas processing or cycling plants. Generally, such liquids consist of propane and heavier hydrocarbons and are commonly referred to as lease condensate, natural gasoline, and liquefied petroleum gases. Natural gas liquids include natural gas plant liquids (primarily ethane, propane, butane, and isobutane; see “Natural Gas Plant Liquids”) and lease condensate (primarily pentanes produced from natural gas at lease separators and field facilities; see "Lease Condensate").

Natural gas plant liquids Those hydrocarbons in natural gas that are separated as liquids at natural gas processing plants, fractionating and cycling plants, and, in some instances, field facilities. Lease condensate is excluded. Products obtained include ethane, liquefied petroleum gases (propane, butanes, propane–butane mixtures, ethane–propane mixtures), isopentane, and other small quantities of finished products, such as motor gasoline, special naphthas, jet fuel, kerosene, and distillate fuel oil.

Natural gasoline and isopentane A mixture of hydrocarbons, mostly pentanes and heavier, extracted from natural gas, that meets vapor pressure, end point, and other specifications for natural gasoline set by the Gas Processors Association. Includes isopentane

NAV (1) Net asset value; (2) Norton antivirus

NC Normally closed

NCEES National Council of Examiners for Engineering and Surveying – the organization that administers the professional engineering exams

NCM (1) Net cash margin; (2) normal cubic meters at 1 Atm, 15 °C

NDE Nondestructive examination

NDT Nondestructive testing

Near-infrared analyzer An analyzer (online or offline) which determines composition of a sample by measuring absorption or transmittance of near infrared light through the sample. Refer to the chapter on controls.

NEC US National Electrical Code

Needle coke Premium grade of petroleum coke used in metallurgy

NEMA National Electrical Manufacturers Association

NESHAP US National Emissions Standards for Hazardous Air Pollutants

Net investment In a project, this includes the capital cost of the plant, which is subject to depreciation, and the associated costs that are not subject to depreciation. It would also include the capitalized construction loan interest.

Net profit margin A measure of profitability based on the ratio of net income to total operating revenues

Netback The price a refiner receives for the sale of petroleum products after deducting the transportation or affiliated costs in shipping the product from its point of origin (i.e., pipeline tariffs, waterborne freight, storage fees, line loss, cost of capital, etc.)

Neutralization Refers to reacting a material with a reagent to bring the pH of the material closer to 7.0 (or "neutral"). This process is used in water effluent treatment to avoid sending water that is too acidic or caustic to a waterway to public treatment works.

Neutralization number The number that expresses the weight in milligrams of an alkali (normally KOH) needed to neutralize the acidic material in 1 g of oil. The neutralization number of an oil is an indication of its acidity.

Neutralizing amine Any of several amines that prevent corrosion by neutralizing acids in a stream – e.g., steam condensate system corrosion control

New York Mercantile Exchange (NYMEX) US commodities exchange where a number of commodities, including WTI crude, heating oil, and unleaded gasoline, are traded on a future basis

Newton's law (particle settling) One of several of Newton's laws is a mathematical relationship that describes the rate of movement of a particle or droplet through another continuous phase in more turbulent conditions. Refer to the environmental chapter section on water and the equipment chapter section on drum design.

NFPA National Fire Protection Association, Inc.

NGL Natural gas liquids – typically propane and butanes recovered with natural gas

NGO Nongovernmental organization

NH_3 Ammonia

NH_3N Ammonia nitrogen. Nitrogen present as ammonia.

NH_4Cl Ammonium chloride – corrosive salt

NH_4HCO_3 Ammonium bicarbonate – corrosive salt

NH_4HS Ammonium bisulfide – corrosive salt

NHT Naphtha hydrotreater

NHV Net heating value

Ni Nickel

Nickel carbonyl ($Ni(CO)_4$) Nickel carbonyl is one of the most toxic substances which may be encountered in a petroleum processing facility anywhere CO is present along with nickel in a reduced state. Refer to the chapter on hazardous materials.

NIOSH US National Institute for Occupational Safety and Health

NIR Near infrared

NLL Normal liquid level

NMR Nuclear magnetic resonance – analytical method

NNF Normally no flow

NO Normally open

Non-energy product refineries This term refers to refineries which primarily produce petroleum products other than fuels. The two major types of non-energy refineries are (1) the lube oil refinery and (2) the petrochemical refinery. These types of facilities are detailed in the chapter "▶ Non-energy Refineries in Petroleum Processing" in this handbook.

NORM Naturally occurring radioactive material

NOx Nitrogen oxides – generically

NP Normal paraffin

NPDES US National Pollutant Discharge Elimination System

NPDES permit US National Pollutant Discharge Elimination System permit – see "National Pollutant Discharge Elimination System."

NPRA National Petroleum Refiners Association – now AFPM

NPSH Net positive suction head – for a pump. Refer to the equipment chapter section on pumps.

NPSHA Net positive suction head available. Refer to the equipment chapter section on pumps.

NPSHR Net positive suction head required. Refer to the equipment chapter section on pumps.

NPV Net present value

NRC Nuclear Regulatory Commission

NSC National Safety Council

NSPS New Source Performance Standards – US Federal. Refer to the environmental chapter.

NTP Normal temperature and pressure in metric units. Normally at either 0 °C or 15 °C and 1 Atm. Check context.

NTSC National Transportation Safety Board

NYMEX New York Mercantile Exchange

NYSE New York Stock Exchange

O

O&GJ Oil and Gas Journal

O_2 Oxygen

OCAW Oil, Chemical, and Atomic Workers Union. Now combined into the United Steelworkers' Union. Represented refinery union workers in most US refineries for many years

Octane number and octane Octane numbers are a measure of a gasoline's resistance to knock or early detonation in a cylinder of a gasoline engine. The higher this resistance is, the higher will be the efficiency of the fuel to produce work. A relationship exists between the antiknock characteristic of the gasoline (octane number) and the compression ratio of the engine in which it is to be used. The higher the octane rating of the fuel, the higher the compression ratio of engine in which it can be used. By definition, an octane number is that percentage of isooctane in a blend of isooctane and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90-octane gasoline matches the knock characteristic of a blend containing 90 % isooctane and 10 % *n*-heptane. The knock characteristics are determined in the laboratory using a standard single-cylinder test engine equipped with a supersensitive knock meter. Online knock engines have been used during blending for many years. The octane number can also be calculated from near-infrared analysis, which enables improved, continuous online measurement of octane during gasoline blending. The pump octane posted in the United States is (RON + MON)/2. In Europe, often only RON is given.

OE (1) Operations excellence; (2) open-ended; (3) organizational error

OECD Organization for Economic Cooperation and Development

OEL Open-ended lines – environmental

OEM Original equipment manufacturer – usually refers to mechanical or electrical parts that originally were installed or meet the specifications of parts originally installed on equipment

Offsite systems or offsites These are facilities outside the main refining process units that support operation of those units. Among the major facilities found in refinery offsite systems are storage (tanks), product blending, road and rail loading, jetty facilities, waste disposal, and effluent water treating. Refer to the topic "▶ Off-Site Facilities for Petroleum Processing" in this handbook for a more complete description and discussion of these facilities.

OGJ Oil and Gas Journal. Abbreviation is frequently used in reference citations.

OH Over head or overhead

Oil Crude petroleum and other hydrocarbons produced at the wellhead in liquid form

Oil sand crude Heavy hydrocarbons recovered from tar sands or oil sands by thermal methods.

Oily water sewer The sewer system that collects water within a refinery or process facility that may contain oil. The collected water is further processed to remove the oil. Refer to the chapters on utilities and offsites.

OIW Oil in water

Olefins Class of unsaturated paraffin hydrocarbons recovered from petroleum. Typical examples include: butene (butylene), ethene (ethylene), and propene (propylene). They constitute a fourth group of hydrocarbons, in addition to paraffins, naphthenes, and aromatics. They are not naturally present in any great quantity in most crude oils, but are often produced in significant quantities during production processes for heavy oils or refining of the crude oil to products. They are generated in those processes that subject the oil to high temperature for a relatively long period of time. Under these conditions, the saturated hydrocarbon molecules break down permanently, losing one or more of the four atoms attached to the quadrivalent carbon. The resulting hydrocarbon molecule is unstable and readily combines within itself (forming double-bond links) or with similar molecules to form polymers. An example of such an unsaturated compound is ethylene: $H_2C = CH_2$. Note the double bond in this compound linking the two carbon atoms that are the defining characteristic of olefins.

On/off-discrete control See "Gap Control."

OOS Out of service

OP (1) Operating pressure; (2) output – from a controller

OPA 90 US Oil Pollution Act of 1990

Opacity In stacks, a measure of the amount of particulate matter or smoke coming out of a stack

OpCom Britannia Operating Committee

OPEX Operating expense

ORI Octane requirement increase

Orifice meter The most common flow metering device that takes advantage of the Bernoulli effect by introducing a restriction in a pipe to create a *vena contracta*.

The pressure difference between the *vena contracta* and the bulk fluid is a function of the flow rate.

Orsat An analysis method for fired heater flue gases used in determining heater performance. Largely supplanted by analyzers. Refer to the environmental chapter section on air emissions.

OSA Suncor Synthetic A (OSA) crude oil – pre-refined from Canadian bitumen

OSARP Oil Spill Assessment Response Program

OSBL Outside battery limits

OSH Suncor sour synthetic crude – from Canada

OSHA Occupational Safety and Health Administration (US Department of Labor)

OT Operating temperature

OTJ On the job – applied to training

Outage (1) Space left in a product container to allow for expansion during the temperature changes it may undergo during shipment and application. (2) Measurement of space that is *not* occupied in a drum or vessel

Outlet collector The device at the bottom of a catalytic reactor bed where the reactants are collected and exit the reactor. The outlet collector is designed to retain the catalyst in the reactor.

Output (1) The total of all streams from a refinery or process unit. (2) In control systems, the signal coming from a controller to the field control device. These may be 3–15 psi pneumatic signals, 4–20 ma electrical signals, digital, or some other form.

Overflash Overflash is a term normally associated with the design of crude atmospheric or vacuum towers. Its objective is to provide additional heat (over and above that set by the product vaporization) required by the process to generate the internal reflux. It also influences the flash zone conditions of temperature and partial pressure of the hydrocarbon vapor feed. Usually, it is fixed between 3 and 5 vol% on crude. This atmospheric flash temperature is adjusted to the temperature at the previously calculated partial pressure existing in the flash zone. A further description and the purpose of overflash is given in the chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook.

Overhead (1) In processing, refers to the top product from a distillation column or absorber (abbreviated OH); (2) in economics, refers to the operating costs that are not directly used in making the products, such as administrative or building costs

Overlap A measure of separation quality expressed as the amount of one distillation product that is still present in another after processing. Generally, overlaps are expressed as the difference between two distillation reference points – such as the 95 % point of the lighter product and the 5 % point of the next heavier product. An overlap exists when, say, the 5 % point of the heavier product is less than the 95 % point of the lighter product. See also "Gaps and Overlaps."

Overplus Design allowance above minimum required. Essentially the design margin for equipment and processes

Overpressure Overpressure is the pressure increase over the set pressure of the primary relieving device; it would be termed accumulation when the relieving device is set at the maximum allowable working pressure of the vessel.

Overspeed Exceeding the allowable rpm of a piece of rotating equipment – such as a steam turbine without load on it

OVHD Overhead

Oxidation Combining elemental compounds with oxygen to form a new compound. A part of the metabolic reactions

Oxidation pond A surface impoundment for treatment of wastewater by aerating the water and allowing microbiological digestion of the contaminants. These ponds may also be used to prevent sanitary sewage from becoming septic and smelling while it is held before final treatment.

Oxidizing agent Any substance, such as oxygen or chlorine, which can accept electrons. For example, when oxygen or chlorine is added to wastewater, organic substances are oxidized. These oxidized organic substances are more stable and less likely to give off odors or to contain disease bacteria.

Oxygen deficient Refers to an environment with insufficient oxygen concentration to support life. Refer to the safety chapter.

Oxygen enrichment The use of pure oxygen or air with oxygen added to enhance an oxidation process. Oxygen enrichment is used as a debottlenecking option in sulfur plants, FCCs, and other process units. Refer to the chapter on utilities for discussion of supply.

Ozonation The application of ozone to water, wastewater, or air, generally for the purposes of disinfection or odor control.

Ozone O_3. A pollutant in the atmosphere when generated by photochemical reaction with NO_x. May also be used for microbiological control and in certain reactions

P

P Phosphorous

P&ID Process (or piping) and instrumentation diagram or flow diagram – also called MFD or mechanical flow diagram

P/I Pneumatic to current transducer or converter

PA (H, HH, L, LL) Pressure alarm high, high–high, low, or low–low – e.g., PAHH is a high–high-pressure alarm.

Packed tower A distillation or fractionation column containing specially shaped mass transfer packing materials instead of trays. Packing often enables much greater mass and heat transfer rates in less height than trays and offers lower pressure drop in many cases. Packing is also used for small-diameter towers (less than 3 ft) or very-large-diameter towers (like vacuum fractionators) where pressure drop is critical. The packing in the tower may be stacked in beds on a random basis or in a defined structured basis. For practical reasons, and to avoid crushing the packing at the bottom, the packing is usually installed in beds of 15–20 f. in height. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for discussion of packed towers.

Packing (1) The shaped contacting elements (e.g., rings, saddles, etc.) that are placed in a contactor tower to provide surface area for mass transfer; (2) the physical orientation or arrangement of mass transfer packings or catalysts within a tower or reactor; (3) A type of seal around a rotating or reciprocating shaft in a compressor or pump. Refer to the equipment chapter sections on compressors and pumps; (4) a type of seal around a valve shaft to contain process fluids – refer to the chapter on process controls, section on control valves and the environmental chapter section on fugitive emissions controls.

Padding Providing a compatible vapor above a storage tank or vessel, normally to prevent contact with air or development of an explosive mixture. Also known as blanketing. See offsites chapter.

PADD US Federal Petroleum Administration for Defense District – defined regions of the United States

PAH Polycyclic aromatic hydrocarbons (occasionally polyaluminum hydroxide)

Pall ring A type of mass transfer packing for towers. Refer to the chapter on equipment, section on packed towers.

Pantograph An articulated set of beams that are able to extend and contract with the movement of whatever they are attached to. Often used for sample lines and roof drains in tanks

Paraffin A saturated hydrocarbon compound in which all carbon atoms in the molecule are connected by single bonds

Partial oxidation (POX) A process for gasification of hydrocarbons by burning the hydrocarbon sub-stoichiometrically with air or oxygen to produce a gas rich in CO and hydrogen, along with some CO_2. The resulting synthesis gas can be cleaned up and used to make hydrogen, petrochemicals, or paraffinic liquid fuels.

Partial pressure The portion of total pressure exerted by a specific component or compound. Normally equal to the total absolute pressure of the system times the mole fraction of the component. For instance, a gas at 250 psig containing 75 % hydrogen has a hydrogen partial pressure of $75\ \%/100\ \% \times (250\ \text{psig} + 14.7\ \text{psi}) = 198.5\ \text{psi}$.

Particulate Free suspended solid or a discrete particle

Partition wall In a fired heater, refractory wall inside a heater that divides the radiant section into separately fired zones. Refer to the equipment chapter, section on fired heaters.

PB Propane + butane

PBC Propane–butane casing head

PC (1) Pressure controller; (2) personal computer – watch out for context; (3) paired comparisons

PCB See "Polychlorinated Biphenyls."

PCS Process control system

PD (1) Positive displacement – like a piston; (2) project development

PDA Personal digital assistant

PDC Power distribution center. AKA the switch room

PDH Professional development hours – in Professional Engineer licensing

PE (1) Professional engineer; (2) production efficiency

PEL Permissible exposure limit

Pensky–Martens (PMCC) A closed-cup test for flash points of oil

Pentanes plus A mixture of hydrocarbons, mostly pentanes and heavier, extracted from natural gas. Includes isopentane, natural gasoline, and plant condensate

PERC (1) Perchloroethylene; (2) power emergency release coupling

Peristaltic pump A type of positive displacement pump

Permissible exposure limit (PEL) Time-weighted average maximum concentration of a chemical which is considered to be safe (negligible health hazard) for workers over an 8 h period. Regulatory limits set by US OSHA

Pet coke See "Petroleum Coke."

Petrochemical An intermediate chemical derived from petroleum, hydrocarbon liquids, or natural gas, such as ethylene, propylene, benzene, toluene, and xylene

Petrochemical feedstocks Chemical feedstocks derived from petroleum principally for the manufacture of chemicals, synthetic rubber, and a variety of plastics

Petrochemical refineries See the previous item on "Non-Energy Product Refineries."

Petroleum A generic name for hydrocarbons, including crude oil, natural gas liquids, natural gas, and their products

Petroleum Administration Defense District (PADD) Five geographic areas into which the United States was divided by the Petroleum Administration for Defense for purposes of administration during federal price controls or oil allocation. They are:

- PADD1: Connecticut, Delaware, District of Columbia, Florida, Georgia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, North Carolina, Pennsylvania, Rhode Island, South Carolina, Vermont, Virginia, and West Virginia
- PADD2: Illinois, Indiana, Iowa, Kansas, Kentucky, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Oklahoma, South Dakota, Tennessee, and Wisconsin
- PADD3: Alabama, Arkansas, Louisiana, Mississippi, New Mexico, and Texas
- PADD4: Colorado, Idaho, Montana, Utah, and Wyoming
- PADD5: Alaska, Arizona, California, Hawaii, Nevada, Oregon, and Washington

Petroleum coke A solid residue, high in carbon content and low in hydrogen, which is the final product of thermal decomposition in the condensation process in cracking. This product is reported as marketable coke. The conversion is 5 barrels (of 42 US gallons each) per short ton. Coke from petroleum has a heating value of about 6.024 million Btu per barrel.

Petroleum products Petroleum products are obtained from the processing of crude oil (including lease condensate), natural gas, and other hydrocarbon compounds. Petroleum products include unfinished oils, liquefied petroleum gases, pentanes plus, aviation gasoline, motor gasoline, naphtha-type jet fuel, kerosene-type jet fuel, kerosene, distillate fuel oil, residual fuel oil, petrochemical feedstocks, special naphthas, lubricants, waxes, petroleum coke, asphalt, road oil, still gas, and miscellaneous products.

PFA Perfluoroalkoxy

PFD (1) Process flow diagram; (2) probability of failure on demand

pH pH is an expression of the intensity of the basic or acidic condition of a liquid. Mathematically, pH is the logarithm (base 10) of the reciprocal of the hydrogen ion concentration. The pH may range from 0 to 14, where 0 is most acidic, 14 most basic, and 7 is neutral. Natural waters usually have a pH between 6.5 and 8.5.

PHA Process Hazards Analysis. Refer to the chapter on safety.

Phenol An organic compound that is an alcohol derivative of benzene

Photovoltaic A device for generating electrical energy from light – like a solar cell

PHR Process Hazards Review (MOC related)

PI (1) Pressure indicator – a pressure gauge; (2) process input; (3) performance indicator; (4) process or plant information – system that collects and retrieves process operating data for analysis (may include a licensed system); (5) profitability index; (6) project implementation; (7) proportional–integral (controller)

PIB Product information bulletin. General information on a product

PID (1) Proportional–integral–derivative (controller). See the chapter on controls. (2) See also "P&ID."

Pilot A small, self-contained burner in a fired heater that burns continuously to ensure ignition of any fuel that enters the firebox. Also used on flare tips

Pilot-operated pressure relief valve A pilot-operated pressure-relief valve is one that has the major flow device combined with and controlled by a self-actuated auxiliary pressure relief valve. This type of valve does not use an external source of energy.

PIMS Linear program. Used for planning refinery operations. PIMS = Process Industry Modeling System.

Pinch technique A calculation and analysis method used for optimizing heat recovery and other similar problems

PIP Process Industry Practices

Pipe fitting Refers to elbows, tees, and other items used to connect straight pipe together into a system

Pipe hanger Device for supporting pipe by hanging it off a structure above the pipe. These may be fixed or may be spring loaded or counterweighted to account for pipe movement.

Pipe support Device for supporting pipe from below or alongside the pipe. Pipe supports may be fixed or may be spring loaded or counterweighted to account for pipe movement.

Pipeline(s) A piping network that allows crude oil, refined products, and gas liquids to move across the country, usually from either refineries to terminals or from coastal (import) locations to terminals and refineries further inland

Piping element General term for anything that goes into a piping system, including elbows, tees, flanges, valves, reducers/enlargers, etc.

PIS Protective instrument systems

Pitch (1) Same as vacuum resid – extremely heavy oil. (2) Attack angle of blades in a fan. (3) Layout angle of the tubes or shell-side baffles in a heat exchanger. Refer to the equipment chapter, section on heat exchangers.

PL Protection layer

Planning refinery operations This term refers to the activities required to define and coordinate the products, crudes, unit rates, unit feeds, and economics to ensure optimum refinery operation and profitability within the constraints of the refinery. Refer to the chapter titled "▶ Petroleum Refinery Planning and Economics" in this handbook for a detailed discussion of these activities.

Plant air Also called utility air. Compressed air used for general plant services, such as pneumatic tools. Separated from the instrument air system for security purposes. Refer to the discussion in the utilities chapter.

Plant commissioning The sequence of events starting with a newly completed process facility and ending with an operating plant. Commissioning includes pre-energizing activities, energizing the plant, conditioning equipment, calibrating instruments, setting relief valves, final checking and closure of vessels and towers, loading catalysts, preparation for "startup," startup, lining out, and performance and guarantee test runs. Commissioning is discussed in detail in the chapter titled "▶ Petroleum Processing Projects" in this handbook.

Plant water Also called utility water. This is water available in a facility for general use. May not necessarily be drinkable or potable. See the discussion in the chapter on utilities.

Play In the oil and gas industry, this refers to a general area in which significant quantities of hydrocarbon oil or gas can be found. Development of a "play" results in commercial production, hopefully.

PLC Programmable logic controller

Plenum A chamber enclosing equipment used to conduct flow into the equipment. Normally refers to a preheated air chamber surrounding the burners in a fired heater with louvers to control the airflow. Refer to the equipment chapter, section on fired heaters.

Plug flow Two-phase piping flow regime where alternate plugs of liquid and gas move through the pipe. This is an undesirable regime that can result in damage. Refer to the equipment chapter, section on two-phase pressure drop.

PM (1) Particulate matter – normally refers to dust and the like in the air. When followed by a number, the number refers to the maximum size particles considered (e.g., PM10 means particles less than 10 μm in size). (2) Preventative maintenance. (3) Performance management. (4) Project manager

PMCC Pensky–Martens closed cup – a flash point test

PMI Positive materials identification

PMS (1) Piping material specifications; (2) power management system; (3) platform maintenance system

PNA Polynuclear aromatics – big, multi-ring aromatic compounds – AKA polyvinyl chicken wire or "red death" in hydroprocessing

Pneumatic Operated by air or other gas pressure

Point In finance, 1/100th of a cent ($0.0001)

Poison In refining, in addition to health hazards, this term refers to compounds, elements, or characteristics that reduce catalyst activity over a period of time. Normally, the term applies to permanent activity reductions.

Pollution The impairment (reduction) of air, water, or other environmental condition by agriculture, domestic, or industrial wastes (including thermal and radioactive wastes) to such a degree as to hinder any beneficial use of the resource or render it offensive to the senses of sight, taste, or smell or when sufficient amounts of waste creates or poses a potential threat to human health or the environment

Polyaromatic hydrocarbon A hydrocarbon having an aromatic structure that includes two or more conjugated or conjoined rings. These tend to condense into larger polyaromatic structures when heated to high temperatures.

Polychlorinated biphenyls (PCBs) Difficult to remediate chemical used in old-style transformers. Concentrated PCBs used to be referred to as "1268". Includes polychlorobiphenyls

Polymer A chemical formed by the union of many monomers (a molecule of low molecular weight). See also "Gums."

Polymerization Process of combining two or more simple molecules of similar type, called monomers, to form a single molecule having the same elements in the same proportion as in the original molecules, but having increased molecular weight. The product of the combination is a polymer.

PON Posted octane number; (RON + MON)/2

PONA Analysis method for paraffins, olefins, naphthenes, and aromatics

Porosity (1) Ability of a bed of solids or a rock formation to permit movement of oil and gas through the solids. High porosity means fluids can easily move through the solids. (2) A measure of the % of the internal volume of a solid particle that is open space. Specifically refers to catalyst particles

PORV Pilot-operated relief valve

Potable water Water that is fit for human consumption. Refer to the chapter on utilities.

POTW Publically owned treatment works. For example, the city or county sewer treatment plant

Pour point The "pour point" of an oil is the temperature at which the oil ceases to flow. It is usually a test applied to middle distillates, lube oils, and fuel oils. The test itself is simple and requires the sample oil to be carefully treated before the test and to reduce its temperature in a controlled and orderly way. Unlike most other petroleum properties, pour points of two or more components cannot be blended directly to give a pour point of the blended stock. Blending indices are used with the volumetric composition of the blend components for this purpose. Details of the blending for "pour point" are given in the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook, while details of the test itself are given in the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook.

Power recovery A system for recovering power from high-pressure fluids as they are reduced to lower pressure. Power may be recovered through direct coupling of a letdown device to a pump or compressor or by power generation. Power recovery devices include letdown turbines and turboexpanders.

POX See "Partial Oxidation."

PP (1) Propane/propylene; (2) pour point

ppb Parts per billion – normally by weight, but may be by volume in gases

PPD Pollution prevention design. Reducing plant pollution during the design phase by appropriate process modifications – i.e., designing lower pollution into the process

PPE Personal protective equipment – hard hat, safety glasses, steel-toed boots, etc., to protect an individual from hazards

PPG Polypropylene glycol

ppm Parts per million – normally by weight, but may be by volume in gases

PR Pressure recorder

Practical (or Puckorius) Scale Index (PSI) A measurement of fouling potential of water. This index attempts to account for buffering. Refer to the chapter on utilities.

PRC Pressure recorder and controller

Preheat and preheat exchanger train In most processes, heat recovery by heat exchange is of great importance. In the design of major processes, such as the crude oil distillation unit, cracker recovery units, and the like, the optimization of this heat recovery concept is of paramount importance. One method for heat recovery design is described in the chapter titled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" of this handbook. Briefly, the method consists of examining several configurations of a heat transfer train, applying "pinch" analysis a cost data to the equipment and to determine the terminal feed temperature of each configuration. This end temperature relates to the heater duty required and therefore to the fuel required by the heater. An economic balance may then be made to select the optimum heat exchanger configuration. Developing the various configurations uses the total enthalpy of the feed (in this case, the crude oil feed to the atmospheric distillation unit) and the total enthalpies of the exchanged streams.

Preprocessing See "Pre-refining."

Pre-refining Many unconventional feedstocks require removal of impurities before they can be processed in a normal refinery. This cleanup is referred to as pre-refining or preprocessing.

Pressure regulator Device for controlling a set pressure. A regulator is normally a local controller that is self-actuating.

Pressure relief valve Pressure relief valve (PRV) is a generic term applied to relief valves (RV), safety valves (SV), pressure safety valves (PSV), or safety relief valves (SRV).

Pressure swing adsorption (PSA) A cyclic process where gas containing impurities is contacted with an adsorbent at high pressures. Some compounds in the gas will "stick" to the adsorbent, while others will not be adsorbed significantly and will pass through. When the adsorbent has collected a target amount of material, the adsorbent bed is taken out of service and regenerated by reducing the pressure, which allows adsorbed components to be desorbed and removed. The sorbent is then repressurized and put back in service. PSAs are used extensively in purifying hydrogen streams, producing essentially 100 % hydrogen and a tail gas containing all the impurities. PSAs normally employ multiple beds connected by valves and headers to mimic a continuous process.

Pre-startup safety review (PSSR) A team review to evaluate a new or modified facility before it is operated. The PSSR confirms the changed plant is ready to operate safely.

Presulfiding See "Sulfiding."

Pretreatment or pretreating Refers to steps taken to prepare a stock for a primary refining process. For instance, hydrotreating naphtha to remove sulfur and nitrogen ahead of a reformer is a type of pretreating.

Primary storage Petroleum storage tanks at refineries, pipelines, and oil company terminals. Product inventory changes at these facilities are what constitute API and EIA demand computations.

Prime driver See "Prime Mover"

Prime mover A drive motor or turbine for a compressor, pump, or other piece of equipment

Process Refers generically to a method for physical or chemical conversion applied to a feedstock to produce a desired product

Process control Management of process operating conditions to meet product objectives safely and efficiently within equipment limitations

Process guarantees Among the items of major concern to the operating refinery staff and the engineering contractor in the design, procurement, and construction of a grassroots process or a revamped process are the final process guarantees that are developed and accepted. The process guarantees may begin to be developed as soon as a firm process has been established and manufacturers' guarantees obtained for the performance of the various manufactured items of equipment. The process performance is usually tied to a guarantee of process efficiency, such as utility consumption in the plant while operating on the design throughput and conditions. These items are described and discussed in to the chapter titled "▶ Petroleum Processing Projects" in this handbook with examples of both the performance guarantee and its associated utility guarantee in Appendices 1 and 2 of that chapter.

Process configurations Process configurations are represented in the form of block flow diagrams. They are prepared usually as the first step in deciding the

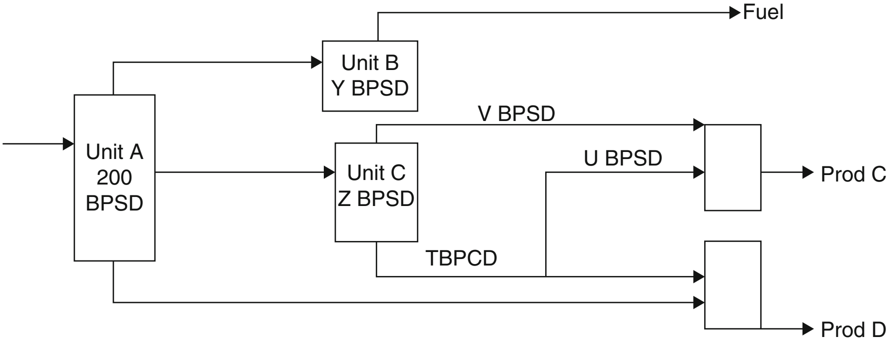


Fig. P.1 A typical block flow diagram

type of process units that will make up a desired complex. The units are shown in sequence to each other by blocks which will be labeled with their throughput size (in the case of a petroleum refinery, in barrels per stream day or in cubic meters or metric tonnes per stream day). The diagram is further developed showing the product and feed lines from and to the unit blocks. The measure of flow is shown on each line. Several block flow diagrams of differing configurations but meeting the end product objectives will be developed prior to the decision on which process route meets all the company's objectives. An example of a simplified block flow diagram is Fig. P.1. Refer to the chapter titled "▶ Petroleum Processing Projects" in this handbook for discussion of process configuration development. Refer to the topic "▶ Petroleum Products and a Refinery Configuration" in this handbook for discussion of the common general refinery types and configurations.

Processing gain or loss The volumetric amount by which total output is greater than or less than input for a given period of time. This difference is due to the processing of crude oil into products which, in total, have a lower or high specific gravity than the crude oil processed, respectively.

Product blending Finished products are blended using two or more components which are rundown stream products from the refinery processes. The blending in most modern refineries is done "in-line"; that is to say that a metered amount of each component is mixed with metered amounts of the other blend components in a pipe that finally enters the respective finished product storage tank. The flow of each of the components is controlled "online" by analyzers which are programmed to fine-tune the component flow control rates to meet the specified product blend recipes. Although these analyzers are quite accurate, the final contents of the finished tanks are always checked by laboratory tests before dispatch out of the refinery. The topic "▶ Petroleum Products and a Refinery Configuration" in this handbook discusses the product properties. That chapter also illustrates the blending recipes in a typical process configuration. Blender design is discussed further in the topic "▶ Off-Site Facilities for Petroleum Processing" in this handbook.

Product information bulletin A summary of product properties for commercial or safety purposes

Product properties The physical and chemical properties of a process product. Normally these are defined by the product specifications and must be measured during operations to ensure the product stays on specification. They may also be estimated or predicted from available information about the stock or operation.

Product property prediction Product properties are predicted from the composition and properties of real components and of pseudo components that make up the product streams. Refer to the handbook topics "▶ Introduction to Crude Oil and Petroleum Processing," "▶ Petroleum Products and a Refinery Configuration," and "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries" for more detailed discussions of property predictions.

Product safety data sheet See "Material Safety Data Sheet."

Production In an oil company, the organization that drills wells, removes the oil and gas from the ground, and initially separates the raw production (oil and gas) for transportation to further processing

Production capacity The maximum amount of product that can be made from processing facilities

Programmable logic controller (PLC) An electronic control system that uses programmed logic to carry out repetitive, sequential process tasks. Outputs from the PLC are used to control field elements. It may interface with other control systems but is intended to perform its function stand-alone.

Progressing cavity Using rotation to isolate a volume of fluid and move it from one pressure to another – examples: Moyno pump or liquid-ring compressor

Project duty specification Among the first activities to initiate a refinery project is the development of the "project duty specification," also known as the project basis or the project premises within different companies. This document describes in detail the plant or complex of plants the company wishes to build. Among the major items of the project specification are process specification, general design criteria, any preliminary flow sheets (duly labeled "Preliminary"), utilities specification, basis for economic evaluations, materials of construction, equipment standards and codes, instrument standards required, and company preferences. These items are described more fully in the chapter titled "▶ Petroleum Processing Projects" in this handbook.

Propane (C_3H_8) A normally gaseous straight-chain hydrocarbon. It is a colorless paraffinic gas that boils at a temperature of − 43.67 °F. It is extracted from natural gas or refinery gas streams. It includes all products designated in ASTM Specification D1835 and Gas Processors Association Specifications for commercial propane and HD-5 propane.

Propant In oil production, especially hydraulic fracturing, a propant is part of the mixture pumped down a well which will hold open the fissures created and help maintain permeability around the well so oil and gas can get to the well. The most common propant is sand.

Proportional band This determines the response time of the controller. Normally a proportional band is adjustable between 5 % and 150 %. The wider the proportional band, the less sensitive is the control. If a slower response time is required, a wider proportional band is used.

Proportional control A control mode where the controller output is determined by the deviation from setpoint times a constant. See "Proportional Band."

Proportioning pump A positive displacement pump that can be adjusted to deliver a precise flow rate

Propylene (C_3H_6) AKA propene. An olefinic hydrocarbon recovered from refinery processes or petrochemical processes. Nonfuel use propylene includes chemical-grade propylene, polymer-grade propylene, and trace amounts of propane. Nonfuel use propylene also includes the propylene component of propane/propylene mixes where the propylene will be separated from the mix in a propane/propylene splitting process.

PRV Pressure relief valve

PSA Pressure swing absorption

PSD Prevention of significant deterioration – environmental – US Federal requirements. Refer to the environmental chapter.

PSE Pressure safety element – a rupture disk. Refer to the chapter on safety.

Pseudo components See "Product Property Prediction." Essentially, pseudo components are mathematically derived, narrow boiling range cuts of a petroleum stock that are treated as a single compound for calculations using average properties estimated for the specific cut boiling range.

PSI or psi (1)lb/square inch pressure; (2) process safety information; (3) Process Safety Institute

Psia or PSIA Pounds per square inch, absolute (gauge pressure +14.7 psi)

Psig or PSIG Pounds per square inch, gauge (read from a gauge referencing atmospheric pressure – a normal pressure gauge reading)

PSM Process Safety Management. Refer to the chapter on safety.

PSSR Pre-startup safety review – part of the MOC process

PSV Pressure safety valve – a relief valve

PT (1) Pressure transmitter; (2) physical testing; (3) project team; (4) primary tower; (5) process technology; (6) dye penetrant testing

PTASCC Polythionic acid stress corrosion cracking

PTB Pounds per thousand barrels – usually refers to salt in crude

PTOH Primary tower overhead

Pulsation dampener or bottle (PD) A device for reducing the pressure variation around reciprocating pumps or compressors. In some cases, a PD may take the form of a wide spot in the line or an actual vessel. For instruments, PD may be achieved by a flow restriction. Refer to the chapter on process equipment, section on reciprocating compressors.

Pumpage Material being pumped

Pumparound This is the term given to any reflux stream which is created inside a distillation tower by taking off a hot liquid stream, cooling it, and returning the

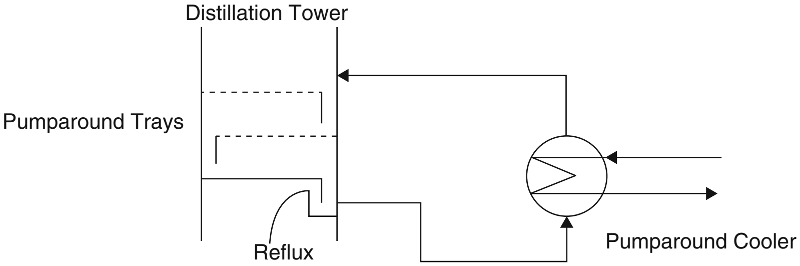


Fig. P.2 A typical pumparound arrangement

stream back into the tower two or three trays above the draw-off tray. Figure P.2 illustrates a typical pumparound system.

Pumps Mechanical device for moving liquids throughout a processing facility. Two types of pumps are typically used in a petroleum processing facility: (1) variable head capacity and (2) positive displacement. Pumps are discussed in detail in the handbook topic "▶ Process Equipment for Petroleum Processing."

Purifier A machine used for a liquid–liquid separation in which the two intermixed liquids which are insoluble in each other have different specific gravities. Solids with specific gravities higher than those of the liquids can be separated off at the same time. A purifier bowl has two outlets, one for the light-phase liquid and one for the heavy-phase liquid. A centrifugal separator

PV (1) Process value; (2) process variable

PVC Polyvinyl chloride

PVDC Polyvinylidene chloride

PVDF Polyvinylidene fluoride

PVF Pipes, valves, and fittings

PWHT Post-weld heat treatment – stress relief

Pyrolysis Breaking down a substance by high temperature

Pyrolysis oil Any oil made by pyrolysis

Q

QA Quality assurance

QC Quality control

QRA Quantitative risk assessment

Quench zone In a multi-bed, exothermic, catalytic reactor, this is a zone or reactor section where reactants are collected, mixed with cooler material (lowering the temperature), and redistributed to the next catalyst bed. Refer to the chapters on hydrotreating, hydrocracking, and equipment (bed pressure drop calculations).

R

R, R', R", etc. Shorthand for any hydrocarbon group

R&D Research and development

Radiant tube or coil In a fired heater, a tube exposed directly to flames

Raffinate The residual product left after a refining process. For instance, the product from solvent extraction, with the material that is removed called the "extract." Also, more generally used in reference to any low-octane product left over after any secondary refining process

RAGAGEP Recognized and generally accepted good engineering practice

RAM Reliability, availability, and maintainability

Ramsbottom coke A carbon residue test originated by Dr. J.R. Ramsbottom in England

Rangeability The rangeability of a control valve is the ratio of the flow coefficient at the maximum flow rate to the flow coefficient at the minimum controllable flow rate.

RAQ In China, Regional Air Quality. Refers to air emissions regulations. Refer to the environmental chapter section on air emissions.

Raschig ring A hollow cylindrical-shaped mass transfer packing or catalyst base. Refer to the chapter on equipment.

RBI Risk-based inspection

RBOB Reformulated blendstock for oxygenate blending – gasoline without the ethanol

RCA Root cause analysis

RCFA Root cause failure analysis

RCM Reliability-centered maintenance – focuses on improving equipment and plant reliability

RCOOH Generic for an organic acid (carboxylic acid)

RCR Ramsbottom carbon residue

RCRA US Federal Resource Conservation and Recovery Act – especially important for disposal of hazardous wastes

RD Rupture disk – pressure relief device. See chapter on safety.

REAC Reactor effluent air cooler – in a hydroprocessing unit

Reacceleration Automatically restarting a piece of rotating equipment after a temporary power loss. Normally refers to electrical equipment that can restart in the event of a power dip without negative consequences or which must be restarted immediately to prevent worse consequences, such as cooling. Reacceleration is sometimes an alternative to providing a spare operated from a different commodity – for instance, a critical service may have one steam turbine-driven pump and one electric motor-driven pump for the service or there may be two electric motors with reacceleration. Refer to the discussion in the equipment chapter.

REACH European Union Registration, Evaluation, Authorization, and Restrictions of Chemicals. Refer to the environmental chapter section on water.

Reactivity Hazardous waste characteristic of being capable of generating a hazardous condition or product when reacted with other materials or air. Refer to the environmental chapter section on hazardous wastes.

Reagent A pure chemical substance that is used to make new products or is used in chemical tests to measure, detect, or examine other substances

Reboiler(s) Reboilers are one of two heat energy input systems to a fractionation unit. The other source is the heat delivered by the feed or feeds to the unit. Reboilers are usually associated with the light ends distillation units and the product stabilizers and splitters on catalytic or thermal cracking units. In most cases, the reboiler is of a shell and tube or a kettle type. In some cases, a fired heater may be used as a reboiler. This reboiler may be fed either by the liquid phase from the bottom tray of the tower or by vaporizing a portion of the bottom product. The first method uses thermosyphon (alt. thermosiphon) as the driving force for flow through the heat exchanger. In the second case, the reboiler feed may be pumped or flow into the kettle section of the exchanger. In both cases, the flow from the reboiler is returned to the tower below the bottom fractionating tray. Exchanger and kettle reboiler arrangements are depicted in Figs. R.1 and R.2. Details on reboiler design are in appropriate sections of this handbook, with additional information in the handbook topic "▶ Process Equipment for Petroleum Processing."

Reciprocating Employing a back-and-forth action – like a locomotive drive cylinder

Reciprocating compressor(s) Reciprocating compressors are positive displacement compressors that are widely used in the petroleum and chemical industries where high discharge pressures are required. They consist of pistons moving in cylinders with inlet and exhaust valves. They are cheaper and more efficient than any other type of compressor where they are applied. Their main advantages are that they are insensitive to gas characteristics and they can handle intermittent loads efficiently. They are made in small capacities and are used in applications where the rates are too small for a centrifugal compressor. They are used almost exclusively in services where the discharge pressures are above 5,000 PSIG. However, reciprocating compressors require more frequent shutdowns for maintenance of valves and other wearing parts than centrifugal compressors. For critical services, this requires either a spare compressor or a multiple compressor installation to maintain plant throughput. The handbook topic "▶ Process Equipment for Petroleum Processing" describes and discusses reciprocating compressors in detail.

Reciprocating pump These are positive displacement pumps that use a piston within a fixed cylinder to pump a constant volume of fluid for each stroke of the piston. In some types, the piston stroke or the cylinder volume may also be mechanically varied to control flow (e.g., metering or proportioning pumps).

Reclaiming (1) In amine absorber systems, reclaiming is the process for removal of contaminants from the circulating amine stream to "reclaim" the amine

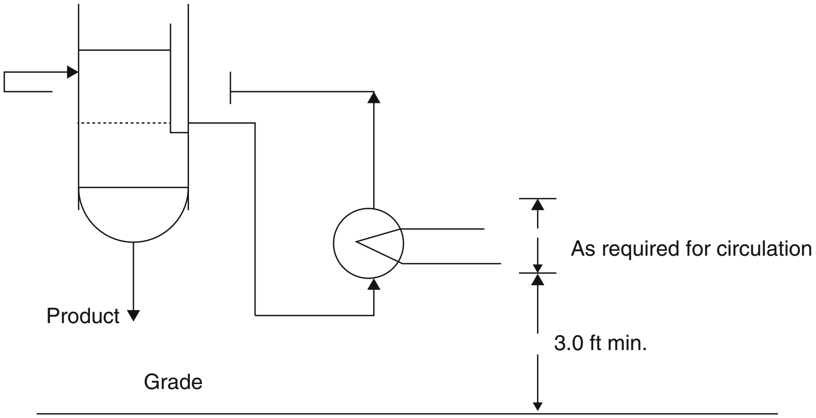


Fig. R.1 A once-through thermosyphon reboiler

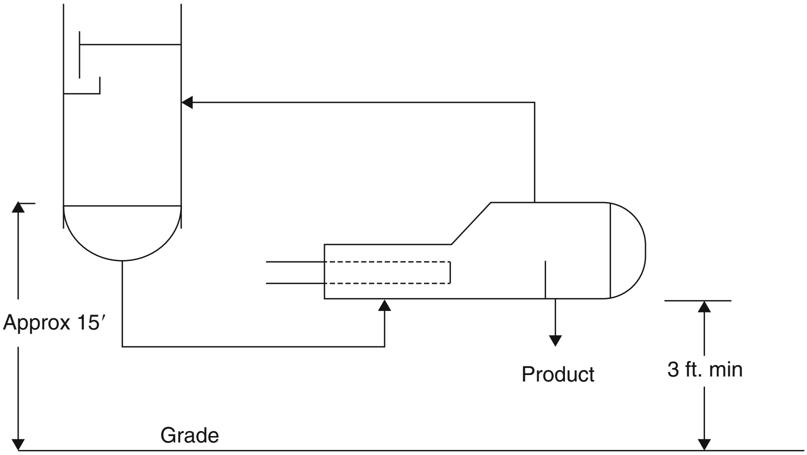


Fig. R.2 A kettle-type reboiler

component (see the chapter on gas treating). (2) In waste management, reclaiming refers to processing of a waste to recover useful metals or other components for reuse and recycle.

Recommended exposure limit (REL) An exposure limit that has been recommended by the US NIOSH to OSHA for adoption as a permissible exposure limit (PEL). Often taken as a limit before official adoption by OSHA. Normally a weighted average concentration over 10 h

Recovered oil See "Slops."

Recycle The reuse of any stream within (internally) a facility: e.g., reusing hydrogen-rich gas in a hydrotreater using a recycle gas compressor

RED In the EU, Renewable Energy Directive. Refer to the environmental chapter section on air emissions.

Reduced crude oil (reduced crude) Crude oil that has undergone at least one distillation process to separate some of the lighter hydrocarbons. Reducing crude lowers its API gravity but increases the handling safety by raising the flash point.

Reducing agent Any substance, such as the base metal (iron) or the sulfide ion that will readily donate (give up) electrons. The opposite of an oxidizing agent

Redwood viscosity The number of seconds required for 50 ml of an oil to flow out of a standard Redwood viscosimeter at a definite temperature; British viscosity standard

Refinery A plant used to separate the various components present in crude oil and convert them into usable products or feedstock for other processes

Refinery-grade butane (C_4H_{10}) A refinery-produced stream that is composed predominantly of normal butane and/or isobutane and may also contain propane and/or natural gasoline. These streams may also contain significant levels of olefins and/or fluorides contamination

Refinery input – crude or total In reference to crude, refers to the total crude oil input to the crude oil distillation units and other refinery processing units (such as direct feed to cokers). Total input refers to all the raw materials and intermediate materials processed at refineries to produce finished petroleum products. These include crude oil, products of natural gas processing plants, unfinished oils or intermediates, other hydrocarbons and oxygenates, motor gasoline and aviation gasoline blending components, and finished petroleum products.

Refinery production Petroleum products produced at a refinery or blending plant. Published production of these products equals refinery production minus refinery input. Negative production will occur when the amount of a product produced during the month is less than the amount of that same product that is reprocessed (input) or reclassified to become another product during the same month. Refinery production of unfinished oils and motor and aviation gasoline blending components appear on a net basis under refinery input.

Refinery types Most of this handbook is focused on the energy refinery, that is, a refinery that converts the crude oil feed to energy products such as gasoline, diesel, turbine fuel, fuel oil, and the like. The topic "▶ Petroleum Products and a Refinery Configuration" in this handbook discusses configurations within this type of refinery. There are two major refinery complexes, however, that convert the crude oil into non-energy products. These are the lube oil refinery and the petrochemical refinery. Very often, these complexes are located adjacent to the energy refinery and they are often integrated into one major refinery complex. The chapter "▶ Non-energy Refineries in Petroleum Processing" in this handbook describes and discusses these two alternate refinery complexes. They are also summarized in the topic "▶ Introduction to Crude Oil and Petroleum Processing" in this handbook.

Refinery yield Refinery yield (expressed as a percentage) represents the percent of finished product produced from input of crude oil and net input of unfinished oils. It is calculated by dividing the sum of crude oil and net unfinished input into the individual net production of finished products. Before calculating the yield for finished motor gasoline, the input of natural gas liquids, other hydrocarbons, and oxygenates and net input of motor gasoline blending components must be subtracted from the net production of finished motor gasoline. Before calculating the yield for finished aviation gasoline, input of aviation gasoline blending components must be subtracted from the net production of finished aviation gasoline.

Refining Converting crude oil into useful products like gasoline, jet fuel, diesel, fuel oil, and olefins

Reflux Returning a cooled liquid stream to a distillation or stripper tower to improve separation and control heat balance in the tower.

Reflux drum A drum that collects fluids to be refluxed to a tower and provides surge volume.

Reflux ratio Normally, volume of reflux per volume of overhead product from a distillation column; although several other definitions are also used. Watch out for the context.

Reformate A naphtha which has been upgraded in octane by catalytic or thermal reforming

Reforming An oil refining process in which naphthas are changed chemically to increase their octane level. Paraffins convert to isoparaffins and naphthenes, and naphthenes change to aromatics. The catalyst used is usually platinum, though sometimes palladium.

Reformulated gasoline The requirements in the United States of the Clean Air Act of 1990 (CAA), and additions to it since, have changed refining requirements to meet this product's need quite significantly. Prior to this date, much of the finished gasoline product recipe consisted of normal light naphtha, reformate, usually some cracked naphtha, and possibly alkylate, with some butane added to meet volatility. The CAA and its subsequent additions forced a reduction of both reformate and cracked stock and replacement of them with oxygenates, such as ethanol, MTBE, and TAME to meet octane number. Oxygenates were used originally simply as additives to improve octane number. However, because of their oxygen content, their addition was also required to reduce the carbon monoxide and hydrocarbons in the emitted gases from combustion. There are a number of oxygenates used in gasoline manufacture; some of the more common are given in Table R.1.

Table R.1 Oxygenates commonly used in gasoline

Name	Formula	RON	RVP, psig	Oxygen, wt%	[a]Water solubility, %
Methyl tertiary-butyl ether (MTBE)	$(CH_3)_3COCH_3$	110–112	8	18	4.3
Ethyl tertiary-butyl ether (ETBE)	$(CH_3)_3COC_2H_5$	110–112	4	16	1.2
Tertiary-amyl methyl ether (TAME)	$(CH_3)_2(C_2H_5)COCH_3$	103–105	4	16	1.2
Ethanol	C_2H_5OH	112–115	18	35	100

[a]wt% soluble in water

The EPA established limits for the use of each oxygenates in gasoline blends. The use of MTBE in the United States was essentially discontinued by the end of 2002 due to concern over groundwater contamination. MTBE is still widely used outside the United States, although the trend in Western Europe is to use ETBE instead. More details on the manufacture of gasolines are given in the topic "▶ Petroleum Products and a Refinery Configuration" in this handbook. More recent regulations are reducing sulfur levels in gasoline in the United States below 10 ppm. This adds more processing requirements.

Refractory (1) Insulating material used in fired heaters (and some other places) to keep heat in and prevent damage to the outer casing. Refer to the equipment chapter, section on fired heaters. (2) Refers to a contaminant that is difficult to remove. For instance, certain nitrogen compounds are much more difficult to remove from oil than others and are termed "refractory nitrogen compounds."

Regeneration (1) In absorber or adsorber systems, regeneration is the process of removing impurities from the sorbent so the sorbent can be reused. (2) In catalysts, regeneration is the process of burning off accumulated coke and impurities from the catalyst to return it to a usable state.

Register A large, loose-fitting butterfly valve or set of louvers that control air entering a burner in a fired heater. These are a primary adjustment for excess O_2 in the firebox.

Regulatory control In control systems, refers to the basic process control system

Reid vapor pressure (RVP) The vapor pressure at 100 °F of a product determined in a volume of air four times the liquid volume. Reid vapor pressure is an indication of the ease of starting and vapor-lock tendency of a motor gasoline as well as explosion and evaporation hazards. This test is the standard test for low-boiling-point distillates. It is used for naphtha, gasoline, light-cracked distillates, and aviation gasoline. For the heavier distillates with vapor pressures expected to be below 26 psig at 100 °F, the apparatus and procedures are different. Only the Reid vapor pressure for those distillates with vapor pressures above 26 psig at 100 °F is described in the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook.

REL Recommended exposure limit

Reliability Ensuring equipment is available, functional, and safe to operate when needed

Relief valves These are devices designed to avoid exceeding allowable equipment operating pressures by controlled venting of excess vapors if a pressure vessel's MAWP is exceeded. Full details and discussion on relief systems, which include the relief valves, used in the petroleum industry are given in the chapter on "▶ Safety Systems for Petroleum Processing" in this handbook.

Relieving conditions Relieving conditions pertain to pressure relief device inlet pressure and temperature at a specific overpressure. The relieving pressure is equal to the valve set pressure (or rupture disk burst pressure) plus the overpressure.

Renewable As normally used, a material that can be replaced by natural sources – like renewable diesel from plant oils or animal fats or fuel ethanol produced by fermentation of sugars

Re-refining Refers to reprocessing of hydrocarbon stocks. Normally used in reference to waste lube oils which can be cleaned up and reused through specific processing methods

Research octane number (RON, CFRR, F-1) A measure of antiknock quality of a gasoline stock or blend. Technically, this is the percentage by volume of isooctane in a blend of isooctane and n-heptane that knocks with the same intensity as the fuel being tested. A standardized test engine operating under standardized conditions (600 rpm) is used. Results are comparable to those obtained in an automobile engine operated at low speed or under city driving conditions: ASTM D2722. Alternative near-infrared analysis methods can also be used to estimate the RON.

Reset The rate at which a control system makes changes to a process. A high reset rate will make more frequent changes to the system. In a PID or PI controller, this may result in windup of controller output which causes it to overshoot the setpoint. A low reset rate may never reach its target.

Resid The heaviest portion of crude oil boiling above 650 °F. Atmospheric resid typically boils above 650 °F. Vacuum resid typically boils above 1,050 °F.

Residual fuel oil Heavy fuel oils produced from the nonvolatile residue from the fractional distillation process. Heavy oils that are "leftovers" from various refining processes. Heavy black oils used in marine boilers and in heating plants

Residue conversion There are several processes used to reduce or eliminate the residues from crude oil refining. The most common processes included here are thermal cracking (e.g., coking, visbreaking, Flexicoking), "deep oil" fluid catalytic cracking (e.g., heavy oil cracking or HOC), and residuum hydrocracking and desulfurization (e.g., H-Oil, LC-fining). The processes are discussed in the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook.

Residue In petroleum refining, the term "residue" refers to the unvaporized portion of the heated crude oil entering either the atmospheric crude oil distillation tower or vacuum tower that leaves these towers as their bottom product. The stream from the atmospheric column is often referred to as the "long" residue, while that from the vacuum unit is often called the "short" residue or bitumen. Both residues are black in color; the atmospheric residue has a specific gravity usually between 0.93 and 0.96, while the vacuum residue will be 0.99 and higher.

Residuum See "Resid" and "Residue."

Resilient seat In a valve, a resilient seat is one in which the plug closes against a rubbery or elastomeric surface.

Respirator Breathing device to prevent personnel exposure to hazardous atmospheres. Includes supplied air and cartridge-type systems. Refer to the safety chapter.

Retort A process for high-temperature thermal decomposition of materials, like oil shale, to produce hydrocarbon oil and gas. Similar to destructive distillation

Return bend A U-shaped pipe fitting or tube to connect two adjacent tubes in a fired heater. Refer to the equipment chapter, section on fired heaters.

Revenues Money taken in

Reverse osmosis A membrane process which purifies a water stream by passing the water through a membrane module at high pressure. The water molecules preferentially pass through the membrane to a lower pressure, leaving the impurities at higher pressure

RFG Reformulated gasoline

RFI (1) Request for information; (2) radio-frequency interface

RFID Radio-frequency identification

RFP Request for proposal

RFQ Request for quotation

RG Recycle gas – in a hydroprocessing unit

RGG Reducing gas generator

RH Relative humidity

RIE Remote instrument enclosure – in the field

RO Restriction orifice

Road and rail loading facilities These are the facilities used to transfer crude, intermediates, or finished products to and from bulk carriers such as tank trucks and rail cars. Refer to the relevant discussion in "▶ Off-Site Facilities for Petroleum Processing" in this handbook.

ROCE Return on capital employed

ROI Return on investment

ROL Reliability operating limit – limit that, if exceeded for an extended time, will result in failure including loss of containment

RON See "Research Octane Number."

ROR Rate of return

Rotary compressor A class of compressors including screws, lobes, and sliding vanes. Refer to the equipment chapter, section on compressors.

Rotary pump A class of positive displacement pumps. Unlike the centrifugal-type pump, these types do not throw the pumping fluid against the casing but push the fluid forward in a positive manner similar to the action of a piston. These pumps however do produce a fairly smooth discharge flow unlike that associated with a reciprocating pump. See the equipment chapter, section on pumps.

Rotating equipment Pumps, compressors, etc. – anything that performs its process function by rotational action, except control valves

Routine maintenance Maintenance done on a daily or schedule basis

RPM or rpm Revolutions per minute – rotational speed

RS Generic for an organic sulfide

RSC US Regional Supply Corridors

RSH Generic for mercaptan or thiol

RSOP Refining standard of practice

RSR' Generic for a conjugated sulfide

RSSR' Generic for a disulfide

RTD Resistance temperature detector – a type of temperature measuring element. See the chapter on controls.

RTR Residual risk and technology review. Refer to the chapter on environmental engineering.

RUL gasoline Regular unleaded gasoline (no ethanol)

Runaway reaction Loss of positive reaction control of an exothermic reaction, resulting in rapidly increasing process temperatures and accompanying increases in reaction rate. Refer to the chapter on safety.

Rupture disk (RD or PSE) A relief device that consists of a thin metal plate or disk designed to burst or fail when a specific pressure differential is imposed on the disk. Once the disk has failed, it must be replaced. It will not stop flowing after the overpressure condition is relieved.

RV Relief valve

RVP See "Reid Vapor Pressure."

Ryznar stability index (RSI) A measure of water fouling potential. Refer to the chapter on utilities.

S

S Sulfur

S/D Shutdown

S/U Startup

S_8 Sulfur – liquid form

Safe park A condition in which a process unit can be held indefinitely without damage to the equipment or catalyst

Safety data sheet See "Material Safety Data Sheet"

Safety integrated system (SIS) AKA safety integrity system, safety instrumented system, or safety interlock system. This is a system that takes secure process information parallel to other control systems and applies specific limits to the measured variables. If one of the variables goes outside the predefined limits, the system first alarms at low deviation and then takes a predefined set of emergency actions at high or sustained deviation. The system is similar to a PLC but is normally triple redundant to ensure high integrity.

Safety shower A deluge system, usually located near a potential chemical exposure area, where personnel can be washed down with copious amounts of clean water to eliminate or control damage from chemical exposure. Refer to the safety chapter.

Safety systems These are the systems that prevent process and other safety incidents in a refinery. Safety systems include fire protection facilities and equipment, emergency shutdown systems, emergency depressuring systems, fired heater safety interlocks, and many other systems. These systems are designed, operated, maintained, and managed to prevent fire, explosion, loss of containment, and other hazardous situations. The chapters on "▶ Safety Systems for Petroleum Processing" and "▶ Fire Prevention and Firefighting in Petroleum Processing" in this handbook discuss the systems in detail. The handbook topic "▶ Hazardous Materials in Petroleum Processing" further highlights the properties and safe handling of several hazardous materials commonly found in refineries.

SAGD Steam-assisted gravity drain. A production process for bitumens and extra-heavy oils where high-pressure, superheated steam is injected into a horizontal well. The hot fluids reduce the viscosity of the oil in the formation and push it toward a lower depth horizontal well from which it is produced. See the discussion on this process in the chapter on unconventional crudes.

Sanitary sewer Sewer system that accepts domestic waste (toilets, showers, etc.) and conveys it to treatment

SAP (1) Sulfuric acid plant; (2) common oil industry enterprise software accounting system offered by SAP AG in Germany

SARA US Superfund Amendments and Reauthorization Act

Saybolt Furol viscosity A viscosity test similar in nature to the Saybolt Universal viscosity test but one more appropriate for testing high-viscosity oils. Certain transmission and gear oils and heavy fuel oils are rated by this method. The results obtained are approximately one tenth the viscosity which would be shown by the Saybolt Universal method.

Saybolt Universal viscosity A measure of kinematic viscosity. The methods determines the time required for 60 cm^3 of oil to flow through a standard, calibrated tube at a controlled temperature. This method is used for oils with flowing time up to 5,600 s (low to medium viscosity). The results are reported as Saybolt Universal Seconds (SUS or SSU). For higher-viscosity oils, the Saybolt Furol viscosity method is used. See "Saybolt Furol Viscosity."

Saybolt viscosity See "Saybolt Universal Viscosity."

SC/RC Sour crude/resid conversion

SCADA Supervisory control and date acquisition

Scavenger In refining, this refers to a chemical used to remove the final traces of an undesirable compound from a material. Examples include oxygen scavengers to remove traces of oxygen from boiler feed water and H_2S scavengers to remove H_2S for safety before shipping or handling an oil.

SCBA Self-contained breathing apparatus

SCC Stress corrosion cracking

SCFD or scfd or scf/d Standard cubic feet per day (1 Atm, 60 °F)

SCFM or scfm or scf/m Standard cubic feet per minute (1 Atm, 60 °F)

SCO (1) Synthetic crude oil; (2) stabilized crude oil

SCR Selective catalytic reduction – NO_x control by reacting ammonia with NO_x over a catalyst in a fired heater flue gas stream

SCSR Self-contained self-rescuer

SD or S/D (1) Shutdown; (2) sustainable development; (3) stream day

SDWA US Safe Drinking Water Act

SE Stack effect – in a fired heater – drives the heater draft profile

Seal Device for preventing loss of fluids past a rotating or reciprocating shaft. Refer to the equipment chapter sections on pumps and compressors. Includes packing, mechanical seals, liquid seals, and gas seals.

SEC US Securities and Exchange Commission

Selective catalytic reduction (SCR) NO_x control by reacting ammonia with NO_x over a catalyst in a fired heater flue gas stream

Selective non-catalytic reduction (SNCR) NO_x control by thermally reacting ammonia with NO_x in a fired heater flue gas stream

Sensing element The field device that measures a physical or chemical property to be used in controlling the process. The most common elements measure things like flow, temperature, pressure, and level.

Sensor See "Sensing Element."

Separator A vessel used to effect separation of a mixture phases into separate phases, such as vapor separation from liquid or water separation from vapor and oil. Refer to the equipment chapter, section on drums and vessels.

Service factor (1) In refinery terms, the service factor is the percentage of the time that a given type of process unit is expected to be operable during a year. The service factor depends on the average amount of scheduled shutdown time the particular unit requires over 1 year for maintenance. Typical service factors are listed in Table S.1 below. (2) In electric motors, from a practical standpoint, the service factor indicates the amount of current a motor can draw over a sustained period and still maintain reasonable life. A service factor of 1.0 means the motor can only provide its design power reliably. A motor with a service factor of, say, 1.15 means the motor could draw about 15 % higher amps that rated without major damage.

Setpoint The desired value of a process variable that is provided to a controller. The controller tries to make the process measurement match the setpoint.

Set pressure Set pressure, in psig or barg, is the inlet pressure at which the pressure relief valve is adjusted to open under service conditions.

Setting (1) The setpoint of a controller (or act of changing the setpoint). (2) In a fired heater, all parts that form the coil supports and enclosure (housing). Refer to the equipment chapter, on fired heaters.

SEU Solvent extraction unit

Sewer systems Generally underground piping systems that collect wastewater or chemicals and transport them to treatment facilities. Sewers may include storm runoff, oily water, chemical wastes, and others. Refer to the discussions in the chapters on utilities, offsites, and environmental engineering.

SGP Saturate gas plant

SGR Saturate gas recovery

Shale crude or gas Not the same as shale oil. This is crude or gas produced by hydraulically fracturing tight shale formations to allow crude and gases in the formation to be recovered, e.g., Bakken or Eagle Ford crudes.

Shale oil Not the same as shale crude. This is oil produced by destructive distillation of a rock called kerogen, either in place (in situ) or after mining the rock

Table S.1 Some typical service factors for refinery processes

Unit	Service factor percent
Crude distillation unit	95–98
Light ends distillation	98
Vacuum crude distillation	95–98
Visbreaker and thermal cracker	90
Cat reformer	90–92
Naphtha hydrotreaters	90–92
Gas oil hydrotreaters	90
Fluid catalytic crackers	85–90
Hydrocrackers (distillate feed)	90–95
Hydrocrackers (residue feed)	80–82 (includes residue hydrotreating)
Cokers	85

(ex situ). This oil has low sulfur but high nitrogen, arsenic, and olefins. Not generally available on the market

SHE Safety, health, and environment

Shield tube See "Shock Tube."

Shell In a shell-and-tube exchanger, the chamber surrounding the tubes on the outside which contains the shell-side fluid

Shell-and-tube heat exchanger An exchanger consisting of an outer pressure shell containing multiple, small tubes inside the shell. A channel directs flow in and out of the tubes. Baffles direct flow around the outside of the tubes. Refer to the discussion in the chapter on equipment, section on heat exchangers.

Shell storage capacity The design capacity of a petroleum storage tank which is always greater than or equal to working storage capacity

Shock tube or coil The first rows of tubes in the convection section of a fired heater that is exposed to the highest temperature flue gases. Normally not finned. May be exposed directly to radiant heat, also

Short ton An avoirdupois measure of weight equal to 2,000 lb

Short-term exposure limit (STEL) The maximum average concentration of a compound which is considered a safe (negligible health hazard) exposure for a short period of time, normally 15 min

Shot coke Spherically shaped petroleum coke that is difficult to control in a coker. Causes equipment damage and potential safety issues

SIC US Standard Industrial Classification Code

Sidestream A stream that is pulled from a distillation tower between the overhead and bottoms. See also "Sidestream Stripping."

Sidestream stripping Sidestreams from multicomponent distillation towers are stripped free of entrained lighter products in "sidestream strippers" (or side strippers). Stripping may be accomplished by injection of steam through the hot sidestream in a trayed column, by injection of an inert gas instead of steam, or by reboiling the bottom product of the stripper tower. Steam stripping is probably the most common approach. The most common application is on the atmospheric crude distillation unit. Figure S.1 is an example of the bottom distillate sidestream stripper of a crude distillation unit.

Sieve tray A type of tray used in distillation, absorber, or stripper columns that promotes contact between vapor and liquid on the tray using holes distributed over the tray

SIF Safety instrumented function

SIL Safety integrity level

SimDist Distillation curve (vol% distilled vs. temperature) using ASTM D2887 method normally. This method is for all ranges of hydrocarbons and employs a gas chromatograph.

SIP In the United States, a State Implementation Plan for reduction of air emissions. See the environmental chapter.

SIS (1) Safety instrumented system; (2) safety interlock system; (3) safety integrity system

SIT Spontaneous ignition temperature. The temperature at which an oil ignites of its own accord in the presence of air or oxygen under standard conditions

Skirt Generally cylindrical supports for vertical vessels and towers. The skirt holds the vessel at the proper elevation and connects the vessel to the foundation. A skirt is normally about the same or slightly smaller diameter as the vessel or tower it supports.

Slack wax Mixture of oil and wax, a by-product from the refining of lubricating oil, from which paraffin wax can be recovered

Slagging Formation of hard deposits on boiler tubes and/or piston crowns, usually due to the presence of sodium, vanadium, and sulfur

SLC Single-loop controller

Slops Also called recovered oil and other site-specific terms. Oil that is collected from leaks, off-spec production, equipment flushing, etc., that does not meet any product specifications or may be contaminated. The oil may be reprocessed or otherwise managed. Refer to the chapter on utilities.

Sludge Deposits in fuel tanks and caused by the presence of wax, sand, scale, asphaltenes, tars, water, etc. The “sludge” formed in a #6 fuel oil storage tank is mostly composed of heavy hydrocarbons.

Slug flow Piping flow regime that is an extreme form of wave flow where the waves are periodically picked up and “slugged” through the pipe. This regime is undesirable as it causes excessive pipe movement and hammer that is potentially damaging. Refer to the equipment chapter, section on two-phase pressure drop.

Slurry oil The heaviest oil product from an FCC

Smoke point A measure of kerosene tendency to smoke. Measured in millimeters of flame height before smoking. Relates to turbine blade path temperatures in a jet engine. Specific ASTM test.

SMR Steam-methane reformer

SMTP Simple Mail Transfer Protocol (Internet e-mail)

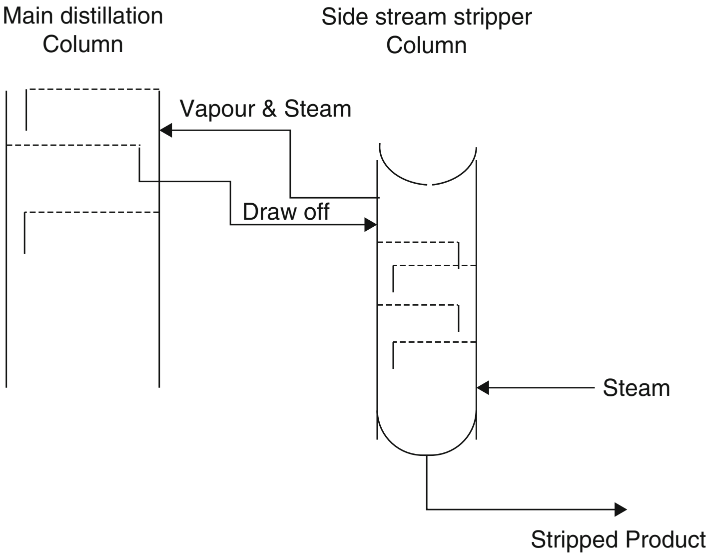


Fig. S.1 Sidestream steam stripper

SNCR Selective, non-catalytic reduction – NO_x control by thermally reacting ammonia with NO_x in a fired heater flue gas stream

Soaking volume factor (SVF) The design of a thermal cracker is keyed to the configuration and temperature profile across the heater and soaking drum or soaking coil. The degree of cracking is dependent on this temperature profile and the residence time of the oil under these conditions. The soaking volume factor (SVF) is related to product yields and the degree of conversion. Definition of these items is given in the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook. A design calculation using the SVF is given as Appendix 1 of that topic.

SOCMI Synthetic Organic Chemical Manufacturing Industry

Soda ash Sodium carbonate (Na_2CO_3)

Soft seat See "Resilient Seated."

SOL Safe operating limit – limit that, if exceeded for a short time, will result in failure including loss of containment

Solid waste A waste that is solid or semisolid (like a mud or gel)

Solomon Associates A company that does semiannual surveys of refining business and provides comparisons of refineries relative to each other

Soluble Matter or compounds capable of dissolving into a solution

Solvent A substance, normally a liquid, which is capable of absorbing another liquid, gas, or solid to form a homogeneous mixture

Soot blowing Removal of soot from the firebox side of a furnace by blowing high-velocity air through the furnace to loosen the soot. The released solids go out with the flue gas.

SOP Standard operating practice or procedure

SOR (1) Start of run; (2) statement of requirements

Sorbent Generic term for material used to remove specific components from a stream. May refer to absorbents (chemical or solution removal) or adsorbents (surface adsorption)

Sour crude Crude with high sulfur, typically >0.5–0.8 w% sulfur

Sour water stripper (SWS) A process which removes H_2S and ammonia from sour waters generated in a refinery by distillation. Refer to the environmental chapter section on air emissions.

SOW Scope of work

SO_x Sulfur oxides – generically

SOX US Federal Sarbanes–Oxley Legislation

SP (1) Set pressure. (2) Setpoint

SPA Solid phosphoric acid

Spalling Removal of scale deposits and coke from heater tubes by forcing the materials to flake off the tubes using temperature changes

Sparing Providing more than one piece of equipment for a service to enable continued operation in the event of single equipment failure

SPC Statistical process control

SPCC Spill prevention, control, and countermeasures

Spec. sheet Specification sheet. Detailed information about a product or equipment

Special naphthas All finished products within the naphtha boiling range that are used as paint thinners, cleaners, or solvents. These products are refined to a specified flash point. Special naphthas include all commercial hexane and cleaning solvents conforming to ASTM Specification D1836 and D484, respectively. Naphthas to be blended or marketed as motor gasoline or aviation gasoline or that are to be used as petrochemical and synthetic natural gas (SNG) feedstocks are excluded.

Specific gravity The specific gravity of a liquid is the weight of a known volume of the liquid at a known temperature compared with water under the same conditions. The standard weight is taken as 1 g, and the standard temperature is usually 60 °F or 15 °C. The specific gravity of a petroleum compound is the basis for development of the material balance in design work and most measurements within the refinery. Abbreviated as Sp.Gr, SpGr, or SG

The basic specific gravities are given as an essential part of the crude assay. They are usually presented as a curve of specific gravities (usually quoted as °API) against midpoint distillation temperatures. API gravities are related to specific gravities by the equation: specific gravity = 141.5/(131.5 + °API). The specific gravity of any petroleum compound may be calculated using the method provided in the topic "Introduction to Crude Oil and Petroleum Processing" in this handbook.

The specific gravity of crude oil and its products are obtained in the refinery using the test method described in the chapter on "▶ Quality Control of Products in Petroleum Refining" in this handbook. The method uses a properly calibrated hydrometer under laboratory conditions.

Specific heat The quantity of heat required to raise the temperature of a unit weight of a substance by 1°; usually expressed as calories/gram/°C or Btu/lb/°F

Specification (1) Detailed engineering definition of requirements for a product, equipment, or facility; (2) Term referring to the properties of a given crude oil or petroleum product, which are "specified" since they often vary widely even within the same grade of product. In the normal process of negotiation, seller will guarantee buyer that product or crude to be sold will meet certain specified limits and will agree to have such limits certified in writing. Generally, the major qualities of oil for which a buyer would demand a guarantee are API gravity (or specific gravity, in some cases), sulfur content, pour point, viscosity min/max, BS&W, etc.

SPL Sound pressure level. Refer to the environmental chapter section on noise.

Splitter, naphtha In all hydroskimming refineries, the key process next to the crude distillation process is the catalytic reformer. The correct design and subsequent operation of this process produces the hydrogen stream that is required by many refinery operations. Important to the efficient operation of this process is the correct boiling point range of the naphtha feed. This is ensured by the fractionation of the full range naphtha stream from the crude unit overhead distillate. This is accomplished as part of the light ends unit complex. Typically, the total overhead distillates plus, in some cases, other naphtha distillates (from thermal crackers) are first debutanized in the light ends debutanizer column. The bottom product from this column is the debutanized full range naphtha. This stream is delivered hot to a naphtha splitter fractionator which produces a light naphtha overhead and a heavy naphtha bottom product. The fractionation between these two products maximizes the naphthene content of the heavy naphtha. As this heavy naphtha is fed to the catalytic reformer, the amount of naphthenes in its composition will, to a large extent, determine the amount of hydrogen the unit will produce. Splitter towers contain between 25 and 35 actual distillation trays and operate at overhead reflux ratios of between 1.5 and 2.0. Further details and description are given in the topic "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing" in this handbook.

SPOC Single point of contact

SPR See "Strategic Petroleum Reserve."

Spot price The current value of any product on a volume basis on the open market

Spread In futures markets, applies to the difference between prices of futures contracts for different delivery months or to the difference in prices for different commodities. Spread traders try to capitalize on likely fluctuations in these relationships, and initial spread margins are often considerably lower than for outright positions.

SQC Statistical quality control

Squat A short, unplanned shutdown for repairs

SR1 Seconds Redwood # 1 at 100 °F. Measure of viscosity

SRD Safety and Reliability Directorate (UK Atomic Energy Authority)

SRHGO Straight-run heavy gas oil

SRU Sulfur recovery unit or sulfur plant

SRV Safety relief valve

SRxxx See "Straight Run."

SS Stainless steel

SSDC Single-station digital controller

SSF Seconds Saybolt Furol – a measure of viscosity. See "Saybolt Furol Viscosity."

SSSC Solid-state sequence controller

SSU Saybolt Seconds Universal. A viscosity measure. See "Saybolt Universal Viscosity."

ST Short ton = 2,000 lb.

Stabilize To convert a stock to a form that is stable to change or safe for storage. For example, stripping of light or sour gases from a hydrocarbon stock before sending it to tankage

Stack(s) Stacks are used to create an updraft of air from the firebox of a fired heater. The purpose of this is to cause a small negative pressure in the firebox and enable the introduction of combustion air from the atmosphere to the burners. This negative pressure also allows for the removal of the products of combustion from the firebox. The stack must have sufficient height to achieve these objectives and overcome the frictional pressure drop in the firebox and the stack itself. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for the discussion of fired heater design.

Staged combustion Introduction of fuel to a burner in stages to reduce NO_x emissions

Static mixer A motionless mixer which has a series of fixed, geometric elements enclosed within a tubular housing. The internal elements impart flow division and radial mixing to materials flowing through the housing to produce a uniform mixture of the materials.

Steam and condensate systems In most plants, steam condensate, accumulated in the various processes, is collected into a single header and returned to the boiler or steam-generating plant. It is stored separately from the treated raw water because condensates may contain some oil contamination. A stream of treated water and condensate are taken from the respective storage tanks and pumped to a deaerator. The condensate stream passes through a simple filter on route to the deaerator to remove any oil contamination. Low-pressure steam is introduced immediately below a packed section of the deaerator and flows upwards countercurrent to the liquid stream to remove any entrapped air in the liquid. The deaerated boiler feed water (BFW) is pumped by the boiler feed water pumps into the steam drum of the steam generator. The steam drum is located above the generator firebox. The liquid in the drum flows through the steam generator coils located in the firebox by gravity thermosyphon or is circulated by pump. A mixture of steam and water is generated in the coils and flows back to the steam drum. Here, the steam and water are separated with the steam leaving the drum to enter the superheater coil. This coil, located in the lower section of the convection side of the heater, superheats the saturated steam to the high-pressure refinery steam mains. Letdown stations may be located at various points in the refinery to create lower pressure main systems. Desuperheaters are used to establish the correct temperature levels in these lower-pressure mains. There are also normally waste heat recovery steam generation systems and cogeneration systems that use boiler feed water and contribute to the total plant steam production. The handbook topic "▶ Utilities in Petroleum Processing" gives details of about steam generation systems and condensate recovery.

Steam chest In a steam turbine or exchanger, the chamber where steam is initially admitted to the equipment

Steam drum A drum for separating steam from boiler water. The steam is produced from the drum and the boiler water is recirculated through one or more heat sources and back to the drum. There are internal steam separators inside the drum.

Steam-methane reforming (SMR) The most common process for making hydrogen or synthesis gas ($CO + H_2$) by reacting steam with hydrocarbon at very high temperatures and moderate pressure over a catalyst inside tubes suspended in a furnace. The hydrocarbon is converted to methane before or as it is process, hence the term steam-*methane* reforming.

Steam out Using steam to purge volatile materials and other contaminants from a piece of equipment or piping

Steam turbine A driver that uses steam pressure letdown and possible condensation to translate energy in the steam to rotational mechanical energy

STEL Short-term exposure limit

Stiff–Davis index (SDI) A measure of water fouling potential. See the utilities chapter.

Still gas (AKA refinery gas) Any form or mixture of gases produced in refineries by distillation, cracking, reforming, and other processes. The principal constituents are methane, ethane, ethylene, normal butane, butylenes, propane, propylene, etc. Still gas is used as a refinery fuel and a petrochemical feedstock. The usual conversion factor is 6.05 million Btus per fuel oil equivalent barrel.

Stoke The unit of kinematic viscosity

Stoke's law A mathematical relationship that describes the rate of movement of a particle or droplet through another continuous phase in laminar conditions. Refer to the environmental chapter section on water and the equipment chapter section on drums and separators.

Stop–check valve A valve normally used in steam systems on the steam drum which serves as a check valve and block valve for steam production off the drum

Storage facilities The term "storage facilities" generally refers to the tankage or tank farm areas of a petroleum processing facility. Please refer to the topic "▶ Off-Site Facilities for Petroleum Processing" in this handbook.

Stove oil Canadian term used to describe kerosene. Stove oil in Canada is the equivalent of US low-sulfur No. 1 oil or kerosene.

STP Standard temperature and pressure – in US refining, normally 60 °F and 1 Atm. In the metric system, normally 15 °C and 1 atm

STPD Short tons per day

Straight run or straight-run Refers to a petroleum product produced by the primary distillation of crude oil, free of cracked components. A crude cut "run straight from the still."

Strategic Petroleum Reserve (SPR) Petroleum stocks maintained by the US Federal Government for use during periods of major supply interruption

Stratification Phenomenon that occurs in mixed fuels or tanks that results in layers of materials in a tank with differing compositions

Stratified flow Flow regime that normally occurs in a horizontal flow when the gas and liquid separate as they flow through long horizontal pipes. The gas moves at a higher velocity than the liquid, with the liquid flowing along the bottom of the pipe. This is a regime that is a concern for vertical flow because it can cause slugging or pipe hammer. Refer to the equipment chapter, section on two-phase flow pressure drop.

Stream day Actual operating day where feedstock is being charged to a process unit. Stream days determine a unit's sizing capacity or rate. Stream days differ from calendar days by the amount of unit downtime. Stream days are always less than or equal to calendar days.

Stress relieve (or relief) Controlled heating and cooling of a metal to relieve residual stresses after forming or welding

Stripping steam ratio Normally, lb steam per barrel of product in a steam stripper

Stuffing box On rotating equipment, this is a chamber surrounding the shaft in which the packing or other sealing system is installed (or "stuffed" in the old vernacular). Refer to the chapter on equipment for details.

SU or S/U Startup

Sub-octane Usually applies to a gasoline that does not meet the 87-octane standard which most suppliers mandate for regular unleaded distinction. Sub-octanes are typically utilized by those using oxygenated components.

Sulfidation Reaction of sulfur with the surface of a metal

Sulfiding Activation of a hydroprocessing catalyst by reacting the catalytically active metals with sulfur to create the active sulfide form of the metals

Sulfiding chemical Refers to several types of sulfur-containing chemicals used to activate petroleum processing catalysts or temporarily suppress cracking activity in reformers. The most common sulfiding chemicals are DMS, DMDS, TBPS, TNPS, and H_2S.

Sulfinol A proprietary Shell Oil system that uses a regenerable solution containing both a chemical (DIPA) and physical solvent (sulfolane) to remove acid gases

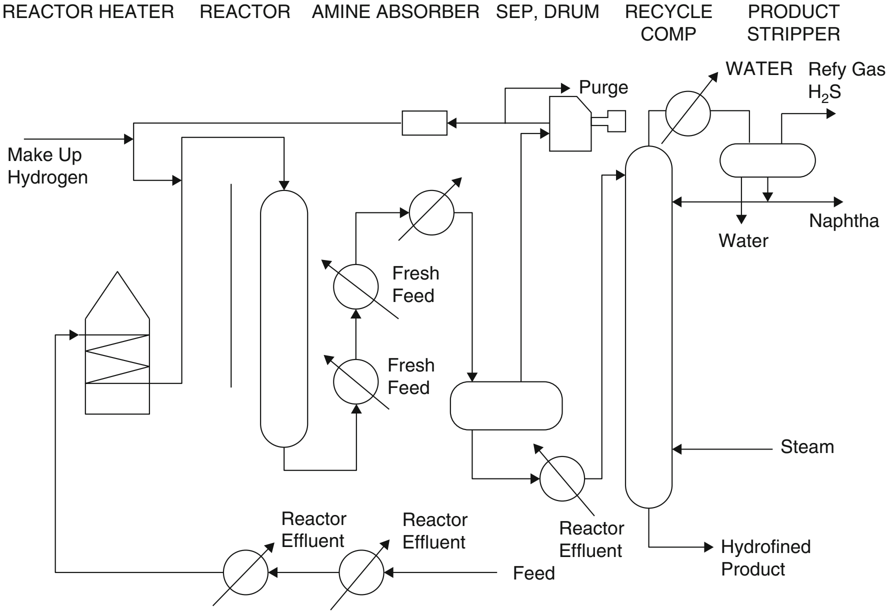


Fig. S.2 A typical middle distillate desulfurizer

(H_2S, CO_2) and some nonacidic gases (COS, RSH) from vapor streams. See the chapter on refinery gas processing.

Sulfolane ($(CH_2)_4SO_2$) Tetrahydrothiophene-1-1-dioxide. A physical solvent component used for sulfur removal from foul gases. A component of sulfinol solution

Sulfur An element that is present in crude oil and natural gas as an impurity in the form of its various compounds.

Sulfur content Sulfur content of a petroleum product or cut is always quoted as a percent or parts per million by weight of the sample. One common laboratory test for sulfur content is “the lamp method ASTM D1266”; this is described in detail in the chapter on “▶ Quality Control of Products in Petroleum Refining” in this handbook. This method has been largely replaced by X-ray fluorescence analysis and other instrumental methods of analysis.

Sulfur removal Removal of sulfur from a petroleum stock. This is normally accomplished by hydrotreating, which converts the organic sulfur compounds to H_2S gas for separation from the hydrocarbons. Some sulfur compounds (notably mercaptans in light hydrocarbons) can also be removed by contact with caustic soda solutions (sweetening). Refer to the chapter “▶ Hydrotreating in Petroleum Processing” in this handbook for the hydrotreating discussion and the chapter “▶ Refinery Gas Treating Processes” for gas sweetening. Figure S.2 illustrates the flow sheet for a simple distillate hydrotreater for sulfur removal.

Sulfuric acid Common aqueous acid used in refineries for pH control and as a catalyst. H_2SO_4. Refer to the chapter on hazardous materials for additional information.

Sump Low spot for collection of a liquid and from which a pump suction may be taken. Sumps may collect liquid from vapors or from other, less dense, liquids.

Superheated A vapor that is heated to a temperature above its saturation temperature. For example, steam at atmospheric pressure and 450 °F is said to be superheated by 450–212 = 238 °F.

Superheater A coil or heat exchanger that provides additional sensible heat to steam above the boiling point

Superimposed back pressure Static pressure existing at the outlet of a pressure relief device at the time the device is required to operate. It is the result of pressure in the discharge system from other sources.

Supervisory control Basic control system for operating units

Surfactant Surface-active agent. The active agent in detergents that possesses a high cleaning ability. A surfactant enables hydrocarbons to be taken into solution or suspended in water by linking the hydrocarbon with the aqueous phases. A surfactant can also make emulsion breaking difficult.

Surge vessel A vessel intended to provide surge volume in a process. Refer to the chapters on equipment and controls.

Surge volume This is the volume of liquid between the normal liquid level (NLL) and the bottom (tan line) of a vessel. Refer to the equipment and controls chapters.

SUS Saybolt Universal Seconds viscosity measure. See “Saybolt Universal Viscosity.”

SU/SD Start up/shut down

SV Safety valve – pressure relief valve

SVP Senior vice president

Sweet crude Crude with low sulfur, usually less than 0.5–0.8 w% sulfur

Swing capacity In crude planning, the total crude storage capacity plus seasonal storage. See the chapter on economics.

Swoopdown A short, unplanned shutdown for repairs

SWOT Strengths, weaknesses, opportunities, and threats analysis

SWP Safe work practice

SWPPP Stormwater Pollution Prevention Plan

SWS Sour water stripper or stripping – recovers H_2S and ammonia out of sour water by driving them out with heat. Refer to the environmental chapter section on air emissions control.

SWSOG Sour water stripper overhead gas

SynBit A blend of synthetic crude and bitumen. Some Canadian crudes fall in this category being blends of bitumen from tar/oil sands and partially refined bitumens.

Synthetic crude (or Syncrude) A crude-like hydrocarbon produced by methods that are not conventional. Basically an unconventional crude. Usually involves taking a raw, nonconventional crude and pre-refining it to remove the worst characteristics that would prevent its sale as a high-quality crude. Effort is made to give the Syncrude properties like a conventional crude. Can then be processed like a conventional crude

S Zorb Sulfur removal process for naphtha and distillates

T

T&C (or Ts and Cs) Terms and conditions in a contract

T&M Time and materials

T/A or TA Turnaround

TA (H, HH, L, LL) Temperature alarm high, high–high, low, or low-low. E.g., TAHH is a high–high temperature alarm.

Tag-Robinson colorimeter An instrument used to determine the color of oils. Also a scale of color values

Tail gas treating Generally refers to processing Claus sulfur recovery plant effluent gas to remove the final traces of sulfur compounds before emission to the air. Refer to the environmental chapter section on air emissions control.

Tallow Animal fat. See the discussions on renewables and unconventional stocks.

TAME Tertiary-amyl methyl ether – oxygenate blendstock for gasoline

TAN Total acid number. A measure of oil corrosivity due to carboxylic acids. Expressed as mg KOH per 100 g oil

Tank farm An installation used to store crude oil and products.

Tanker Vessel used to transport crude oil or petroleum products

Tar Tar is an ill-defined general term that describes heavy petroleum fractions that are solid or semisolid at room temperature. An alternative term is *bitumen* although the latter is better used to denote naturally occurring tar deposits, as in tar pits or tar sands. In addition to being very viscous or non-flowing materials (viscosity >10,000 cP), tars are also characterized by having relatively high densities lower than about 10 API degrees, which corresponds to a specific gravity (60/60) greater than 1.0. Depending on their physical properties, tars may be easily confused with asphalts. The main difference being that tars are usually either naturally occurring or unprocessed heavy fractions recovered as by-products from other sources (e.g., petroleum residues or coal processing), while asphalts are typically processed or manufactured materials, whether air-blown or solvent extracted. Sometimes, tars are further processed to recover the more volatile components. If so, the remaining very heavy residue is usually called *pitch* (Gerd Collin, "*Tar and pitch*." *Ullmann's Handbook of Industrial Chemistry*, Wiley-VCH Verlag GmbH, 2002). See also the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook.

Tar sands Tar sands or bituminous sands or oil sands are several porous rock formations that contain highly viscous heavy hydrocarbon materials that cannot be recovered by conventional oil recovery methods, including enhanced oil recovery techniques. These hydrocarbon resources and the oils that come from them are discussed in the topic "▶ Unconventional Crudes and Feedstocks in Petroleum Processing."

Tariff A schedule of rates that a common carrier pipeline is permitted to charge to transport petroleum products or crude

TBA (1) Tertiary butyl alcohol; (2) tertiary butyl amine; (3) in marketing: tires, batteries, and accessories

TBN Total base number. ASTM D2896. This is measured in mg of KOH needed to neutralize an acidic solution through a reverse titration. TBN is the ability of the product to neutralize acid. In a motor oil, this is a property which allows the oil to neutralize acids from combustion that would otherwise degrade the oil.

TBP True boiling point

TC Temperature controller

TCC Thermal catalytic cracking unit

TCF Trillion cubic feet

TCU Thermal cracking unit

TDAF Tertiary dissolved air flotation

TEA See "Triethanolamine"

TEG Triethylene glycol

TEL Tetraethyl lead – octane booster – no longer used in United States. See "Tetraethyl Lead."

Tetraethyl lead (TEL) A former additive used as an antiknock additive to boost the octane number in gasoline. It was produced commercially from ethyl chloride. It was used at a dosage in 0–3 ml/gal range depending on the gasoline composition, sulfur content, and lead sensitivity. The use of tetraethyl lead has largely been discontinued worldwide, in particular, as a result of the introduction of catalytic converters to clean up the exhaust from internal combustion engines. The use of lead irreversibly poisons the oxidation catalysts used in such converters. Also, lead itself is a highly toxic substance that was present in automobile exhaust before it was banned with the advent of catalytic converters.

TEMA Tubular Exchanger Manufacturers Association – sets standards for heat exchangers

Tertiary-amyl methyl ether (TAME, $(CH_3)_2(C_2H_5)COCH_3$) An oxygenate blendstock formed by the catalytic etherification of isoamylene with methanol

Tertiary butyl alcohol (TBA, t-butanol, $(CH_3)_3COH$) An alcohol primarily used as a chemical feedstock, a solvent or feedstock for isobutylene production for MTBE; produced as a coproduct of propylene oxide production or by direct hydration of isobutylene

Tertiary storage Refers to petroleum storage tanks of end users, such as vehicle gasoline tanks or home heating oil storage

Test run A defined period of process unit operation where detailed performance data, sample analyses, and other information are recorded. The data are analyzed to define a process unit and equipment performance at a point in time. Test runs can be used to evaluate performance for guarantees, decisions on catalyst, or to determine alternate operations options, among many other uses. They also establish baseline equipment performance in new facilities.

TF Tank farm

TFE or PTFE Polytetrafluoroethylene

TGU or TGT Tail gas unit or tail gas treating unit. Refer to the chapter on environmental controls, air emissions section.

Thermal cracking Thermal cracking was the first commercial process used for the conversion of heavy petroleum fractions into more useful products. Though largely superseded by other processes (in particular catalytic cracking), thermal cracking was used for many years for the decomposition (cracking) of heavy, high-molecular-weight hydrocarbons into smaller molecules and is still used commercially in the processing of very heavy fractions, as in visbreaking or coking. Refer to the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook for additional discussion.

Thermal reforming Thermal reforming is similar to thermal cracking applied to gasoline boiling range hydrocarbons. The smaller molecules in naphtha are more difficult to crack and require higher severities than thermal cracking, with furnace outlet temperatures of up to about 600 °C. Good per-pass conversions and good octane improvements can be obtained while coke formation is limited because of the lighter nature of the feedstock. An excellent review of thermal processes, both cracking and reforming, can be found in the Petroleum Processing Handbook, edited by John J. McKetta, Marcel Dekker (1992). To a large extent, thermal reforming has been superseded by catalytic reforming and thermal cracking by fluidized catalytic cracking (FCC).

Thermal relief A pressure relief valve intended to avoid overpressure of a liquid-filled line due to external heating.

Thermal value Calories per gram or Btu per pound produced by burning fuels

Thermocouple The most common temperature measuring element. Takes advantage of the tiny voltage generated at a dissimilar metal junction that changes with temperature in a defined manner. See the chapter on process controls.

Thermofor The commercial name of a continuous moving bed process used either for catalytic cracking or catalytic reforming. A distinctive feature of this process is that the catalyst, usually chromia/alumina, flows down through the reactor concurrently with the hydrocarbons. A mechanical conveying system is used to circulate the catalyst back to the top of the reactors. The process is not common today. For more information, refer to James G. Speight and Baki Özüm, *Petroleum Refining Processes*, Marcel Dekker, 2002.

Thermosiphon or thermosyphon An equipment arrangement, often used for reboilers, which uses the density difference created by heating a fluid to induce natural convection flow in the fluid. Refer to the section on heat exchangers in the chapter on equipment.

Thermowell A device inserted into a process in which the temperature measuring element is inserted. The thermowell protects the temperature element from damage by the process fluids.

Threshold limit value (TLV) The average concentration of a compound which is considered a safe (negligible health hazard) working environment over an 8 h period

Throttle valve A valve normally controlling steam rate entering a steam turbine or gas rate entering a compressor. Refer to the equipment chapter.

Throttling Controlling flow rate by a restriction, such as a valve

TIC Total indicated cost – in a project

Tight oil or tight shale oil See "Shale Crude and Gas." Oil produced from shale formations with negligible natural permeability. The rock must be fractured to create permeability before oil or gas can be produced.

TLV Threshold limit value

TMEL Targeted mitigating event likelihood – in LOPA

TOC Total organic carbon – in wastewater

Toluene ($C_6H_5CH_3$) Colorless liquid of the aromatic group of petroleum hydrocarbons, made by the catalytic reforming of petroleum naphthas containing methylcyclohexane. A high-octane gasoline-blending agent, solvent, and chemical intermediate base for TNT

Ton 2,000 lb in English engineering units

Tonne 1,000 kg or 1 metric ton. 2,205 lb. On average, there are 7 barrels of crude per metric ton.

Topped crude oil Oil from which the light ends have been removed by a simple refining process. Also referred to as "reduced crude oil"

Topping "Topping" or "skimming" is the name used for the distillation of crude oil to remove the lighter fractions. The crude oil with such fractions removed is sometimes called "topped crude." Some refineries are only designed to be topping units, but these facilities are severely disadvantaged by limited crude options and poor product quality. Very few simple topping plants are in operation any more.

Total existent sediment Combination of inorganic and hydrocarbon sediments existing in a stock as delivered

Tower Generally refers to a tall vessel with internals for fractionation, absorption, or stripping. Refer to the equipment chapter, section on vessel and tower design.

Tower fractionation A fractionation tower is a distillation column, typically with multiple trays or fractionation stages and with at least one feed and two product streams – top and bottom – but often having also provision for multiple feeds and multiple withdrawal points or side cuts. Design of these towers is discussed in the handbook topics on atmospheric and vacuum crude distillation units, light ends distillation, and process equipment design. The mechanical design of a fractionation tower is far more complex than just the specification of the operating conditions or the number of theoretical stages. Also needed are the specifications and designs for its internal components, such as dimensions, plates or packing, risers, downcomers, internal supports, distributor nozzles, reboilers, condensers, etc. Refer to the handbook topic "▶ Process Equipment for Petroleum Processing" for some details of tower internals.

Toxic Property of being poisonous to a living organism

Toxicity (1) The relative degree of being poisonous or toxic. A condition which may exist in wastes and will inhibit or destroy the growth or function of certain organisms. (2) Hazardous waste characteristic of being poisonous to living organisms. Refer to the environmental chapter section on hazardous wastes.

TPD Tons per day

TQ Threshold quantity

TR Temperature recorder

Trade secret Information that provides a company with an economic advantage. Proprietary information. Such information does not need to be disclosed except in an emergency.

Tramp compound A contaminant or undesired material in a process stream

Tramp air Air that enters a fired heater by leakage other than through the burners or stack cooling vents, wasting efficiency

Transesterification Reaction of a heavy polyorganic ester with a light alcohol to form lighter esters. See the discussion of renewables and unconventional stocks.

Transmix The interface material between shipments of different products through a pipeline. The interface does often not meet the specifications for either product, but may be blended into one product (generally downgrading) or reprocessed.

Transportation System used to move oil and gas from the field to the market

Trap A device for elimination of either condensed liquid from a vapor system (e.g., a steam trap to eliminate condensate from the steam header) or trapped gases from a liquid-filled system

TRC (1) Temperature recorder and controller; (2) total recordable cases (injuries)

TRI Toxic release inventory – environmental

Trickle filter A biological digestion unit for removal of BOD from wastewater by passing the water through a rock bed covered with organisms and exposed to air.

Triethanolamine (TEA, $(HOC_2H_4)_3N$) An early regenerable solvent used for removal of acid gases (mainly H_2S) from streams. Refer to the chapter on refinery gas treating. This material is not normally used for this service anymore because of the availability of better solvents.

Trip Unplanned shutdown caused by a process or equipment failure

True boiling point (TBP) The true boiling point distillation curve can be obtained in a laboratory apparatus. TBP distillation differs from an ASTM or *Engler* distillation. In process design, especially in fractionation, the TBP curve is critical. Various correlations exist to relate TBP, ASTM, and other laboratory distillation procedures. See the handbook topics "▶ Introduction to Crude oil and Petroleum Processing" and "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries." Another good reference is: Nelson, W. L. *Petroleum Refining Engineering*, McGraw-Hill, 4th edition, 1958.

TRV Thermal relief valve

TSAP EU Thematic Strategy for Air Pollution. Refer to the environmental chapter.

TSCA US Toxic Substances Control Act

TSV (1) Thermal or temperature safety valve – a relief valve for thermal expansion of fluids in a packed line; (2) total system value

TT Temperature transmitter

Tube hanger A device to support a tube in a fired heater

Tube sheet In a shell-and-tube exchanger, the plate where the tubes start and/or end and which isolates the tube-side fluid from the shell-side fluid

Tube skin The surface of a tube. Generally refers to furnace tube surface temperatures, which are normally the hottest part of the tube exposed to the firebox

Tube trailer A large trailer consisting of multiple high-pressure tubes (2,000–5,000 psig) used to supply relatively small specialty gas needs, such as hydrogen or nitrogen without requiring additional compression. Refer to the discussions in the chapters on utilities and hydrogen production.

Tube wall Literally, the wall of a tube. Usually applied in furnaces or exchangers

Turnaround A major, periodic shutdown maintenance period to inspect, repair, and renew equipment in a process unit

Turndown Reducing a unit's feed rate or production rate. Most units have a limited turndown capability before they become hard to control. Turndown may be described as % turndown; however, often what this number means is unclear: 33 % turndown sometimes means the plant can be run as low as 33 % of design rate or it can only be turned down to 67 % of design rate. It is always best to clarify what is meant.

Turnout gear In firefighting, these are the heavy, fire-resistant clothing and boots used to protect personnel

TUV Technischer Uberwachungs-Verein e.V. (Technical Inspection Association of Germany)

TW Thermowell

Two-phase Having two distinct phases, such as a mixture of liquid and vapor

U

Ubbehohde viscosimeter A suspended-level apparatus for accurately determining the viscosity of a liquid

UCARSOL A proprietary solution from Dow Chemical for absorbing acid gases. Refer to the environmental chapter on air emissions

UCC US Uniform Commercial Code

UFD Utility flow diagram

UL Underwriters Laboratory, Inc.

ULCC See "Ultra-Large Crude or Cargo Carrier."

Ullage The amount which a tank or vessel lacks of being full

ULNB Ultralow NO_x burner

ULS Ultralow sulfur – may apply to any product. ULSD = ultralow-sulfur diesel.

ULSD Ultralow-sulfur diesel – usually refers to diesel with <10 wppm sulfur

ULSK Ultralow-sulfur kerosene – usually refers to kerosene with <10 wppm sulfur

Ultra-large crude or cargo carrier (ULCC) The largest category of tanker, generally holding at least 3.5 million barrels of product

Unbranded A supply arrangement with a supplier that is usually not contractual and does not usually guarantee a specific amount of supply

Unconventional crude Crude that is produced by methods other than conventional – like shale oil that must be thermally decomposed from rocks or oil sands that must be thermally removed from sand via mining or special production methods. There are many types of unconventional crudes. Renewable fuels are in this category.

Underwood equation This correlation is used to estimate the minimum vapor flow above the feed in a distillation column. See the chapters on crude distillation, light ends processing, and equipment.

Unfinished oils All oils requiring further processing, except those requiring only mechanical blending. Unfinished oils are produced by partial refining of crude oil and include naphthas and lighter oils, kerosene and light gas oils, heavy gas oils, and residuum. AKA intermediates

Unfired vent stack See "Vent Stack."

UOP Originally Universal Oil Products – now UOP LLC, part of the Honeywell group. Independent refining process developer and licensor

UOP K (AKA Watson K) The *UOP K*, or the *Watson K*, or the *Watson characterization factor*, is a parameter identified by Kenneth Watson who defined it as

$$K = [T_B]^{1/3}/(\mathrm{Sp.Gr.})$$

where $[T_B]^{1/3}$ represents the cube root of the average molal boiling point of the hydrocarbon mixture $[T_B]$ in degrees Rankine (°R = °F + 460), divided by the specific gravity at 60 °F, relative to water at 60 °F. This is a correlation parameter based on the observation that $K \sim 12.5$ corresponds to paraffinic materials, while $K \sim 10.0$ indicates a highly aromatic material. It provides a means for roughly identifying the nature of a feedstock solely on the basis of two observable physical parameters. The characterization factor has also been related to viscosity, aniline point, molecular weight, critical temperature, percentage of hydrocarbons, etc., so it can be estimated using a number of laboratory methods. Refer also to (1) Characterization of petroleum fractions, *Ind. Eng. Chem.*, **27**, 1460, 1935 and (2) Nelson, W. L., Petroleum Refinery Engineering, McGraw-Hill, 4th edition, 1958.

UPS Uninterruptible power supply – a battery-backup power supply

Upstream Organization that finds and produces crude oil and natural gas

Urea dewaxing A process for making low pour point oils in which straight-chain paraffins are removed from the feedstock by complexing them with urea to form a crystalline adduct that can be separated by filtration. Refer to the chapter on "▶ Non-energy Refineries in Petroleum Processing" in this handbook and John J. McKetta (ed), *Petroleum Processing Handbook*, Marcel Dekker, 1992.

USD United States dollar

UST Underground storage tank

Utility Refers to fluids used by several pieces of equipment in refinery units – steam, air, water, cooling water, instrument air, power, nitrogen, etc.

Utility air See "Plant Air."

Utility station or utility drop A set of outlets provided at selected locations in a plant where utility connections are available. A utility station normally has plant air, plant water, and steam available. Some stations may have nitrogen or other utilities available. Refer to the chapter on utilities.

Utility water See "Plant Water."

UV Ultraviolet

V

V Vanadium

Vacuum distillation unit (VDU) Vacuum distillation unit refers to the further distillation of the residue portion of atmospheric distillation of the crude. The boiling curve range of this portion of the crude is too high to permit further vaporization at atmospheric pressure. Cracking of the residue would occur long before any temperature level for effective distillation would be reached. By reducing the pressure, the danger of cracking on further heating the residue oil for further distillation is reduced. Figure V.1 is a process diagram of a typical crude oil vacuum distillation unit. These units operate at overhead pressures as

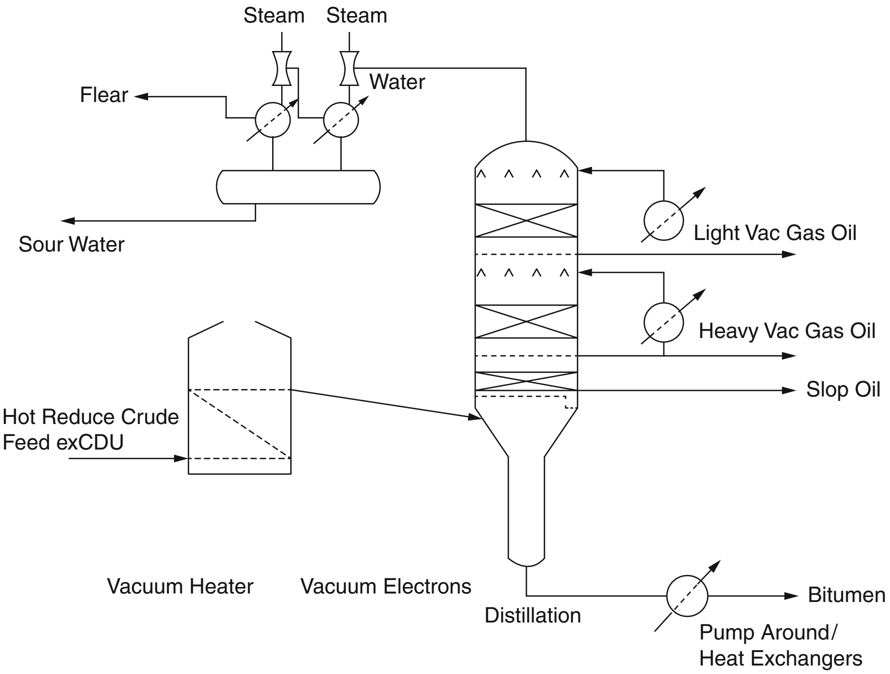


Fig. V.1 Vacuum distillation

low as 10 mmHg. This type of unit is further described and discussed in the handbook topics on atmospheric and vacuum distillation and process equipment design.

Vacuum pump A type of compressor used to create vacuum in a process system. These are normally liquid-ring or reciprocating compressors. They are often used as the last stage in a 3-stage vacuum system, with steam-jet ejectors used for the first two stages.

Vacuum resid See "Resid."

Value chain The string of organizations that bring something from raw material to finished product

Valve loader or lifter See "Loader or Lifter."

Valve tray A type of tray used in distillation, absorber, or stripper columns that promotes contact between vapor and liquid on the tray using simple, lifting valves placed over holes distributed over the tray. Refer to the chapter on process equipment.

Vanadium inhibitor An organic and/or inorganic metal bearing chemical intended to chemically and/or physically combine with the compounds formed during combustion of heavy fuel oil to improve the surface properties of the treated ash compounds

Vapor depressuring (or depressing) system Protective arrangement of valves and piping intended to provide for rapid reduction of pressure in equipment by release of vapors to a safe location, usually the flare, in emergencies.

Vapor disengaging drum Vessel for separation of vapor or gas from a mixture with liquid. Refer to the chapter on equipment, section on drums and separators.

Variable cost A cost that depends on processing rate. For example, energy costs that depend on number of barrels processed

Variable head-capacity pump A pump where the delivered flow rate depends on the back pressure, like a centrifugal pump

Variable speed A technique for controlling flow by changing the speed of a compressor or pump

VC Vertical cylindrical (or Can) heater style – also called petrochem heater – used extensively in refineries

VDU (1) See "Vacuum Distillation Unit"; (2) video display unit

Vena contracta The point of the narrowest flow streamline around an obstruction in a pipe or other flow channel. The pressure at this point has a specific relationship to the flow rate, as defined by the Bernoulli principle, and is used in flow metering.

Vent stack (or unfired vent stack) Elevated vertical termination of a disposal system which discharges vapors into the atmosphere without combustion or conversion of the relieved fluid

Venturi flow meter Similar to an orifice meter, a venturi meter creates a *vena contracta* with a smooth, nonturbulent channel that follows the fluid streamlines. This reduces pressure drop and improves accuracy.

Very large crude carrier (VLCC) A category of ocean-going tanker hauling from 1.5 million to 2.5 million barrels of product.

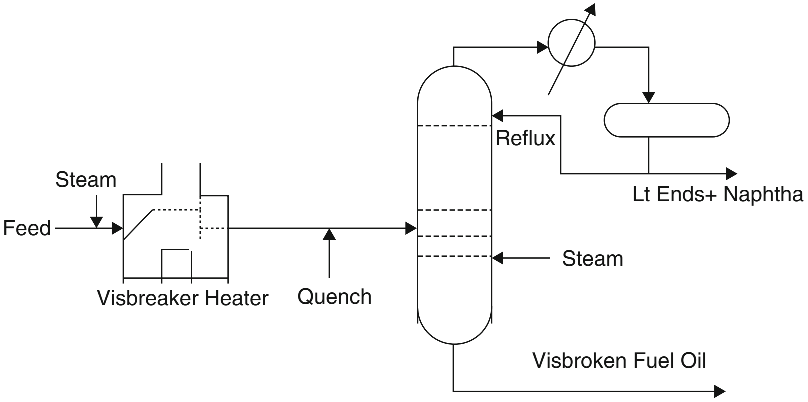


Fig. V.2 Typical visbreaker unit

Vetrocoke (AKA Giammarco-Vetrocoke) A proprietary process normally used for purification of product vapors from a gasifier to remove acid gases. This process uses either arsenite/arsenate or hot potassium carbonate solutions. It is not commonly found in refineries.

VGO Vacuum gas oil

VHAP Volatile hazardous air pollutant

VI Viscosity index

Virgin xxx See "Straight Run."

Visbreaking The visbreaking process is a mild thermal cracking of crude oil residues to reduce oil viscosity without blending. It is used especially to reduce the viscosity of vacuum residue to meet the fuel oil specification. The process configuration is very similar to the conventional, once through thermal cracker except for the routing of the recovery products from the fractionator. Figure V.2 shows the configuration of a typical visbreaker. Refer to the chapter on "▶ Upgrading the Bottom of the Barrel" in this handbook for a more detailed discussion.

Viscosimeter A device for determining the viscosity of oil. There are several methods or devices in general use. Basically, a fixed quantity of oil is allowed to pass through a fixed orifice at a specified temperature over a measured time span and the time is then compared to a standard liquid such as a calibration oil or water.

Viscosity This is a measure of the internal friction or resistance of an oil to flow. As the temperature of an oil is increased, its viscosity decreases, and it is therefore able to flow more readily. Viscosity is measured on several different scales, including Redwood No. 1 at 100 °F, Engler degrees, Saybolt Seconds, etc. The most common method for designation of viscosity is kinematic viscosity, measured in centistokes, cSt at 50 °C (see Saybolt Furol, Saybolt

Universal, Engler, Redwood, Kinematic). This measurement is important in many facets of process design and indeed is an essential quality of many finished products. The topic entitled "▶ Quality Control of Products in Petroleum Refining" describes some of the test methods for viscosity. There are two viscosity parameters normally defined: (1) dynamic or absolute viscosity and (2) kinematic viscosity. Both are related, since the kinematic viscosity may be obtained by dividing the dynamic viscosity by the mass density. The metric unit for viscosity is *poise* (P). The unit most often used in the petroleum industry for this measure is the *centipoise* (cP) which is the poise divided by 100. Thus, dimensions of the poise are grams/(cm × s). The kinematic viscosity dimension in English units is *square foot per second*. And in metric units is *square centimeter per second* called *the stoke*. In the petroleum refining industry, stokes divided by 100 called *the centistoke* (cSt) is the unit most often used. In blending for viscosity, a blending index concept must be used. You cannot blend viscosities directly using just proportions. The viscosity indices are given and discussed in the chapter titled "▶ Introduction to Crude Oil and Petroleum Processing" and again in the topic "▶ Petroleum Products and a Refinery Configuration."

Viscosity index (VI) Measure of the amount the viscosity of a lube oil stock will change with temperature. A high VI indicates less change with temperature. High VI is desired for premium lube oils. See the chapter titled "▶ Non-energy Refineries in Petroleum Processing."

VLCC Very large crude carrier

VOC Volatile organic compounds

Volatile A volatile substance is one that is capable of being evaporated or changed to a vapor at a relatively low temperature.

Volatile organic compound A combination of fugitive chemical pollutants that form ozone or smog. The Clean Air Act was designed in part to reduce VOCs in gasoline in order to reduce ozone pollution from gasoline exhaust and emissions.

Volatility (1) The degree to which an oil product will vaporize or turn from liquid to gas, when heated. (2) Range in price or frequency and magnitude of change in price for a product

VPP US OSHA Voluntary Protection Program

VRU Vapor recovery unit

VTB Vacuum tower bottoms – AKA vacuum resid. See "Resid."

VTU Vacuum tower unit

W

WABIT Weighted average bed inlet temperature – normally catalytic naphtha reformers

WABT Weighted average bed temperature – normally used for hydroprocessing reactors and other fixed bed units

Waste disposal facilities All process plants, including oil refineries, produce quantities of toxic and/or flammable materials during periods of plant upset or emergencies. Properly designed flare and slop handling systems are therefore essential to the plant operation. Facilities for recovery of hydrocarbon slops, safe disposal of excess gases, and environmentally responsible disposal of water effluents are discussed in the topics "▶ Off-Site Facilities for Petroleum Processing" and "▶ Environmental Control and Engineering in Petroleum Processing."

Waste minimization or waste reduction Practice of reducing the amount of net waste produced by a facility or process. Refer to the environmental chapter section on solid wastes.

Water–gas shift (WGS) The reaction of CO with steam to produce CO_2 and hydrogen. This reaction is used extensively in SMR hydrogen plants.

Water rate In a steam turbine, the steam required by a turbine for a given horsepower application. Units are lb/HP-hr. Refer to the chapter on equipment, section on steam turbines.

Water systems The major water systems in most petroleum processing plants include cooling water, treated boiler feed water, plant water, fire water, and potable water. The key elements of these systems are discussed in the topics "▶ Utilities in Petroleum Processing" and "▶ Fire Prevention and Firefighting in Petroleum Processing."

Wave or wavy flow Flow regime similar to stratified flow, but the gas velocity is higher, producing a wavy interface between gas and liquid layers. Again, this regime can give rise to problems when flow is vertical. Refer to the chapter on equipment, section on two-phase pressure drop.

Wax A solid or semisolid material consisting of a mixture of hydrocarbons obtained or derived from petroleum fractions, or through a Fischer–Tropsch-type process, in which the straight-chained paraffin series predominates. This includes all marketable wax, whether crude or refined, with a congealing point (ASTM D938) between 100 °F and 200 °F and a maximum oil content (ASTM D3235) of 50 wt%.

Waxy lube stock (WLS) An intermediate in lube oil production that has a high VI and can be finished into a lube oil blendstock

WBS Work breakdown structure in projects

WBT Web-based training

WC or "WC Inches of water column – a measure of draft in a heater firebox or vacuum

W.C.A. Water column absolute – normally inches of water pressure above vacuum

W.C.G. Water column gauge – normally inches of water pressure above atmospheric pressure

WCS (1) Western Canadian select crude oil blend; (2) worst case scenario

WDT Watchdog timer – in control systems

Weir A small "dam" used to create a controlled liquid level upstream by allowing overflow of excess liquid over the weir. In some typical applications, weirs are used to create liquid seals in distillation column downcomers and to control flow rates and distribution through wastewater treating units.

WFD EU Water Framework Directive

WGS (1) Wet gas scrubber – used for SO_x reduction in stacks, among others; (2) water–gas shift reaction (see "Water–Gas Shift")

What-if analysis A process hazards analysis method based on questions about possible impacts of process changes. Refer to the safety chapter.

WHB Waste heat boiler – recovers heat by generating steam. This will look like a heat exchanger.

WLS Waxy lube stock

Working capital This economic term includes capital items that require a front-end investment but are not part of the physical plant, accrued interest charges, accounts receivable, cash on hand, sorbents, catalysts, metals, warehouse, and spare parts inventories. See the chapter on economics.

Working storage capacity The difference in volume of a tank or other vessel between the maximum safe fill capacity and the quantity below which pump suction is ineffective (bottoms or tank heel/minimum level)

WPS Welding procedure specifications

WTI West Texas intermediate crude – a marker or price-setting crude oil

WTS West Texas sour crude oil

WWT (1) Wastewater treatment; (2) a Chevron process for recovering ammonia from sour wastewater

WWTP Wastewater treatment plant

WWTS Wastewater treatment standards

X

xC Controller – controls condition "x" where x = flow, temperature, pressure, level, etc.

xE Element – a device that detects condition "x" where x = flow, temperature, pressure, level, etc.

XHVGO Extra-heavy vacuum gas oil

xI Indicator – indicates condition "x" where x = flow, temperature, pressure, level, etc.

xIC Indicator–controller – indicates and controls condition "x" where x = flow, temperature, pressure, level, etc.

X-factor The sum of C_7+ hydrocarbons, C_6 naphthenes, and benzene in the feed to a light naphtha isomerization process unit. The higher the X factor, the more difficult the feed is to process.

X-grade Pipeline term for no. 2 fuel oil

XML Extensible Markup Language

xR Recorder – records condition "x" where x = flow, temperature, pressure, level, etc. – not used much anymore

XRD X-ray diffraction analysis method

XRF X-ray fluorescence analysis method

X-ray fluorescence analyzer In these analyzers, a sample is excited by X-rays which causes it to fluoresce or absorb in specific wavelengths that depend on composition. The fluorescence or absorption are detected and translated to composition. Refer to the chapter on controls.

xTL Shorthand for any carbon material converted to a liquid hydrocarbon. Refer to the chapters on unconventional feedstocks and chemicals from natural gas and coal.

xX Transmitter – transmits sensed condition "x" to control system (where x = flow, temperature, pressure, etc.)

Xylenes ($C_6H_4(CH_3)_2$) These are aromatic compounds consisting of two methyl groups attached to a benzene ring. There are three xylenes designated as meta, ortho, and para based on the positions of the two methyl groups around the aromatic ring. In ortho-xylene, the methyl groups are attached to adjacent carbon atoms. In meta-xylene, the methyl groups are separated by one carbon atom in the ring. Para-xylene has the methyl groups on opposite sides of the ring. Xylenes, coupled with benzene, toluene, and ethyl benzene, are the major products from a petrochemical petroleum refinery. These compounds as a whole are usually designated as BTX. Refer to the chapter "▶ Non-energy Refineries in Petroleum Processing" of this handbook for additional discussion.

Y

Yard air See "Plant Air."

Yard water See "Plant Water."

Y-grade Pipeline term for No. 1 Fuel Oil. The feedstocks that are sent to a fractionator in order to extract gas liquids

YTD Year to date

Z

"Z" factor The term "Z factor" is usually found in two contexts:

- Compressibility factor for a gas
- Pseudo heat transfer coefficient for a heat exchanger

(1) *Gas compressibility factor*

"Z" is often the symbol used for the compressibility factor of a gas. This may be derived from the equation:

$$PV = ZnRT$$
$$PV = Z(m/M)RT$$
$$PM = Z\rho RT$$
$$Z = PM/\rho RT$$

where:
V = volume of gas
m = mass of gas
R = gas constant
M = molecular weight of the gas
P = gas pressure (absolute)
T = absolute temperature
ρ = density of the gas at gas temperature and pressure
Typical values for R are:
8.3143 J/(mol × °K)
0.08205341 atm × m^3/(kmol × °K)
1.98716759 cal/(mol × °K)
10.7313 psia × ft^3/(lb mol × °K)
(2) *Pseudo heat transfer coefficient*
When limited data are available in a unit to track heat transfer in an exchanger, a Z factor can be tracked to infer exchanger fouling. The Z factor is developed in the following manner:

$$\Delta Q = U\ A\ \Delta T_{LM}\ \text{and also}\ \Delta Q = C_{effective} DT$$

$$U\ A\,\Delta T_{LM} = C_{effective}\Delta T$$

$$U = C_{effective}\Delta T / A\,\Delta T_{LM}$$

Observe that the heat transferred per degree in an exchanger is roughly constant and the exchanger surface area is constant, assuming no major changes in flow rates on either side of the exchanger. Hence, assume that $C_{effective}/A$ is constant. So, U α $\Delta T/\Delta T_{LM}$ which we define as the Z factor for the exchanger.
ΔQ = Heat transferred in the exchanger per unit time.
U = Overall heat transfer coefficient.
A = Exchanger surface area.
ΔT = Temperature difference for one of the fluids in the exchanger.
$C_{effective}$ = Heat transferred per degree for the fluid chosen as the ΔT basis.
ΔT_{LM} = Exchanger log-mean temperature difference between the hot and cold fluids.
A plot of Z over time will indicate the extent of fouling in an exchanger. Note that this approach assumes relatively constant flow conditions on both sides of the exchanger. It is confounded by large differences in flow rates. It is possible to adjust the Z for flow variations by introducing a correction factor developed from empirical tests.

Zeolite catalysts Zeolite catalysts contain acidic silica–alumina structures that promote cracking of hydrocarbons. They are used in catalytic cracking processes. This together with the technique of “riser cracking” revolutionized these processes (distillate feed crackers and residuum feed). This is described and discussed in detail in the chapter "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining." This type of catalyst is also incorporated into hydrocracking as part of the catalyst base. Discussion of hydrocracking is in the chapter on "▶ Hydrocracking in Petroleum Processing."

Part VI

Appendices

Examples of Working Flow Sheets in Petroleum Refining

Steven A. Treese

Contents

Abstract

This appendix is a collection of working flow sheet examples that are developed for design and operation of refinery and other petroleum processing units. These are only used as illustrations of the format and content for these key documents. Included here are a Process Flow Diagram and accompanying Material Balance, a section of a Mechanical Flow Diagram (or P&ID), and a section of a Utility Flow Sheet.

Keywords

Process flow diagram • Mechanical flow diagram • Material balance • Utility flow diagram • P&ID

Steven A. Treese has retired from Phillips 66.

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_32

Appendix A: Example Flow Sheets

A1a A Typical Process Flow Sheet

See Fig. 1.

A1b The Associated Material Balance

See Fig. 2.

A2 A Section of a Typical Mechanical Flow Sheet

See Fig. 3.

A3 A Section of a Typical Utility Flow Sheet

See Fig. 4.

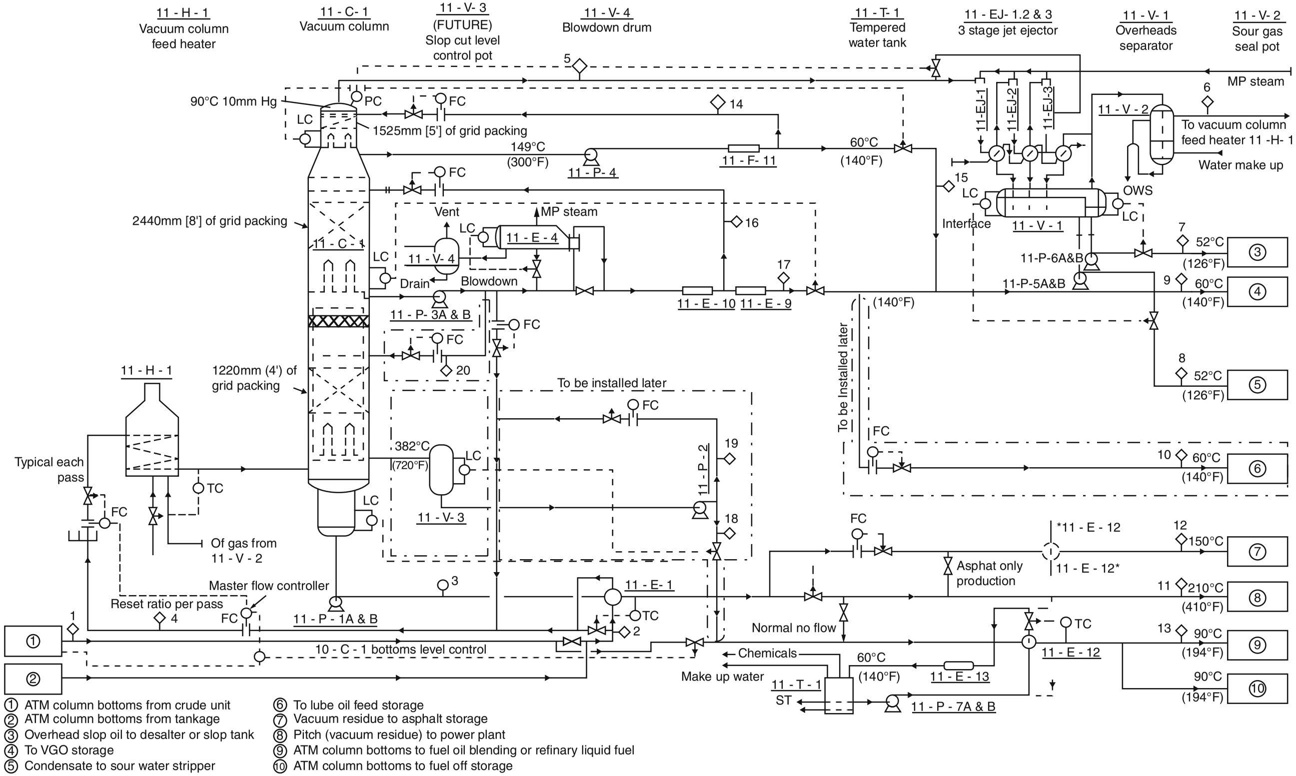


Fig. 1 A Typical Process Flow Sheet

Stream up	1	2	3	4	5
Stream identification	ATM column bottoms from crude column	Feed to vacuum column	Vacuum column residue	Feed to vacuum column	Vacuum column overhead vapour
Normal kg/h	470,269	391,836	245,982	391,836	2971
BPSD based on standard conditions	71,800	60,000	36,000	60,000	
Cut	371°C+	371°C+	80 pen	371°C+	94.1 (Av. mol/wt)
SG @ 15%	0.959	0.989	1.033	0.989	
API	11.5	11.5	5.5	11.5	
Max operating kg/h	470,300	457,070 (69,000 BPSD of 385°C+)	329,460 (48,500 BPSD) @ 800 pen)	457,070 (385°C+ resid)	3,000

Stream up	6	7	8	9	10
Stream identification	Vacuum column inerts exit stream	Vacuum column overhead slop	Condensate water from ejectors	Combined top side cut and heavy V.G.O.	Heavy vacuum gas oil
Normal kg/h	600	2,371		137,900	
BPSD based on standard conditions		407		22,693	
Cut	29 (Av. mol/wt)	218 (Av. mol/wt)	18		
SG @ 15%		0.883			
API		28.7		22.1	20.7
Max operating kg/h	600	2,371	7,710	137,901	

Stream up	11	12	13	14	15
Stream identification	Combined slop cut and vac. resid streams	Asphalt	ATM column botoms to fuel blending	Top circulating reflux	Top cut TBP 370 to 427°C (700 to 800°F)
Normal kg/h	251,565		78,433	174,603	51,279
BPSD based on standard conditions	36,900		11,800		8,593
Cut			371°C+		
SG @ 15%			1.033	0.906	0.906
API	5.5	5.5	5.5	24.6	24.6
Max operating kg/h		11,900	457,000 (385°C+ resid)		51,280

Stream up	16	17	18	19	20
Stream identification	H.G.O. circulating reflux	Heavy vacuum gas oil	Slop cut vacuum column product	Vac. column bottoms recycle	Metals wash out
Normal kg/h	149,206	86,621	5,583	0 to 16,748	8,481
BPSD based on standard conditions		14,100	900	2,700	
Cut					
SG @ 15%	0.930	0.930	0.942	0.948	0.930
API	20.7	20.7	18.7	18.7	20.7
Max operating kg/h		86,621	16,748	16,748	15,964

Fig. 2 Material Balance Associated with the Typical Process Flow Sheet (Fig. 1)

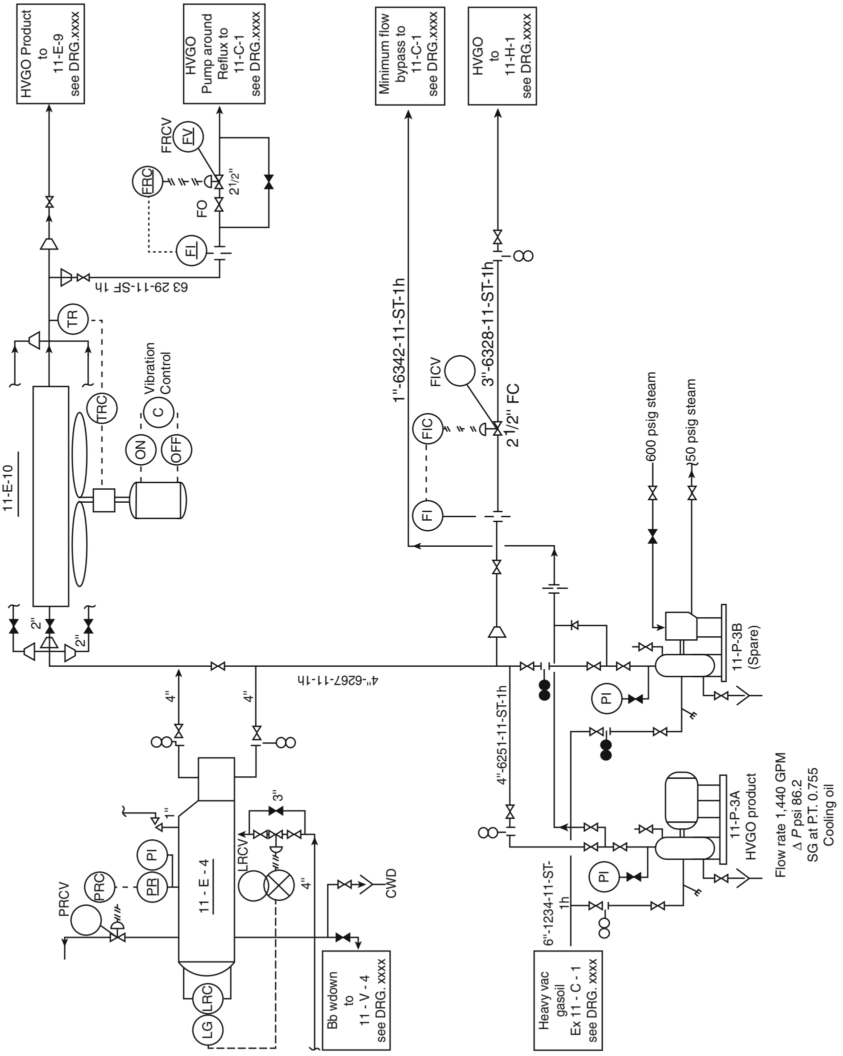


Fig. 3 A Section of a Typical Mechanical Flow Sheet

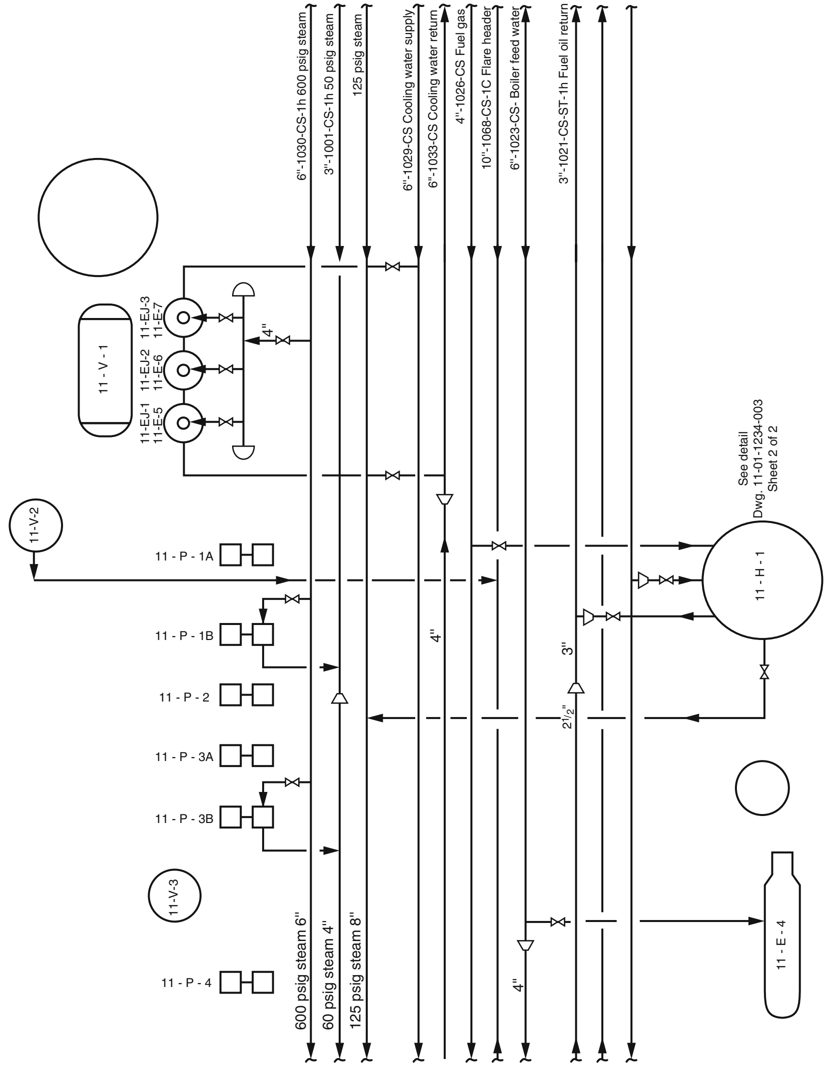


Fig. 4 A Section of a Typical Utility Flow Sheet

General Data for Petroleum Processing

Steven A. Treese

Contents

Abstract

This appendix provides general data for petroleum processing which is used throughout this handbook. Included here are data on (1) viscosity and density/SG of stocks as a function of temperature; (2) relationships for chords, diameters, and areas of circular cross-sections that are used in vessel and tower design; and (3) boiling and freezing points for normal alkanes or paraffins up to a carbon number of 120.

Keywords

Refining • Viscosity • Specific gravity • API gravity • Boiling point • Freezing point • Hydrocarbon • Temperature response

---

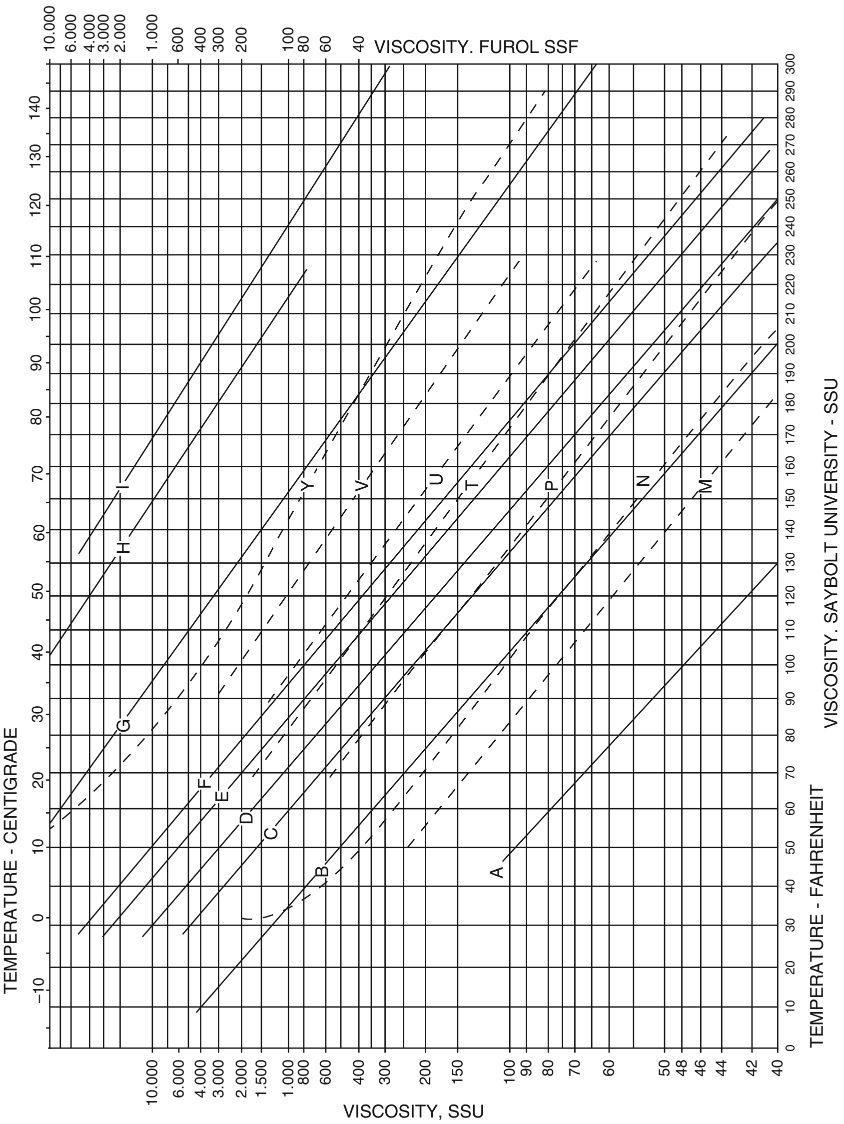
Steven A. Treese has retired from Phillips 66.

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_33

Appendix B: General Reference Data

B1 Hydrocarbon Viscosity Versus Temperature



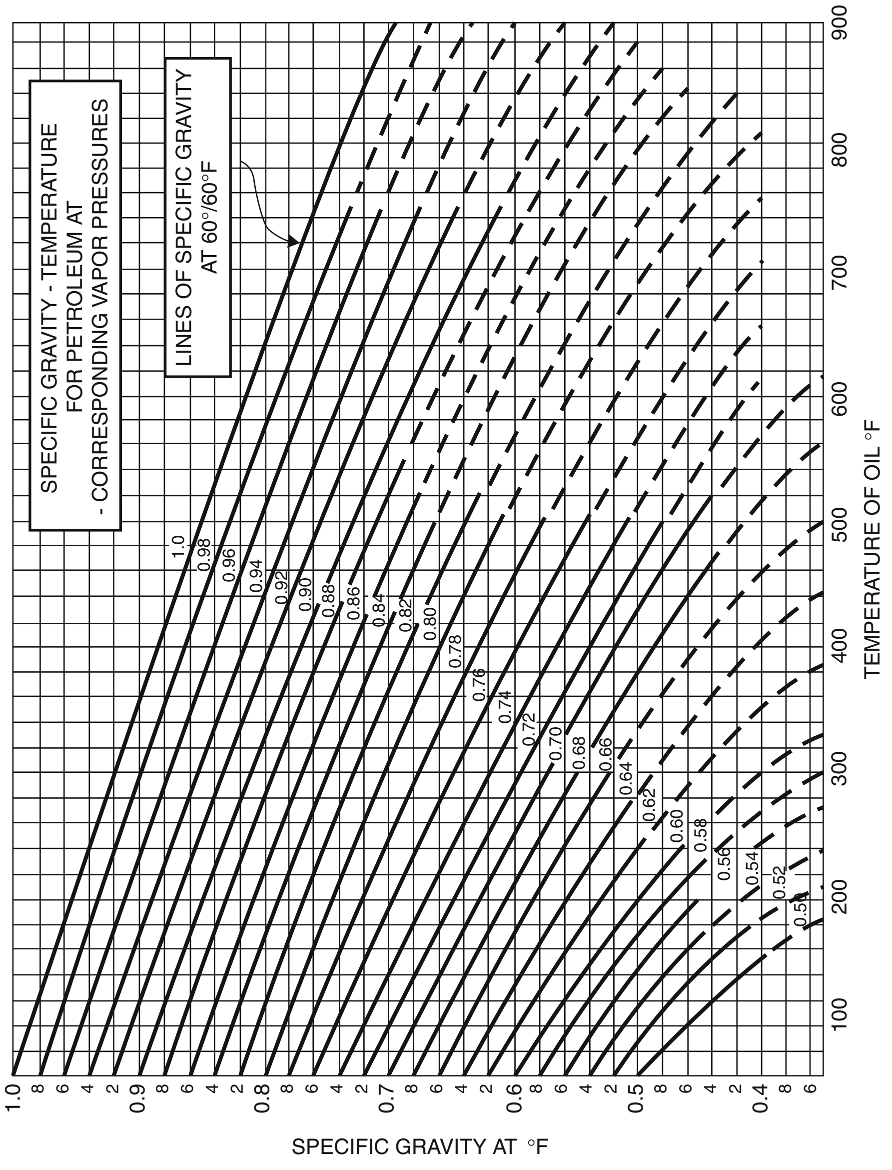
This chart may be used to determine the viscosity of an oil at any temperature provided its viscosity at two temperatures is known.

The lines on this chart show viscosities of representative oils.

Note: This chart is similar to ASTM tentative standard D341-32T which has a somewhat wider viscosity and temperature range.

Courtesy of Texaco, Inc.

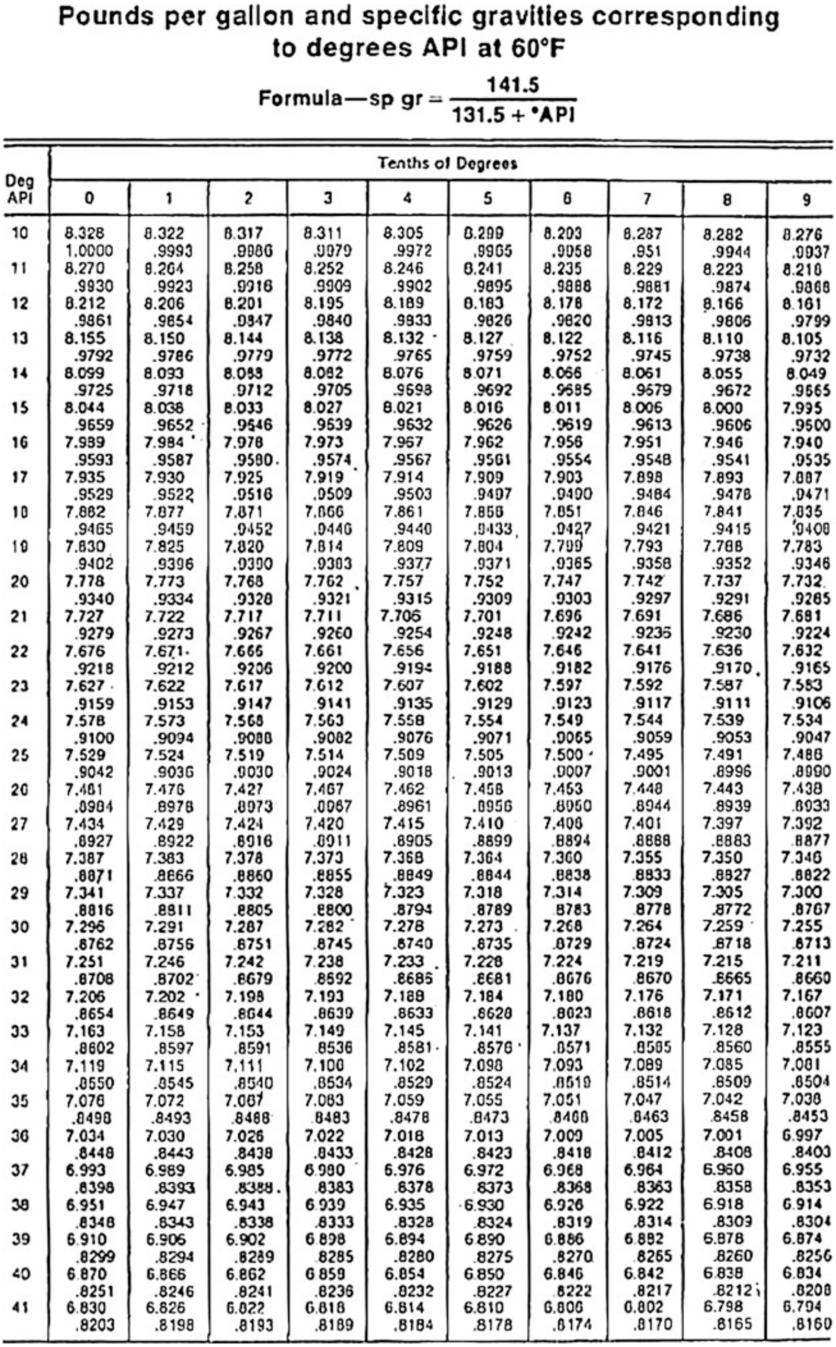
B2 Hydrocarbon Specific Gravity Versus Temperature



Specific Gravity - Referred to water at 60°F
Example: Oil with sp. gr. of 0.82 at 60°F will have sp. gr. of 0.64 at 500°F

Courtesy of Hydraulic Institute.

B3a Relationship of SG, °API, and Lbs/Gal



Pounds per gallon and specific gravities corresponding to degrees API at 60°F

$$\text{Formula—sp gr} = \frac{141.5}{131.5 + °\text{API}}$$

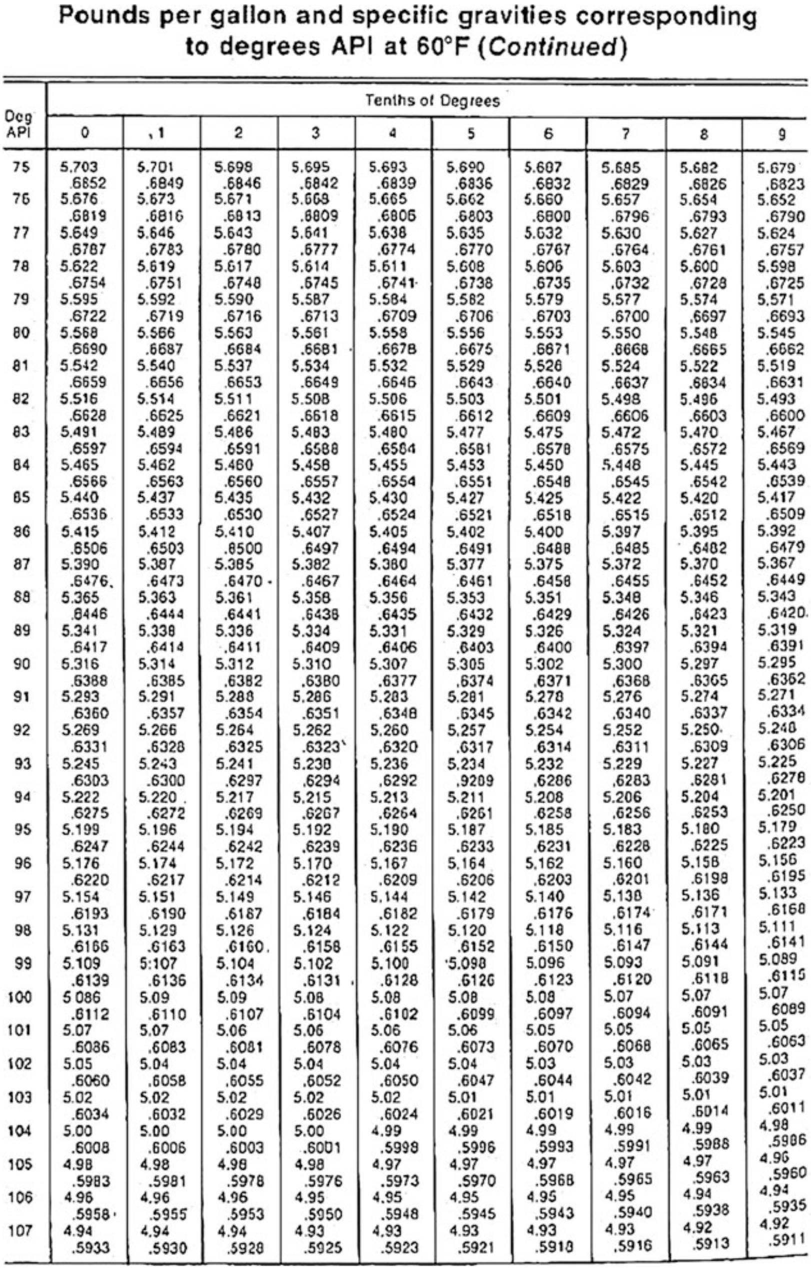
Deg API	Tenths of Degrees									
	0	1	2	3	4	5	6	7	8	9
10	8.328 1.0000	8.322 .9993	8.317 .9986	8.311 .9979	8.305 .9972	8.299 .9965	8.293 .9958	8.287 .951	8.282 .9944	8.276 .9937
11	8.270 .9930	8.264 .9923	8.258 .9916	8.252 .9909	8.246 .9902	8.241 .9895	8.235 .9888	8.229 .9881	8.223 .9874	8.218 .9868
12	8.212 .9861	8.206 .9854	8.201 .9847	8.195 .9840	8.189 .9833	8.183 .9826	8.178 .9820	8.172 .9813	8.166 .9806	8.161 .9799
13	8.155 .9792	8.150 .9786	8.144 .9779	8.138 .9772	8.132 .9765	8.127 .9759	8.122 .9752	8.116 .9745	8.110 .9738	8.105 .9732
14	8.099 .9725	8.093 .9718	8.088 .9712	8.082 .9705	8.076 .9698	8.071 .9692	8.066 .9685	8.061 .9679	8.055 .9672	8.049 .9665
15	8.044 .9659	8.038 .9652	8.033 .9646	8.027 .9639	8.021 .9632	8.016 .9626	8.011 .9619	8.006 .9613	8.000 .9606	7.995 .9600
16	7.989 .9593	7.984 .9587	7.978 .9580	7.973 .9574	7.967 .9567	7.962 .9561	7.956 .9554	7.951 .9548	7.946 .9541	7.940 .9535
17	7.935 .9529	7.930 .9522	7.925 .9516	7.919 .9509	7.914 .9503	7.909 .9497	7.903 .9490	7.898 .9484	7.893 .9478	7.887 .9471
18	7.882 .9465	7.877 .9459	7.871 .9452	7.866 .9446	7.861 .9440	7.856 .9433	7.851 .9427	7.846 .9421	7.841 .9415	7.835 .9408
19	7.830 .9402	7.825 .9396	7.820 .9390	7.814 .9383	7.809 .9377	7.804 .9371	7.799 .9365	7.793 .9358	7.788 .9352	7.783 .9346
20	7.778 .9340	7.773 .9334	7.768 .9328	7.762 .9321	7.757 .9315	7.752 .9309	7.747 .9303	7.742 .9297	7.737 .9291	7.732 .9285
21	7.727 .9279	7.722 .9273	7.717 .9267	7.711 .9260	7.706 .9254	7.701 .9248	7.696 .9242	7.691 .9236	7.686 .9230	7.681 .9224
22	7.676 .9218	7.671 .9212	7.666 .9206	7.661 .9200	7.656 .9194	7.651 .9188	7.646 .9182	7.641 .9176	7.636 .9170	7.632 .9165
23	7.627 .9159	7.622 .9153	7.617 .9147	7.612 .9141	7.607 .9135	7.602 .9129	7.597 .9123	7.592 .9117	7.587 .9111	7.583 .9106
24	7.578 .9100	7.573 .9094	7.568 .9088	7.563 .9082	7.558 .9076	7.554 .9071	7.549 .9065	7.544 .9059	7.539 .9053	7.534 .9047
25	7.529 .9042	7.524 .9036	7.519 .9030	7.514 .9024	7.509 .9018	7.505 .9013	7.500 .9007	7.495 .9001	7.491 .8996	7.486 .8990
26	7.481 .8984	7.476 .8978	7.427 .8973	7.467 .8967	7.462 .8961	7.458 .8956	7.453 .8950	7.448 .8944	7.443 .8939	7.438 .8933
27	7.434 .8927	7.429 .8922	7.424 .8916	7.420 .8911	7.415 .8905	7.410 .8899	7.406 .8894	7.401 .8888	7.397 .8883	7.392 .8877
28	7.387 .8871	7.383 .8866	7.378 .8860	7.373 .8855	7.368 .8849	7.364 .8844	7.360 .8838	7.355 .8833	7.350 .8827	7.346 .8822
29	7.341 .8816	7.337 .8811	7.332 .8805	7.328 .8800	7.323 .8794	7.318 .8789	7.314 .8783	7.309 .8778	7.305 .8772	7.300 .8767
30	7.296 .8762	7.291 .8756	7.287 .8751	7.282 .8745	7.278 .8740	7.273 .8735	7.268 .8729	7.264 .8724	7.259 .8718	7.255 .8713
31	7.251 .8708	7.246 .8702	7.242 .8679	7.238 .8692	7.233 .8685	7.228 .8681	7.224 .8676	7.219 .8670	7.215 .8665	7.211 .8660
32	7.206 .8654	7.202 .8649	7.198 .8644	7.193 .8639	7.188 .8633	7.184 .8628	7.180 .8623	7.176 .8618	7.171 .8612	7.167 .8607
33	7.163 .8602	7.158 .8597	7.153 .8591	7.149 .8536	7.145 .8581	7.141 .8576	7.137 .8571	7.132 .8565	7.128 .8560	7.123 .8555
34	7.119 .8550	7.115 .8545	7.111 .8540	7.106 .8534	7.102 .8529	7.098 .8524	7.093 .8519	7.089 .8514	7.085 .8509	7.081 .8504
35	7.076 .8498	7.072 .8493	7.067 .8488	7.063 .8483	7.059 .8478	7.055 .8473	7.051 .8468	7.047 .8463	7.042 .8458	7.038 .8453
36	7.034 .8448	7.030 .8443	7.026 .8438	7.022 .8433	7.018 .8428	7.013 .8423	7.009 .8418	7.005 .8412	7.001 .8408	6.997 .8403
37	6.993 .8398	6.989 .8393	6.985 .8388	6.980 .8383	6.976 .8378	6.972 .8373	6.968 .8368	6.964 .8363	6.960 .8358	6.955 .8353
38	6.951 .8348	6.947 .8343	6.943 .8338	6.939 .8333	6.935 .8328	6.930 .8324	6.926 .8319	6.922 .8314	6.918 .8309	6.914 .8304
39	6.910 .8299	6.906 .8294	6.902 .8289	6.898 .8285	6.894 .8280	6.890 .8275	6.886 .8270	6.882 .8265	6.878 .8260	6.874 .8256
40	6.870 .8251	6.866 .8246	6.862 .8241	6.859 .8236	6.854 .8232	6.850 .8227	6.846 .8222	6.842 .8217	6.838 .8212	6.834 .8208
41	6.830 .8203	6.826 .8198	6.822 .8193	6.818 .8189	6.814 .8184	6.810 .8178	6.806 .8174	6.802 .8170	6.798 .8165	6.794 .8160

(*continued*)

Pounds per gallon and specific gravities corresponding to degrees API at 60°F (*Continued*)

Deg API	Tenths of Degrees									
	0	1	2	3	4	5	6	7	8	9
42	6.790 .8155	6.786 .8151	6.782 .8146	6.779 .8142	6.775 .8137	6.771 .8132	6.767 .8128	6.763 .8123	6.759 .8118	6.756 .8114
43	6.752 .8109	6.748 .8104	6.744 .8100	6.740 .8095	6.736 .8090	6.732 .8086	6.728 .8081	6.724 .8076	6.720 .8072	6.716 .8067
44	6.713 .8063	6.709 .8058	6.705 .8054	6.701 .8049	6.697 .8044	6.694 .8040	6.690 .8035	6.686 .8031	6.682 .8026	6.679 .8022
45	6.675 .8017	6.671 .8012	6.667 .8008	6.663 .8003	6.660 .7999	6.656 .7994	6.652 .7990	6.648 .7985	6.645 .7981	6.641 .7976
46	6.637 .7972	6.633 .7967	6.630 .7963	6.626 .7958	6.622 .7954	6.618 .7949	6.615 .7945	6.611 .7941	6.607 .7936	6.604 .7932
47	6.600 .7927	6.596 .7923	6.592 .7918	6.589 .7914	6.585 .7909	6.582 .7905	6.578 .7901	6.574 .7896	6.571 .7892	6.567 .7887
48	6.563 .7883	6.560 .7879	6.556 .7874	6.552 .7870	6.548 .7865	6.545 .7861	6.541 .7857	6.537 .7852	6.534 .7848	6.530 .7844
49	6.526 .7839	6.523 .7835	6.520 .7831	6.516 .7826	6.512 .7822	6.509 .7818	6.505 .7813	6.501 .7809	6.498 7805	6.494 .7800
50	6.490 .7796	6.487 .7792	6.484 .7788	6.480 .7783	6.476 .7779	6.473 .7775	6.469 .7770	6.466 .7766	6.462 .7762	6.459 .7758
51	6.455 .7753	6.451 .7749	6.448 .7745	6.445 .7741	6.441 .7736	6.437 .7732	6.434 .7728	6.430 .7724	6.427 .7720	6.423 .7715
52	6.420 .7711	6.416 .7707	6.413 .7703	6.410 .7699	6.406 .7694	6.402 .7690	6.399 .7686	6.396 .7682	6.392 .7678	6.389 .7674
53	6.385 .7669	6.381 .7665	6.378 .7661	6.375 .7657	6.371 .7653	6.368 .7649	6.365 .7645	6.360 .7640	6.357 .7636	6.354 .7632
54	6.350 .7628	6.347 .7624	6.344 .7620	6.340 .7616	6.337 .7612	6.334 .7608	6.330 .7603	6.326 .7599	6.323 .7595	6.320 .7591
55	6.316 .7587	6.313 .7583	6.310 .7579	6.306 .7575	6.303 .7571	6.300 .7567	6.296 .7563	6.293 .7559	6.290 .7555	6.287 .7551
56	6.283 .7547	6.280 .7543	6.276 .7539	6.273 .7535	6.270 .7531	6.266 .7527	6.263 .7523	6.259 .7519	6.256 .7515	6.253 .7511
57	6.249 .7507	6.246 .7503	6.243 .7499	6.240 .7495	6.236 .7491	6.233 .7487	6.229 .7483	6.226 .7479	6.223 .7475	6.219 .7471
58	6.216 .7467	6.213 .7463	6.209 .7459	6.206 .7455	6.203 .7451	6.199 .7447	6.196 .7443	6.193 .7440	6.190 .7436	6.187 .7432
59	6.184 .7428	6.180 .7424	6.177 .7420	6.174 .7416	6.170 .7412	6.167 .7408	6.164 .7405	6.161 .7401	6.158 .7397	6.154 .7393
60	6.151 .7389	6.148 .7385	6.144 .7381	6.141 .7377	6.138 .7374	6.135 .7370	6.132 .7366	6.129 .7362	6.125 .7358	6.122 .7354
61	6.119 .7351	6.116 .7347	6.113 .7343	6.109 .7339	6.106 .7335	6.103 .7332	6.100 .7328	6.097 .7324	6.094 .7320	6.090 .7316
62	6.087 .7313	6.084 .7309	6.081 .7305	6.078 .7301	6.075 .7298	6.072 .7294	6.068 .7290	6.065 .7286	6.062 .7283	6.059 .7279
63	6.056 .7275	6.053 .7271	6.050 .7268	6.047 .7264	6.044 .7260	6.040 .7256	6.037 .7253	6.034 .7249	6.031 .7245	6.028 .7242
64	6.025 .7238	6.022 .7234	6.019 .7230	6.016 .7227	6.013 .7223	6.010 .7219	6.007 .7216	6.004 .7212	6.000 .7208	5.997 .7205
65	5.994 .7201	5.991 .7197	5.988 .7194	5.985 .7190	5.982 .7186	5.979 .7183	5.976 .7179	5.973 .7175	5.970 .7172	5.967 .7168
66	5.964 .7165	5.961 .7161	5.958 .7157	5.955 .7154	5.952 .7150	5.949 .7146	5.946 .7143	5.943 .7139	5.940 .7136	5.937 .7132
67	5.934 .7128	5.931 .7125	5.928 .7121	5.925 .7118	5.922 .7114	5.919 .7111	5.916 .7107	5.913 .7013	5.910 .7100	5.907 .7096
68	5.904 .7093	5.901 .7089	5.898 .7086	5.895 .7082	5.892 .7079	5.889 .7075	5.886 .7071	5.883 .7068	5.880 .7064	5.877 .7061
69	5.874 .7057	5.871 .7054	5.868 .7050	5.866 .7047	5.863 .7043	5.860 .7040	5.857 .7036	5.854 .7033	5.851 .7029	5.848 .7026
70	5.845 .7022	5.842 .7019	5.839 .7015	5.836 .7012	5.833 .7008	5.831 .7005	5.828 .7001	5.825 6998	5.823 .6995	5.820 .6991
71	5.817 6988	5.814 .6984	5.811 .6981	5.808 6977	5.805 .6974	5.802 .6970	5.799 .6967	5.796 .6964	5.793 .6960	5.791 .6957
72	5.788 6952	5.785 .6950	5.782 .6946	5.779 .6943	5.776 6940	5.773 .6935	5.771 .6933	5.768 .6929	5.765 .6926	5.762 6923
73	5.759 .6919	5.757 .6916	5.754 .6913	5.751 .6909	5.748 .6906	5.745 .6902	5.743 .6899	5.740 .6896	5.737 .6892	5.734 .6889
74	5.731 .6886	5.728 .6882	5.726 .6879	5.723 .6876	5.720 .6872	5.718 .6869	5.715 .6866	5.712 .6862	5.709 .6859	5.706 .6856

B3b Relationship of SG, °API, and Lbs/Gal



Pounds per gallon and specific gravities corresponding to degrees API at 60°F (*Continued*)

Deg API	Tenths of Degrees									
	0	.1	2	3	4	5	6	7	8	9
75	5.703 .6852	5.701 .6849	5.698 .6846	5.695 .6842	5.693 .6839	5.690 .6836	5.607 .6832	5.685 .6829	5.682 .6826	5.679 .6823
76	5.676 .6819	5.673 .6816	5.671 .6813	5.668 .6809	5.665 .6806	5.662 .6803	5.660 .6800	5.657 .6796	5.654 .6793	5.652 .6790
77	5.649 .6787	5.646 .6783	5.643 .6780	5.641 .6777	5.638 .6774	5.635 .6770	5.632 .6767	5.630 .6764	5.627 .6761	5.624 .6757
78	5.622 .6754	5.619 .6751	5.617 .6748	5.614 .6745	5.611 .6741	5.608 .6738	5.606 .6735	5.603 .6732	5.600 .6728	5.598 .6725
79	5.595 .6722	5.592 .6719	5.590 .6716	5.587 .6713	5.584 .6709	5.582 .6706	5.579 .6703	5.577 .6700	5.574 .6697	5.571 .6693
80	5.568 .6690	5.566 .6687	5.563 .6684	5.561 .6681	5.558 .6678	5.556 .6675	5.553 .6671	5.550 .6668	5.548 .6665	5.545 .6662
81	5.542 .6659	5.540 .6656	5.537 .6653	5.534 .6649	5.532 .6646	5.529 .6643	5.526 .6640	5.524 .6637	5.522 .6634	5.519 .6631
82	5.516 .6628	5.514 .6625	5.511 .6621	5.508 .6618	5.506 .6615	5.503 .6612	5.501 .6609	5.498 .6606	5.496 .6603	5.493 .6600
83	5.491 .6597	5.489 .6594	5.486 .6591	5.483 .6588	5.480 .6584	5.477 .6581	5.475 .6578	5.472 .6575	5.470 .6572	5.467 .6569
84	5.465 .6566	5.462 .6563	5.460 .6560	5.458 .6557	5.455 .6554	5.453 .6551	5.450 .6548	5.448 .6545	5.445 .6542	5.443 .6539
85	5.440 .6536	5.437 .6533	5.435 .6530	5.432 .6527	5.430 .6524	5.427 .6521	5.425 .6518	5.422 .6515	5.420 .6512	5.417 .6509
86	5.415 .6506	5.412 .6503	5.410 .6500	5.407 .6497	5.405 .6494	5.402 .6491	5.400 .6488	5.397 .6485	5.395 .6482	5.392 .6479
87	5.390 .6476	5.387 .6473	5.385 .6470	5.382 .6467	5.380 .6464	5.377 .6461	5.375 .6458	5.372 .6455	5.370 .6452	5.367 .6449
88	5.365 .6446	5.363 .6444	5.361 .6441	5.358 .6438	5.356 .6435	5.353 .6432	5.351 .6429	5.348 .6426	5.346 .6423	5.343 .6420
89	5.341 .6417	5.338 .6414	5.336 .6411	5.334 .6409	5.331 .6406	5.329 .6403	5.326 .6400	5.324 .6397	5.321 .6394	5.319 .6391
90	5.316 .6388	5.314 .6385	5.312 .6382	5.310 .6380	5.307 .6377	5.305 .6374	5.302 .6371	5.300 .6368	5.297 .6365	5.295 .6362
91	5.293 .6360	5.291 .6357	5.288 .6354	5.286 .6351	5.283 .6348	5.281 .6345	5.278 .6342	5.276 .6340	5.274 .6337	5.271 .6334
92	5.269 .6331	5.266 .6328	5.264 .6325	5.262 .6323	5.260 .6320	5.257 .6317	5.254 .6314	5.252 .6311	5.250 .6309	5.248 .6306
93	5.245 .6303	5.243 .6300	5.241 .6297	5.238 .6294	5.236 .6292	5.234 .9209	5.232 .6286	5.229 .6283	5.227 .6281	5.225 .6278
94	5.222 .6275	5.220 .6272	5.217 .6269	5.215 .6267	5.213 .6264	5.211 .6261	5.208 .6258	5.206 .6256	5.204 .6253	5.201 .6250
95	5.199 .6247	5.196 .6244	5.194 .6242	5.192 .6239	5.190 .6236	5.187 .6233	5.185 .6231	5.183 .6228	5.180 .6225	5.179 .6223
96	5.176 .6220	5.174 .6217	5.172 .6214	5.170 .6212	5.167 .6209	5.164 .6206	5.162 .6203	5.160 .6201	5.158 .6198	5.156 .6195
97	5.154 .6193	5.151 .6190	5.149 .6187	5.146 .6184	5.144 .6182	5.142 .6179	5.140 .6176	5.138 .6174	5.136 .6171	5.133 .6168
98	5.131 .6166	5.129 .6163	5.126 .6160	5.124 .6158	5.122 .6155	5.120 .6152	5.118 .6150	5.116 .6147	5.113 .6144	5.111 .6141
99	5.109 .6139	5:107 .6136	5.104 .6134	5.102 .6131	5.100 .6128	5.098 .6126	5.096 .6123	5.093 .6120	5.091 .6118	5.089 .6115
100	5 086 .6112	5.09 .6110	5.09 .6107	5.08 .6104	5.08 .6102	5.08 .6099	5.08 .6097	5.07 .6094	5.07 .6091	5.07 6089
101	5.07 .6086	5.07 .6083	5.06 .6081	5.06 .6078	5.06 .6076	5.06 .6073	5.05 .6070	5.05 .6068	5.05 .6065	5.05 .6063
102	5.05 .6060	5.04 .6058	5.04 .6055	5.04 .6052	5.04 .6050	5.04 .6047	5.03 .6044	5.03 .6042	5.03 .6039	5.03 .6037
103	5.02 .6034	5.02 .6032	5.02 .6029	5.02 .6026	5.02 .6024	5.01 .6021	5.01 .6019	5.01 .6016	5.01 .6014	5.01 .6011
104	5.00 .6008	5.00 .6006	5.00 .6003	5.00 .6001	4.99 .5998	4.99 .5996	4.99 .5993	4.99 .5991	4.99 .5988	4.98 .5986
105	4.98 .5983	4.98 .5981	4.98 .5978	4.98 .5976	4.97 .5973	4.97 .5970	4.97 .5968	4.97 .5965	4.97 .5963	4.96 .5960
106	4.96 .5958	4.96 .5955	4.96 .5953	4.95 .5950	4.95 .5948	4.95 .5945	4.95 .5943	4.95 .5940	4.94 .5938	4.94 .5935
107	4.94 .5933	4.94 .5930	4.94 .5928	4.93 .5925	4.93 .5923	4.93 .5921	4.93 .5918	4.93 .5916	4.92 .5913	4.92 .5911

(*continued*)

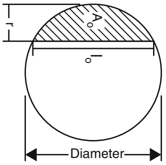
Pounds per gallon and specific gravities corresponding to degrees API at 60°F (*Continued*)

Deg API	Tenths of Degrees 0	1	2	3	4	5	6	7	8	9
108	4.92 .5908	4.92 .5906	4.92 .5903	4.91 .5901	4.91 .5898	4.91 .5896	4.91 .5893	4.91 .5891	4.90 .5888	4.90 .5886
109	4.90 .5884	4.90 .5881	4.90 .5879	4.89 .5876	4.89 .5874	4.89 .5871	4.89 .5869	4.89 .5867	4.88 .5864	4.88 .5862
110	4.88 .5859	4.88 .5857	4.87 .5854	4.87 .5852	4.87 .5850	4.87 .5847	4.87 .5845	4.86 .5842	4.86 .5840	4.86 .5837
111	4.86 .5835	4.86 .5833	4.85 .5830	4.85 .5828	4.85 .5825	4.85 .5823	4.85 .5821	4.84 .5818	4.84 .5816	4.84 .5813
112	4.84 .5811	4.84 .5909	4.83 .5806	4.83 .5804	4.83 .5802	4.83 .5799	4.83 .5797	4.82 .5794	4.82 .5792	4.82 .5790
113	4.82 .5787	4.82 .5785	4.82 .5783	4.81 .5780	4.81 .5778	4.81 .5776	4.81 .5773	4.81 .5771	4.80 .5768	4.80 .5766
114	4.80 .5764	4.80 .5761	4.80 .5759	4.79 .5757	4.79 .5754	4.79 .5752	4.79 .5750	4.79 .5747	4.78 .5745	4.78 .5743
115	4.78 .5740	4.78 .5738	4.78 .5736	4.77 .5733	4.77 .5731	4.77 .5729	4.77 .5726	4.77 .5724	4.76 .5722	4.76 .5719
116	4.76 .5717	4.76 .5715	4.76 .5713	4.76 .5710	4.75 .5708	4.75 .5706	4.75 .5703	4.75 .5701	4.75 .5699	4.74 .5696
117	4.74 .5694	4.74 .5692	4.74 .5690	4.74 .5687	4.73 .5685	4.73 .5683	4.73 .5680	4.73 .5678	4.73 .5676	4.73 .5674
118	4.72 .5671	4.72 .5669	4.72 .5667	4.72 .5665	4.72 .5662	4.71 .5660	4.71 .5658	4.71 .5655	4.71 .5653	4.71 .5651
119	4.70 .5649	4.70 .5646	4.70 .5644	4.70 .5642	4.70 .5640	4.69 .5637	4.69 .5635	4.69 .5633	4.69 .5631	4.69 .5628
120	4.69 .5626	4.68 .5624	4.68 .5622	4.68 .5620	4.68 .5617	4.68 .5615	4.67 .5613	4.67 .5611	4.67 .5608	4.67 .5606
121	4.67 .5604	4.67 .5602	4.66 .5600	4.66 .5597	4.66 .5595	4.66 .5593	4.66 .5591	4.65 .5588	4.65 .5586	4.65 .5584
122	4.65 .5582	4.65 .5580	4.64 .5577	4.64 .5575	4.64 .5573	4.64 .5571	4.64 .5569	4.64 .5566	4.63 .5564	4.63 .5562
123	4.63 .5560	4.63 .5558	4.63 .5556	4.62 .5553	4.62 .5551	4.62 .5549	4.62 .5547	4.62 .5545	4.62 .5542	4.61 .5540
124	4.61 .5538	4.61 .5536	4.61 .5534	4.61 .5532	4.61 .5530	4.60 .5527	4.60 .5525	4.60 .5523	4.60 .5521	4.60 .5519
125	4.59 .5517	4.59 .5514	4.59 .5512	4.59 .5510	4.59 .5508	4.59 .5506	4.58 .5504	4.58 .5502	4.58 .5499	4.58 .5497
126	4.58 .5495	4.57 .5493	4.57 .5491	4.57 .5489	4.57 .5487	4.57 .5484	4.57 .5482	4.56 .5480	4.56 .5478	4.56 .5476
127	4.56 .5474	4.56 .5472	4.56 .5470	4.55 .5468	4.55 .5465	4.55 .5463	4.55 .5461	4.55 .5459	4.54 .5457	4.54 .5455
128	4.54 .5453	4.54 .5451	4.54 .5449	4.54 .5446	4.53 .5444	4.53 .5442	4.53 .5440	4.53 .5438	4.53 .5436	4.53 .5434
129	4.52 .5432	4.52 .5430	4.52 .5428	4.52 .5426	4.52 .5424	4.51 .5421	4.51 .5419	4.51 .5417	4.51 .5415	4.51 .5413
130	4.51 .5411	4.50 .5409	4.50 .5407	4.50 .5405	4.50 .5403	4.50 .5401	4.50 .5399	4.49 .5397	4.49 .5395	4.49 .5393
131	4.49 .5390	4.49 .5388	4.49 .5386	4.48 .5384	4.48 .5382	4.48 .5380	4.48 .5378	4.48 .5376	4.48 .5374	4.47 .5372
132	4.47 .5370	4.47 .5368	4.47 .5366	4.47 .5364	4.47 .5362	4.46 .5360	4.46 .5358	4.46 .5356	4.46 .5354	4.46 .5352
133	4.46 .5350	4.45 .5348	4.45 .5346	4.45 .5344	4.45 .5342	4.45 .5340	4.45 .5338	4.44 .5336	4.44 .5334	4.44 .5332
134	4.44 .5330	4.44 .5328	4.44 .5326	4.43 .5324	4.43 .5322	4.43 .5320	4.43 .5318	4.43 .5316	4.43 .5314	4.42 .5312
135	4.42 .5310	4.42 .5308	4.42 .5306	4.42 .5304	4.42 .5302	4.41 .5300	4.41 .5298	4.41 .5296	4.41 .5294	4.41 .5292
136	4.41 .5290	4.40 .5288	4.40 .5286	4.40 .5284	4.40 .5282	4.40 .5280	4.40 .5278	4.39 .5276	4.39 .5274	4.39 .5272
137	4.39 .5270	4.39 .5268	4.39 .5266	4.38 .5264	4.38 .5262	4.38 .5260	4.38 .5258	4.38 .5256	4.38 .5254	4.37 .5252
138	4.37 .5250	4.37 .5249	4.37 .5247	4.37 .5245	4.37 .5243	4.36 .5241	4.36 .5239	4.36 .5237	4.36 .5235	4.36 .5233
139	4.36 .5231	4.35 .5229	4.35 .5227	4.35 .5225	4.35 .5223	4.35 .5221	4.35 .5219	4.35 .5218	4.34 .5216	4.34 .5214

B4 Relationship of Chords, Diameters, and Areas

*R**	*L**	*A**	*R**	*L**	*A**	*R**	*L**	*A**	*R**	*L**	*A**	*R**	*L**	*A**	*R**	*L**	*A**
0.070	0.511	0.0308	0.120	0.650	0.0680	0.170	0.751	0.113	0.220	0.828	0.163	0.280	0.898	0.230	0.390	0.977	0.361
1	0.514	0.0315	1	0.652	0.0688	1	0.753	0.114	1	0.829	0.164	5	0.903	0.236	5	0.979	0.367
2	0.517	0.0321	2	0.654	0.0697	2	0.755	0.115	2	0.831	0.165						
3	0.521	0.0328	3	0.657	0.0705	3	0.756	0.116	3	0.832	0.166	0.290	0.908	0.241	0.400	0.980	0.374
4	0.524	0.0335	4	0.659	0.0714	4	0.758	0.117	4	0.834	0.167	5	0.913	0.247	5	0.982	0.380
5	0.527	0.0342	5	0.661	0.0722	5	0.760	0.117	5	0.835	0.169	0.300	0.917	0.252	0.410	0.984	0.386
6	0.530	0.0348	6	0.663	0.0731	6	0.762	0.118	6	0.836	0.170	5	0.921	0.258	5	0.986	0.392
7	0.533	0.0355	7	0.665	0.0739	7	0.763	0.119	7	0.838	0.171						
8	0.536	0.0362	8	0.668	0.0748	8	0.765	0.120	8	0.839	0.172	0.310	0.925	0.264	0.420	0.987	0.398
9	0.539	0.0368	9	0.670	0.0756	9	0.786	0.121	9	0.841	0.173	5	0.930	0.270	5	0.989	0.405
0.080	0.542	0.0375	0.130	0.672	0.0765	0.180	0.768	0.122	0.230	0.842	0.174	0.320	0.933	0.276	0.430	0.991	0.412
1	0.545	0.0382	1	0.674	0.0774	1	0.770	0.123	1	0.843	0.175	5	0.937	0.282	5	0.993	0.418
2	0.548	0.0389	2	0.677	0.0782	2	0.772	0.124	2	0.845	0.176						
3	0.552	0.0396	3	0.679	0.0791	3	0.773	0.125	3	0.846	0.177	0.330	0.941	0.288	0.440	0.994	0.424
4	0.555	0.0403	4	0.682	0.0799	4	0.775	0.126	4	0.848	0.178	5	0.945	0.294	5	0.995	0.430
5	0.558	0.0410	5	0.684	0.0808	5	0.777	0.127	5	0.849	0.179	0.340	0.948	0.300	0.450	0.996	0.437
6	0.561	0.0418	6	0.686	0.0817	6	0.778	0.128	6	0.850	0.180	5	0.951	0.306			
7	0.564	0.0425	7	0.688	0.825	7	0.780	0.129	7	0.851	0.181				0.460	0.997	0.450
8	0.567	0.0432	8	0.691	0.0834	8	0.781	0.130	8	0.853	0.182	0.350	0.955	0.312			
9	0.570	0.0439	9	0.693	0.0842	9	0.783	0.131	9	0.854	0.183	5	0.958	0.318	0.470	0.998	0.462
0.090	0.573	0.0446	0.140	0.695	0.0851	0.190	0.784	0.132	0.240	0.855	0.184	0.360	0.961	0.324	0.480	0.998	0.475
1	0.576	0.0454	1	0.697	0.0860	1	0.786	0.133	5	0.860	0.190	5	0.964	0.330			
2	0.578	0.0461	2	0.699	0.0869	2	0.787	0.134							0.490	0.999	0.488
3	0.581	0.0469	3	0.700	0.0878	3	0.789	0.135	0.250	0.866	0.196	0.370	0.967	0.337			
4	0.583	0.0476	4	0.702	0.0887	4	0.790	0.136	5	0.872	0.202	5	0.969	0.343	0.500	1.0	0.50
5	0.586	0.0484	5	0.704	0.0896	5	0.792	0.137	0.260	0.878	0.207	0.380	0.971	0.348			
6	0.589	0.0491	6	0.706	0.0905	6	0.794	0.138	5	0.883	0.213	5	0.977	0.354			
7	0.592	0.0499	7	0.708	0.0914	7	0.795	0.139									
8	0.594	0.0506	8	0.710	0.0923	8	0.797	0.140	0.270	0.888	0.218						
9	0.597	0.0514	9	0.712	0.0932	9	0.798	0.141	5	0.893	0.224						
0.100	0.600	0.0521	0.150	0.714	0.0941	0.200	0.800	0.142									
1	0.603	0.0529	1	0.716	0.0950	1	0.802	0.143									
2	0.605	0.0537	2	0.718	0.0959	2	0.803	0.144									
3	0.608	0.0545	3	0.720	0.0969	3	0.805	0.145									
4	0.610	0.0555	4	0.722	0.0978	4	0.806	0.146									
5	0.613	0.0561	5	0.724	0.0987	5	0.808	0.148									
6	0.615	0.0568	6	0.726	0.0996	6	0.809	0.149									
7	0.618	0.0576	7	0.728	0.1005	7	0.810	0.150									
8	0.620	0.0584	8	0.729	0.1015	8	0.812	0.151									
9	0.623	0.0592	9	0.731	0.102	9	0.813	0.152									
0.110	0.625	0.0600	0.160	0.733	0.103	0.210	0.814	0.153									
1	0.628	0.0608	1	0.735	0.104	1	0.816	0.154									
2	0.630	0.0616	2	0.737	0.105	2	0.817	0.155									
3	0.633	0.0624	3	0.738	0.106	3	0.819	0.156									
4	0.635	0.0632	4	0.740	0.107	4	0.820	0.157									
5	0.638	0.0640	5	0.742	0.108	5	0.822	0.158									
6	0.640	0.0648	6	0.744	0.109	6	0.823	0.159									
7	0.643	0.0656	7	0.746	0.110	7	0.824	0.160									
8	0.645	0.0664	8	0.747	0.111	8	0.826	0.161									
9	0.648	0.0672	9	0.749	0.112	9	0.827	0.162									

* This table relates the downcomer area, the weir length, and the height of the circular segment formed by the weir



$$R = \frac{\text{*Downcomer rise}}{\text{Diameter}} = \frac{r}{\text{Dia}} \qquad L = \frac{\text{*Weir length}}{\text{Diameter}} = \frac{l_o}{\text{Dia}} \qquad A = \frac{\text{*Downcomer area}}{\text{Tower area}} = \frac{A_D}{A_S}$$

B5 Boiling and Freezing Points of Normal Alkanes (Paraffins)

Carbon number	Boiling point °C	Boiling point °F	Freeze point °C	Freeze point °F
3	−42	−44		
4	0	32	−138	−216
5	36	97	−129	−201
6	69	156	−96	−140

(*continued*)

Carbon number	Boiling point		Freeze point	
	°C	°F	°C	°F
7	98	209	−91	−131
8	126	259	−57	−70
9	151	303	−53	−64
10	174	345	−29	−21
11	196	385	−25	−13
12	216	421	−9	15
13	235	455	−6	22
14	254	489	6	43
15	271	520	10	50
16	287	549	18	64
17	302	576	22	72
18	316	601	28	82
19	330	626	32	90
20	344	651	37	98
21	363	685	40	104
22	369	696	44	111
23	380	716	47	117
24	391	736	51	124
26	412	774		
28	431	808		
30	449	840		
32	466	871		
34	481	898		
36	496	925		
38	509	948		
40	522	972		
42	534	993		
44	545	1,013		
46	556	1,033		
48	566	1,051		
50	575	1,067		
52	584	1,083		
54	592	1,098		
56	600	1,112		
58	608	1,126		
60	615	1,139		
62	622	1,152		
64	629	1,164		
66	635	1,175		
68	641	1,186		
70	647	1,197		
72	653	1,207		
74	658	1,216		

(*continued*)

Carbon number	Boiling point		Freeze point	
	°C	°F	°C	°F
76	664	1,227		
78	670	1,238		
80	675	1,247		
82	681	1,258		
84	686	1,267		
86	691	1,276		
88	695	1,283		
90	700	1,292		
92	704	1,299		
94	708	1,306		
96	712	1,314		
98	716	1,321		
100	720	1,328		
110	735	1,355		
120	750	1,382		

Selection of Crude Oil Assays for Petroleum Refining

Steven A. Treese

Contents

Abstract

This appendix provides a selection of several simple crude assays for stocks worldwide. It is intended to illustrate the range of variability and typical assay values. Caution: For final studies and definitive engineering, up-to-date assays from the crude oil suppliers should be used. The assays here are believed to be from reliable public sources, but they should be used only for informational purposes.

Keywords

Crude oil • Assay • Petroleum

Steven A. Treese has retired from Phillips 66.

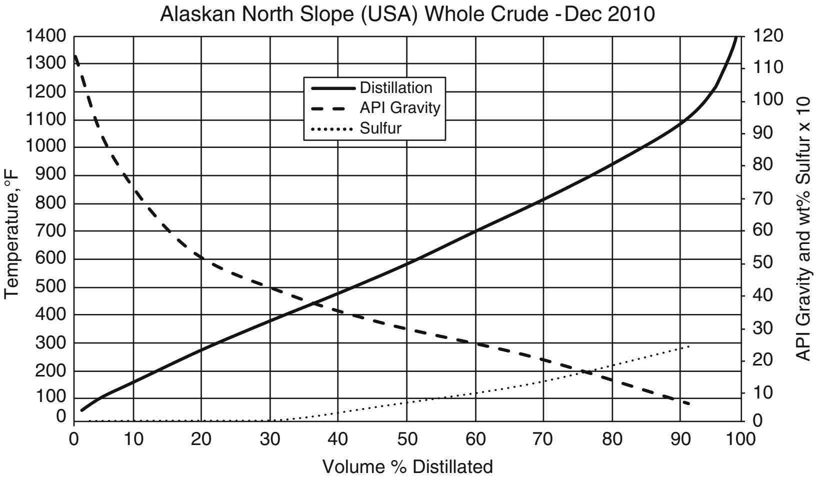
S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_34

Appendix C: A Selection of Crude Assays

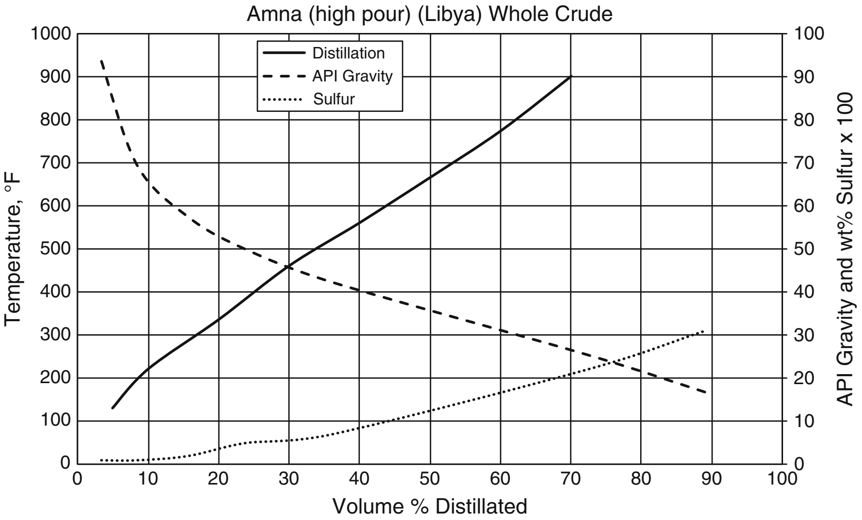
Alaskan North Slope, USA **Dec-10**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Diesel/Lt. Gasoil	Vacuum Gasoil	Vac Residuum
TBP Range, °F	-----	C_4–Minus	C_5–165	165-330	330-480	480-650	650-1000	1000+
Yield, v%	100.0	2.5	8.0	14.1	14.1	16.0	27.1	18.3
Yield, w%	100.0	1.7	6.1	12.4	13.4	16.1	29.0	21.4
Gravity, °API	32.1	113.7	83.77	55.02	41.1	31.4	21.2	6.9
Sulfur, w%	0.93		0.001	0.0107	0.0929	0.5304	1.21	2.34
Nitrogen, wppm	1490		0.01	0.15	1.1	75	1307	6322
CCR, w%	4.38					0	0.5	21.8
Viscosity	12.2 cSt @ 68°F	0.35 cSt @ 68°F	0.39 cSt @ 68°F	0.71 cSt @ 68°F	1.81 cSt @ 68°F	7.57 cSt @ 68°F	286 cSt @ 68°F	
Pour Point, °F	–3				–69	–2	88	121
TAN, mg/g	0.2					0.13	0.34	0.18
Ni, wppm	11					0	0	52
V, wppm	24.8					0	0	119
Paraffins, v%		100	85	43	36	32	19	
Naphthenes, v%		0	14	43	43	37	35	
Aromatics, v%		0	1	14	21	31	46	
RON Clear			71	38				
Freeze Point, °F					–52	14		
Aniline Point, °F					130	148	174	
Cetane Index	30	113	51	29	40	48		
Cloud Point, °F					–60	7		
Smoke Point, mm					22			



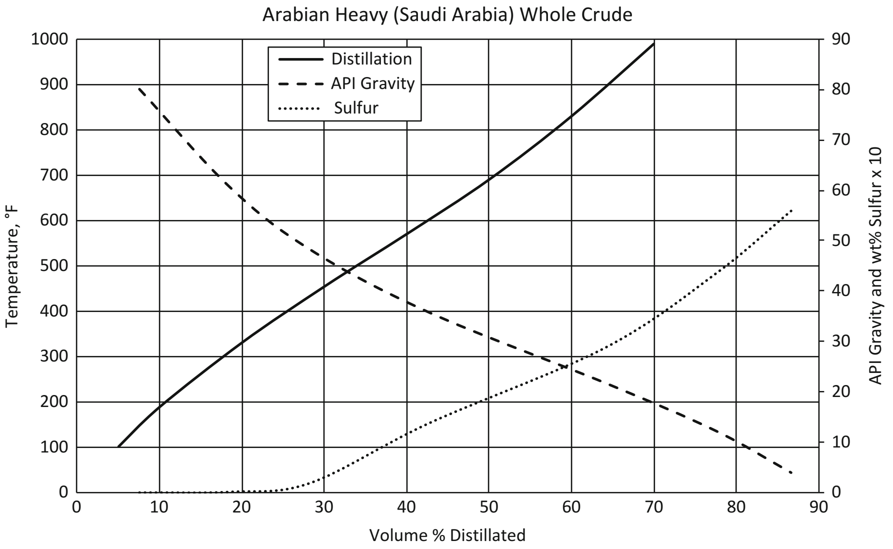
Amna (high pour), Libya **Source: O&GJ**

Cut	Whole Crude	Light Naphtha	Light Naphtha	Heavy Naphtha	Kerosene	Diesel/Lt. Gasoil	Vacuum Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	C_5-120	120-250	250-330	330-443	443-600	600-850	655+	1000+
Yield, v%	100.0	2.4	7.7	6.9	9.4	15.0	23.3	55.4	21.8
Gravity, °API	36.1	93.6	69.5	57.4	49.9	42.3		25.4	16.7
Sulfur, w%	0.15	0.01	0.01	0.02	0.05	0.07	0.13	0.22	0.31
CCR, w%	3.7							6.22	14.5
Viscosity	13.7 cSt @ 100°F								
Pour Point, °F	75				–75	0	80	100	130
Salt, ptb	8.2								
Ni, wppm	5							8.5	20
V, wppm	0.6							1.1	2.5
Paraffins, v%		99	69.9	60.5	60.9				
Naphthenes, v%		1	26.5	33.6	29.9				
Aromatics, v%		0	3.7	5.9	9.2				
RON Clear		78							
Freeze Point, °F					–58				
Aniline Point, °F					150.6	169.1	202		
Diesel Index					75	71	69		
Smoke Point, mm					31				



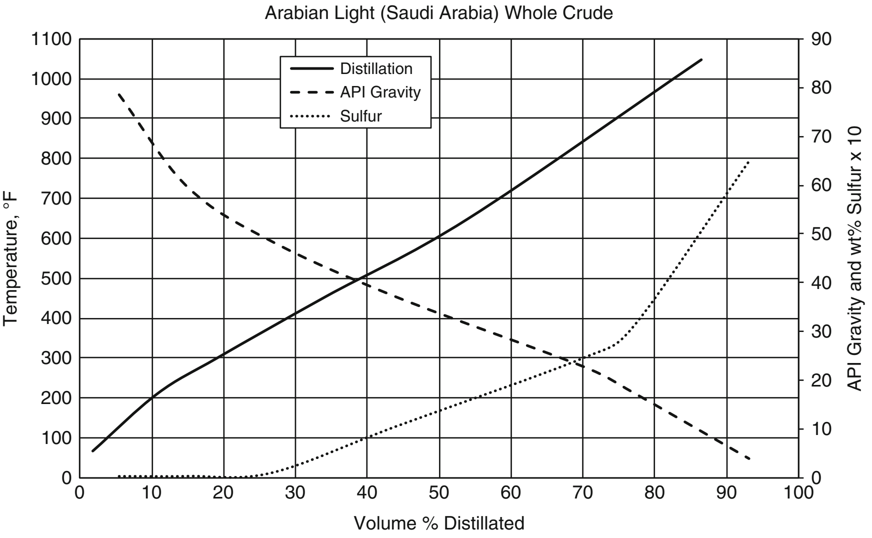
Arabian Heavy, Saudi Arabia **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Diesel/Lt. Gasoil	Vacuum Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	X-68	68-212	212-302	302-455	455-650	650–1049	650+	1049+
Yield, v%	100.0	7.3	7.9	6.8	12.5	16.4	26.3	53.1	26.8
Gravity, °API	28.2		80.1	60.6	48.3	35.8	21.8	12.3	4.0
Sulfur, w%	2.84		0.0028	0.018	0.19	1.38	2.88	4.35	5.6
CCR, w%								13.2	24.4
Viscosity	18.9 cSt @ 100°F				1.12 cSt @ 100°F	3.65 cSt @ 100°F	62.5 cSt @ 100°F	106 cSt @ 210°F	13400 cSt @ 210°F
Pour Point, °F	–30					5	90	55	120
RVP, psi	8.5		10.2						
Ni, wppm								8.5	53
V, wppm								1.1	171
Paraffins, v%			89.6	70.3	58				
Naphthenes, v%			9.5	21.4	23.7				
Aromatics, v%			0.9	8.3	18.3				
RON Clear			59.7						
Freeze Point, °F					–64				
Aniline Point, °F					138	156	172		
Smoke Point, mm					26				


Arabian Heavy (Saudi Arabia) Whole Crude

Arabian Light, Saudi Arabia **Source: O&GJ**

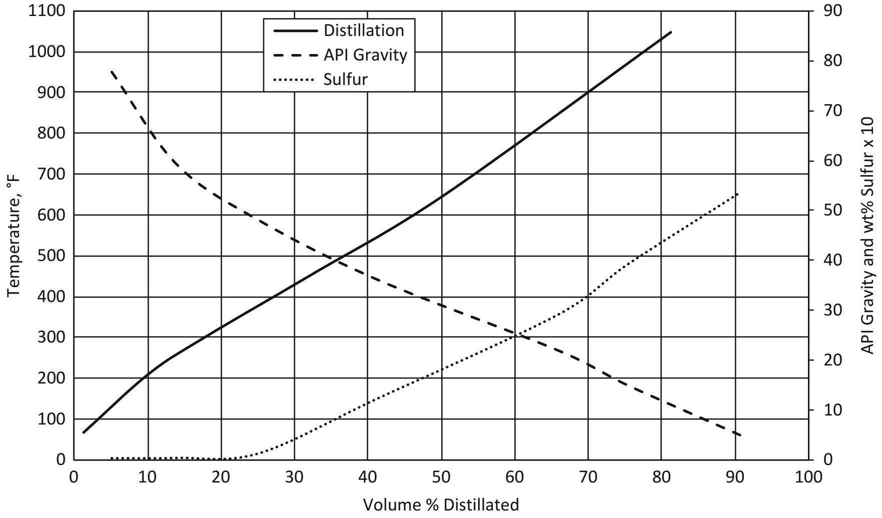
Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Diesel/Lt. Gasoil	Vacuum Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	X-68	68-212	212-302	302-455	455-650	650-1049	650+	1049+
Yield, v%	100.0	1.7	9.0	8.4	15.0	19.8	32.5	46.1	13.6
Gravity, °API	33.4		78.5	59.6	38.5	37.1	22.8	17.6	4.0
Sulfur, w%	1.8		0.024	0.027	0.094	1.05	2.46	3.08	6.5
CCR, w%								7.6	22.4
Viscosity	6.14 cSt @ 100°F					3.28 cSt @ 100°F	52.5 cSt @ 100°F	21.0 cSt @ 210°F	2017 cSt @ 210°F
Pour Point, °F	–30					0	90	40	115
RVP, psi	4.2		8.3						
Ni, wppm									22
V, wppm									94
Paraffins, v%			87.2	69.5					
Naphthenes, v%			10.4	18.2					
Aromatics, v%			2.4	12.3	20.4				
RON Clear			54.7						
Freeze Point, °F					–69				
Aniline Point, °F					135	156	179		
Smoke Point, mm					23				



Arabian Medium, Saudi Arabia **Source: O&GJ**

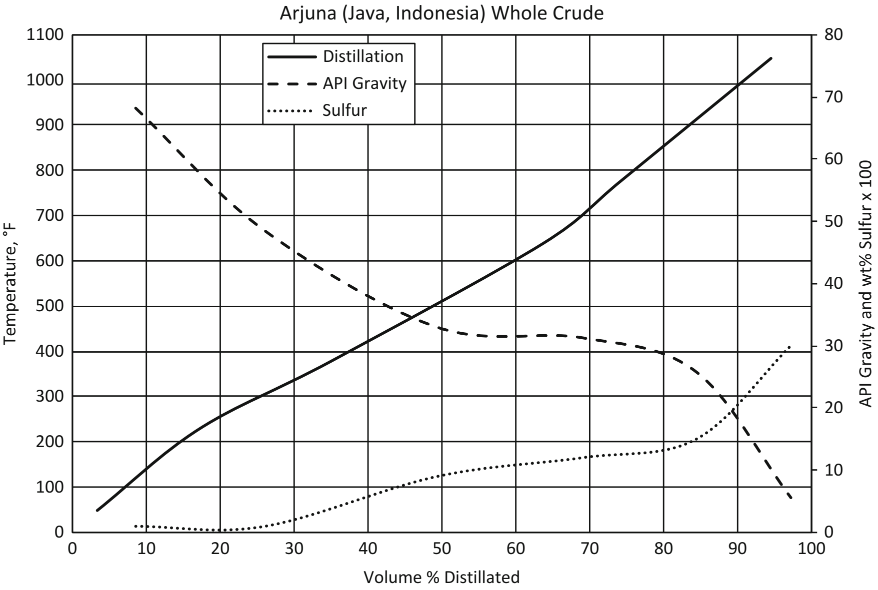
Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Diesel/Lt. Gasoil	Vacuum Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	X-68	68-212	212-302	302-455	455-650	650-1049	650+	1049+
Yield, v%	100.0	1.2	8.9	7.7	14.5	18.1	30.9	49.6	18.7
Gravity, °API	30.8		77.7	59.1	48	36	21.9	15	4.9
Sulfur, w%	2.4		0.043	0.05	0.14	1.24	2.91	3.9	5.35
CCR, w%								9.9	23.3
Viscosity	9.41 cSt @ 100°F				1.13 cSt @ 100°F	3.53 cSt @ 100°F	49.2 cSt @ 100°F	36.0 cSt @210°F	3847 cSt @210°F
Pour Point, °F	5					15	100	55	115
RVP, psi	3.2		7.9						
Ni, wppm									32
V, wppm									96
Paraffins, v%			85.3	68.5					
Naphthenes, v%			12.3	18.7					
Aromatics, v%			2.4	12.7	20.6				
RON Clear			54.5						
Freeze Point, °F					–62				
Aniline Point, °F					136	157	176		
Smoke Point, mm					23				

Arabian Medium (Saudi Arabia) Whole Crude



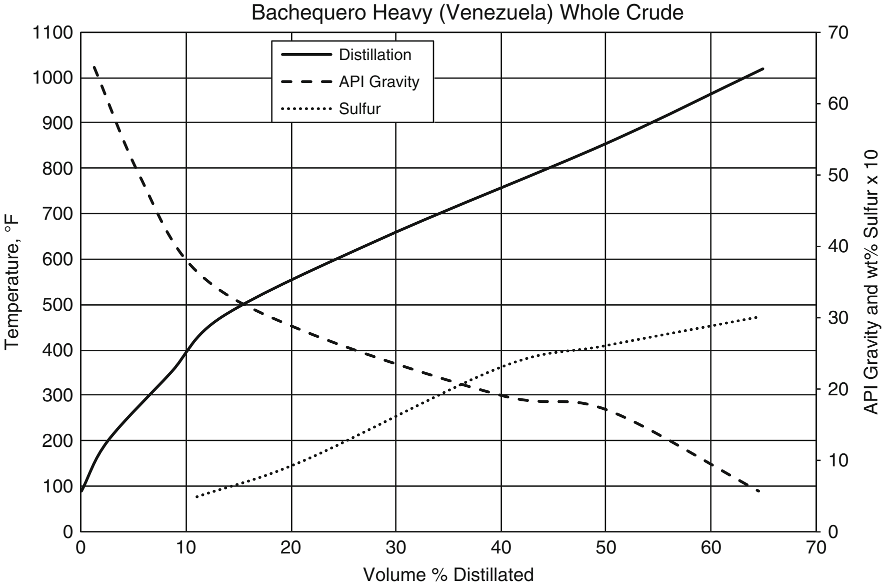
Arjuna, Java, Indonesia **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Distillate	Atm Gasoil	Vac Gasoil	Vac Residuum
TBP Range, °F	-----	X-50	50-230	230-380	380-640	640-780	780-1049	1049+
Yield, v%	100.0	3.3	13.8	17.9	28.7	10.7	20.2	5.4
Gravity, °API	37.7		68.2	48.5	33.0	31.3	25.8	5.6
Sulfur, w%	0.12		0.01	0.01	0.09	0.12	0.15	0.3
CCR, w%						0.08	0.42	
Viscosity	37.7 SUS @ 100°F							4100 cSt @ 275°F
Pour Point, °F	80				15	90	120	
RVP, psi	7		6.9					
Salt, ptb	< 10							
Ni, wppm						0.3	0.9	
V, wppm						0	0.3	
Paraffins, v%			41	43.8				
Naphthenes, v%			34.9	29.1				
Aromatics, v%			5.7	27.1				
RON Clear			72.2	61.6				
Aniline Point, °F						90.2	98.4	
Cetane Number					41			



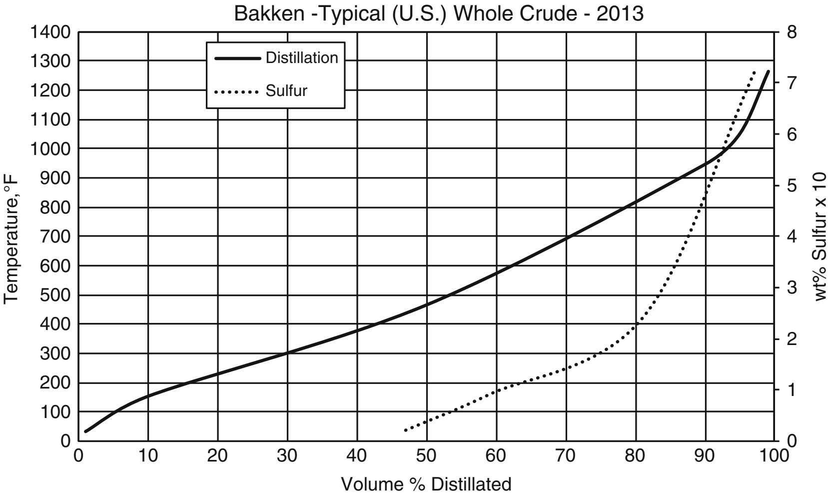
Bachequero (16.8°API) Heavy, Venezuela **Source: O&GJ**

Cut	Whole Crude	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Atm Residuum
TBP Range, °F	-----	90-200	200-350	350-475	475-650	650+
Yield, v%	100.0	2.5	6.0	5.0	15.5	71.0
Gravity, °API	16.8	65.0	50.0	36.4	28.0	5.6
Sulfur, w%	2.4			0.48	0.99	3.0
Viscosity	1362 SUS @ 100°F					4100 cSt @ 275°F
Pour Point, °F	–10			–80		
RVP, psi		2.8				
Paraffins, v%		43.4		19.2		
Naphthenes, v%		51.9		54.8		
Aromatics, v%		4.7		26		
Aniline Point, °F				125	134	



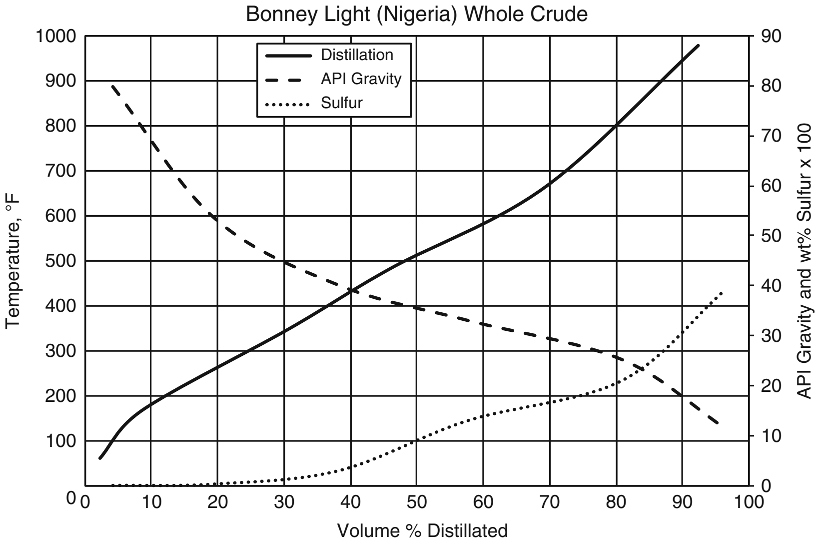
Bakken - Typical (U.S.) **2013**

Cut	Whole Crude	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	375-500	500-620	620-1050	1050+
Gravity, °API	41-42.1				14.0
Sulfur, w%	0.13-0.20	0.02	0.09	0.24	0.68-0.75
Pour Point, °F	–25				
Ni, wppm					7
V, wppm					2



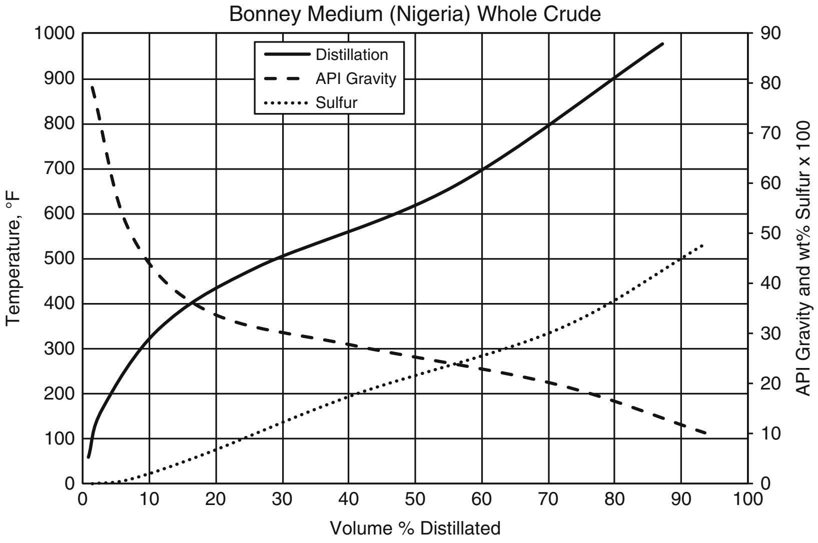
Bonney Light, Nigeria **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Vac Residuum
TBP Range, °F	-----	X-60	60-167	167-347	347-482	482-662	662-977	977+
Yield, v%	100.0	2.2	6.4	22.0	15.4	23.2	23.1	7.7
Gravity, °API	37.6		79.9	53.6	40.2	33.2	25.4	11.8
Sulfur, w%	0.13		0.0002	0.003	0.03	0.13	0.21	0.39
Nitrogen, wppm							1150	
CCR, w%	1.1							12
Viscosity	36 SUS @ 100°F					40.3 SUS @ 100°F	48.1 SUS @ 210°F	2030 SUS @ 210°F
Pour Point, °F	5				–70	20	105	
Ni, wppm	4						<0.1	40
V, wppm	< 0.5						<0.1	3
Paraffins, v%			77	34				
Naphthenes, v%			21.5	55				
Aromatics, v%			1.5	11				
RON Clear			78					
Freeze Point, °F					–53			
Aniline Point, °F				120	136		190	
Diesel Index					55	53		
Cetane Index						51		
Smoke Point, mm					19			



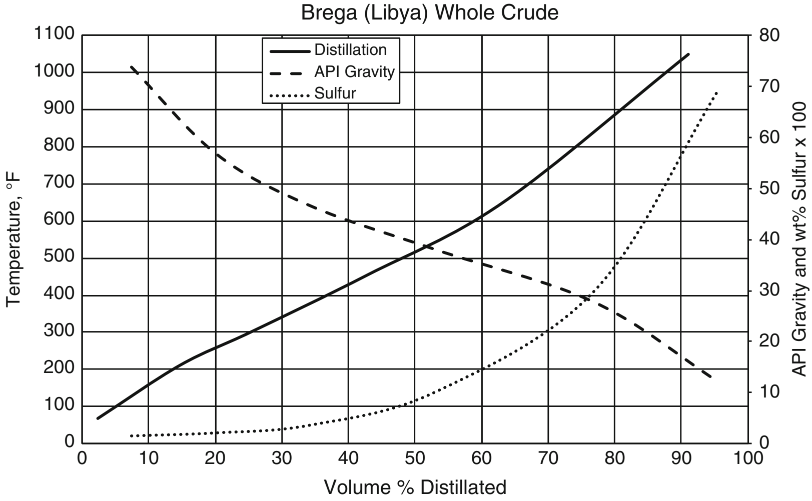
Bonney Medium, Nigeria **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Vac Residuum
TBP Range, °F	-----	X-60	60-167	167-347	347-482	482-662	662-977	977+
Yield, v%	100.0	0.7	2.1	8.7	14.7	29.7	31.3	12.8
Gravity, °API	26		79.2	50.1	34.4	27.5	19.7	10.1
Sulfur, w%	0.23		0.001	0.01	0.063	0.18	0.31	0.48
Nitrogen, wppm								
CCR, w%	1.8							12.7
Viscosity	60.7 SUS @ 100°F					44.6 SUS @ 100°F	53.1 SUS @ 210°F	3690 SUS @ 210°F
Pour Point, °F	<–5				<–70	–15	80	
Ni, wppm	7						<0.1	52
V, wppm	1						<0.1	7
Paraffins, v%			73	27.5				
Naphthenes, v%			24	58.5				
Aromatics, v%			3	14				
RON Clear			80					
Freeze Point, °F					–85			
Aniline Point, °F				110	123		163	
Diesel Index					42	37		
Cetane Index						40		
Smoke Point, mm					17			



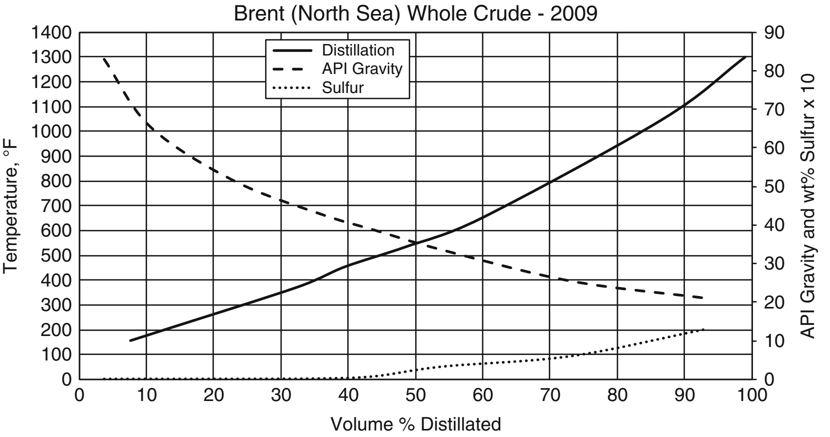
Brega, Libya **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	X-68	68-212	212-302	302-455	455-650	650–1049	650+	1049+
Yield, v%	100.0	2.4	12.4	10.7	17.4	20.3	27.8	36.8	9.0
Gravity, °API	40.4		73.8	56.8	46.7	38.1	27.7	23.6	12.3
Sulfur, w%	0.21		0.014	0.02	0.035	0.10	0.30	0.41	0.69
Nitrogen, wppm									
CCR, w%								4.1	14.6
Viscosity	3.56 cSt @ 100°F				1.17 cSt @ 100°F	3.61 cSt @ 100°F	6.1 cSt @ 210°F	14.1 cSt @ 210°F	620 cSt @ 210°F
Pour Point, °F	30					15	105	95	>120
RVP, psi	6.4		7.4						
Ni, wppm									32
V, wppm									24
Paraffins, v%			72.5	53	51.2				
Naphthenes, v%			25.3	39.3	34.7				
Aromatics, v%			2.2	7.7	14.1				
RON Clear			59.9						
Freeze Point, °F					–68				
Aniline Point, °F					144	172	206		
Smoke Point, mm					27				



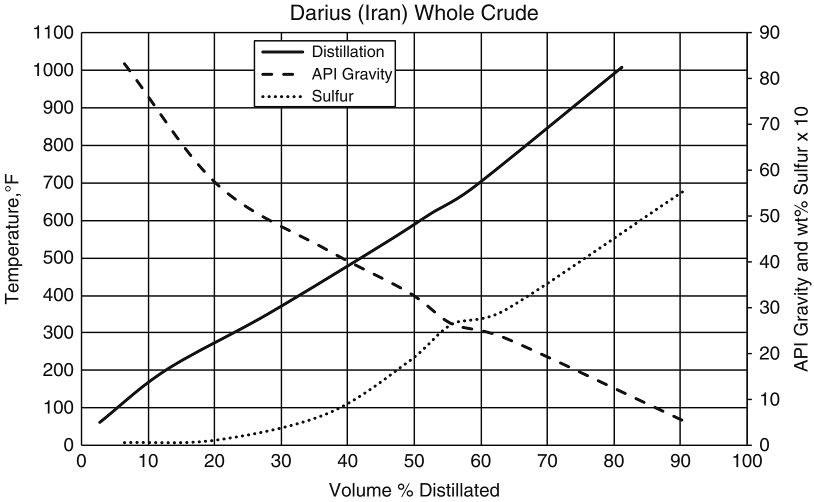
Brent (North Sea) **2009**

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	7.6	6.3	18.6	7.0	9.1	11.1	27.1	12.3
Yield, w%	100.0	6.0	5.4	17.3	6.8	9.1	11.4	29.3	13.7
Gravity, °API	38.3	82.9	65.3	51.3	42.8	38.6	33.4	25.4	21.0
Sulfur, w%	0.4	0	0.001	0.002	0.012	0.07	0.327	0.603	1.303
CCR, w%	2.1							0.1	15.8
Viscosity	3.9 mm^2/s @ 100°F				1.4 mm^2/s @ 100°F	2.4 mm^2/s @ 100°F	5.0 mm^2/s @ 100°F		400 mm^2/s @ 200°F
Pour Point, °F	–44				–65	3	73		
TAN, mg/g	0.1								
Ni, wppm	1								7.8
V, wppm	6								46.6
Naphthenes, v%			28.6	35					
Aromatics, v%			9.6	17.5	22	22.9			
RON Clear		71.8	62.5	43.2					
Freeze Point, °F					–83	–27			
Aniline Point, °F					282	304	329	379	
Cetane Index					44	44.3	51.5		
Smoke Point, mm					20	17			



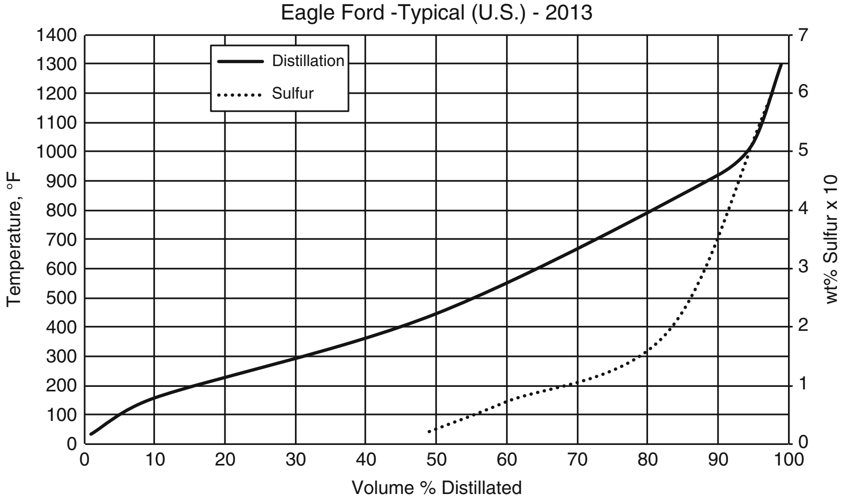
Darius, Iran **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Atm Gasoil	Vac Gasoil	Vac Residuum
TBP Range, °F	-----	X-60	60-200	200-350	350-540	540-620	620-690	690-1010	1010+
Yield, v%	100.0	2.8	10.0	15.3	17.6	7.0	6.4	22.2	18.9
Gravity, °API	33.9		83.3	56.9	42.7	33.4	26.4	23.4	5.3
Sulfur, w%	2.45		0.07	0.13	0.70	1.84	2.67	2.97	5.57
Nitrogen, wppm							0.055	0.093	
RCR, w%									18.9
Viscosity	40 SUS @ 130°F								620 cSt @ 210°F
Pour Point, °F	0				–23	57			
RVP, psi	6.4								
Ni, wppm								1.4	Ni+V
V, wppm								Equivalent	195
Naphthenes, v%				N+A					
Aromatics, v%				30.2					
Arom. Carbon,w%							15.1	14.7	
RON Clear			57.2						
Cetane Index					51.5	54			



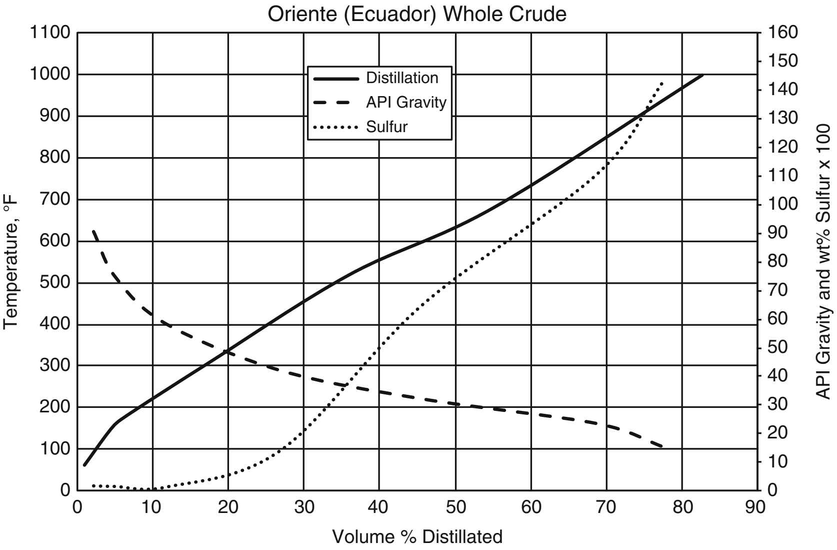
Eagle Ford - Typical (U.S.) **2013**

Cut	Whole Crude	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	375-500	500-620	620-1050	1050+
Gravity, °API	47-59				
Sulfur, w%	0.05-0.11	0.02	0.07	0.19	0.600
CCR, w%	0.07-0.24				
Viscosity	29-35 SSU @ 100°F				
Pour Point, °F	6-15				
RVP, psi	6.5-9.7				
Salt, ptb	0-1				
TAN, mg/g	0.02-0.03				
Ni, wppm	0.1-0.21				2-4
V, wppm	0.03-0.5				0.5-0.6



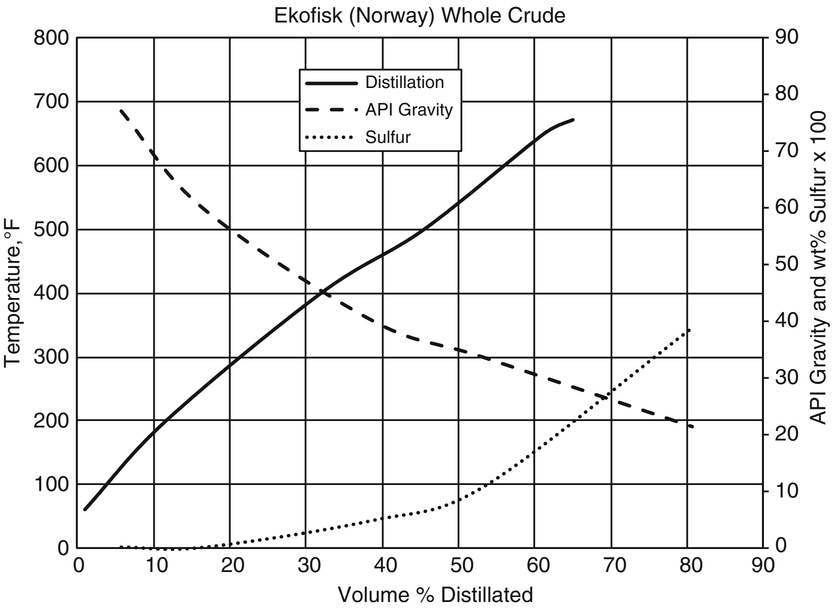
Ecuador Oriente, Ecuador **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Atm Residuum
TBP Range, °F	-----	X-60	60-140	170-310	310-520	520-680	680-1000	680+
Yield, v%	100.0	0.9	3.2	11.9	18.4	18.9	27.7	44.94
Gravity, °API	30.4		90.6	58.2	41.9	32.0	23.3	15.2
Sulfur, w%	0.87		0.019	0.015	0.144	0.65	1.11	1.43
Nitrogen, wppm							1300	
CCR, w%								11.3
Viscosity	61.8 SUS @ 100°F					44.3 SUS @ 100°F	55.5 SUS @ 210°F	325 SUS @ 210°F
Pour Point, °F	20					25	105	95
RVP, psi	4.8							
Salt, ptb	5							
Ni, wppm	28						<0.1	56
V, wppm	61						<0.1	123
Paraffins				49.4				
Naphthenes				43.9				
Aromatics				6.7	18			
RON Clear			80.1					
Freeze Point, °F					–52			
Aniline Point, °F				131	137		198	
Diesel Index						51.2		
Cetane Index					46	52.4		
Smoke Point, mm					20			



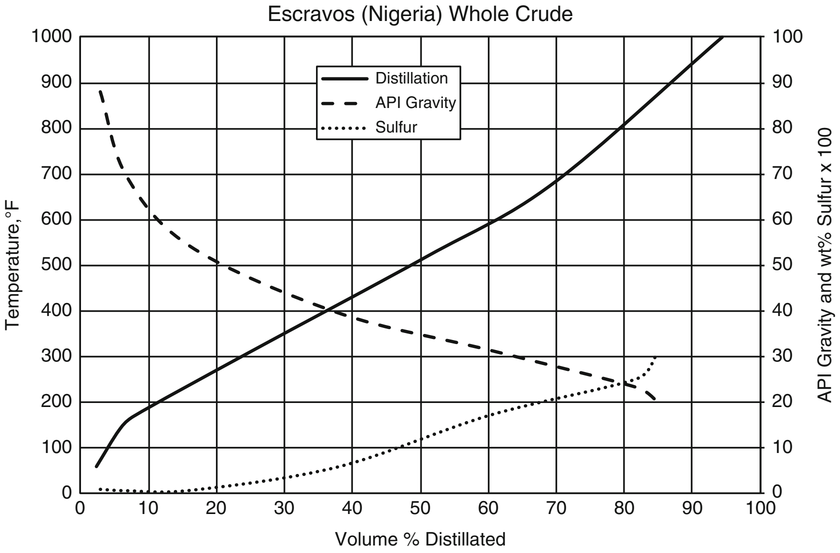
Ekofisk, Norway **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Gasoline	Kerosene	Distillate	Atm Residuum
TBP Range, °F	-----	X-60	60-200	60-400	400-500	500-650	650+
Yield, v%	100.0	1.0	10.7	31.0	13.5	15.7	38.8
Gravity, °API	36.3		77.2	60.1	40.2	33.7	21.5
Sulfur, w%	0.21		0.003	0.0024	0.05	0.11	0.39
RCR, w%						0.08	4.0
Viscosity	42.5 SUS @ 100°F				32.3 SUS @ 100°F	43.8 SUS @ 100°F	80.3 SFS @ 122°F
Pour Point, °F	68					25	85
RVP, psi	5.1						
Salt, ptb	14.5						
BS&W, v%	1.0						
Ni, wppm							5.4
V, wppm							1.95
Paraffins, v%				56.5			
Naphthenes, v%				29.5			
Aromatics, v%				14.0	13.1		
RON Clear			74.4	52			
Freeze Point, °F					–38		
Aniline Point, °F					146	164	
Cetane Index						56.5	
Smoke Point, mm					21		



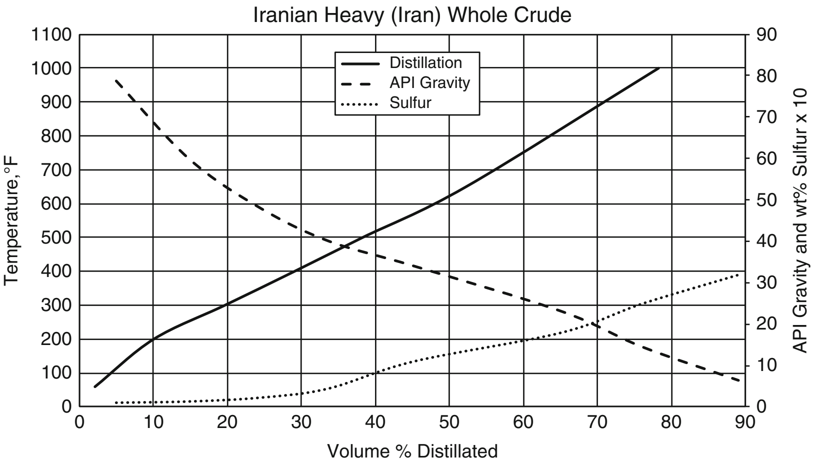
Escravos, Nigeria **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Atm Residuum
TBP Range, °F	-----	X-60	60-140	170-310	310-520	520-680	680-1000	680+
Yield, v%	100.0	2.3	3.4	17.0	26.2	18.6	24.9	30.51
Gravity, °API	36.2		88.1	54	39.6	31.4	23.2	20.4
Sulfur, w%	0.16		0.008	0.006	0.057	0.17	0.25	0.3
Nitrogen, wppm							1200	
CCR, w%	1.3							3.62
Viscosity	38.0 SUS @ 100°F					44.1 SUS @ 100°F	56.4 SUS @ 210°F	93.2 SUS @ 210°F
Pour Point, °F	50					30	110	105
RVP, psi	4.5							
Salt, ptb	10							
Ni, wppm	5.1						1	15
V, wppm	0.2						<0.1	0.7
Paraffins, v%			89	38				
Naphthenes, v%			10	47.1				
Aromatics, v%			1	14.9	21.5			
RON Clear			81.2					
Freeze Point, °F					–48			
Aniline Point, °F				117	133		194	
Diesel Index						49.9		
Cetane Index					42	50.5		
Smoke Point, mm					19			



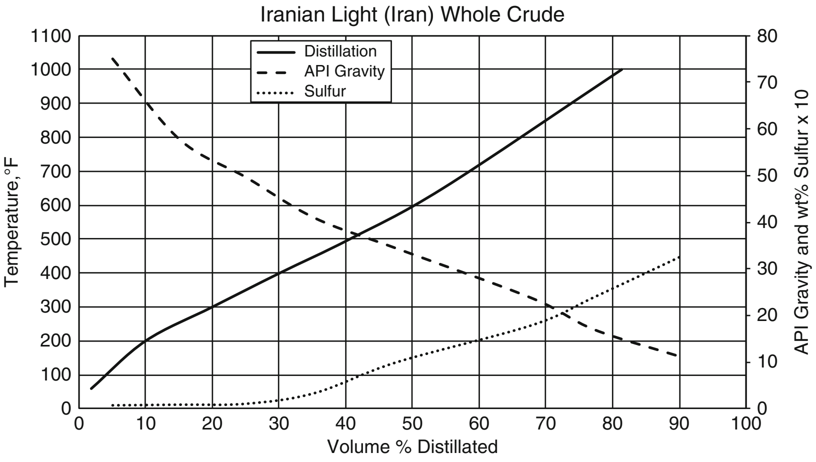
Iranian Heavy, Iran **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Gasoline	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	X-60	60-200	200-300	300-400	400-500	500-650	650-1000	650+	1000+
Yield, v%	100.0	2.1	7.9	9.6	9.4	9.2	14.0	26.0	47.8	21.8
Gravity, °API	30.8		78.8	60	48.2	40.1	34.0	23.0	14.4	6.3
Sulfur, w%	1.6		0.1	0.13	0.22	0.44	1.1	1.8	2.5	3.2
RSH, wppm			340	340	100	14				
Nitrogen, wppm								1600	4700	8300
Ethane, v%		0.1								
Propane, v%		0.5								
I-Butane, v%		0.3								
N-Butane,v%		1.2								
CCR, w%	5								9.5	
Viscosity	9.81 cSt @ 100°F							30.0 cSt @ 130°F	500 cSt @ 130°F	4250 cSt @ 210°F
Penetration, 77°F										47
Pour Point, °F	–5					–40	15	90	75	135
RVP, psi	6.6									
Ni, wppm	30									
V, wppm	88									
Paraffins, v%				53	50	27				
Naphthenes, v%				34	35	43				
Aromatics, v%				13	15	30				
RON Clear			66.1	49.6						
Freeze Point, °F						–35				
Aniline Point, °F					130	140	157	176		
Smoke Point, mm					23	19				



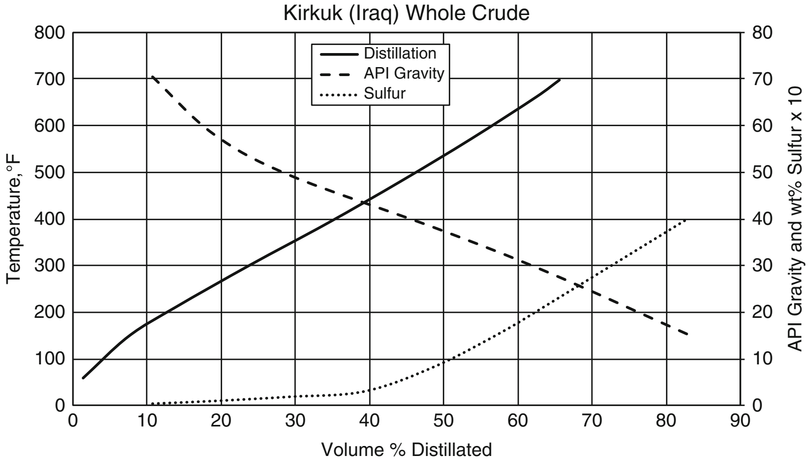
Iranian Light, Iran **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light Gasoline	Light Naphtha	Heavy Naphtha	Kerosene	Distillate	Vac Gasoil	Atm Residuum	Vac Residuum
TBP Range, °F	-----	X-60	60-200	200-300	300-400	400-500	500-650	650-1000	650+	1000+
Yield, v%	100.0	1.9	8.1	10.0	10.1	10.5	14.0	26.8	45.4	18.6
Gravity, °API	33.5		75	57.8	49.6	40.9	34.4	23.7	17	11.0
Sulfur, w%	1.4		0.076	0.09	0.11	0.34	1	1.8	2.4	3.3
RSH, wppm			210	210	20	23				
Nitrogen, wppm								1300	2900	5100
Ethane, v%		0.1								
Propane, v%		0.4								
I-Butane, v%		0.3								
N-Butane,v%		1.1								
CCR, w%	3.4								6.8	
Viscosity	6.41 cSt @ 100°F							20.0 cSt @ 130°F	190 cSt @ 130°F	930 cSt @ 210°F
Penetration, 77°F										285
Pour Point, °F	–20					–35	20	90	75	100
RVP, psi	6.5									
Ni, wppm	13									
V, wppm	35									
Paraffins, v%				50	54	30				
Naphthenes, v%				33	30	41				
Aromatics, v%				17	16	29				
RON Clear			64.7	47.4						
Freeze Point, °F						–30				
Aniline Point, °F					135	146	162	183		
Smoke Point, mm					25	21				



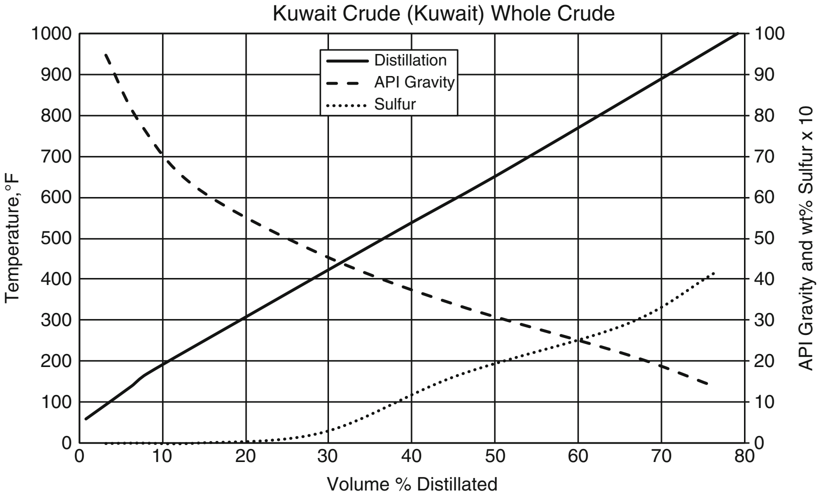
Kirkuk, Iraq **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light SR	Light Naphtha	Heavy Naphtha	Kerosene	Light Distillate	Heavy Distillate	Extra Hvy Distillate	Vac Residuum
TBP Range, °F	-----	X-60	60-149	149-212	212-302	302-392	392-482	572-662	662-698	698+
Yield, v%	100.0	1.4	6.1	6.4	10.0	10.5	9.9	8.8	3.1	34.4
Gravity, °API	35.9			70.4	58.2	49.4			28.6	15.4
Sulfur, w%	1.95			0.0333	0.0903	0.181	0.3	1.6	2.17	4
CCR, w%	3.8									10
Viscosity	4.61 cSt @ 100°F						1.68 cSt @ 100°F			43.9 cSt @ 210°F
Pour Point, °F	-33									86
Ni, wppm										<3
V, wppm										58
Paraffins, v%			97	80	69					
Naphthenes, v%				18	21					
Aromatics, v%				2	10					
RON Clear			73	52	38					
Aniline Point, °F						130.64				
Cetane Index							53			
Smoke Point, mm						24				
Wax Content, w%	3.6									
Asphaltenes, w%	1.5									



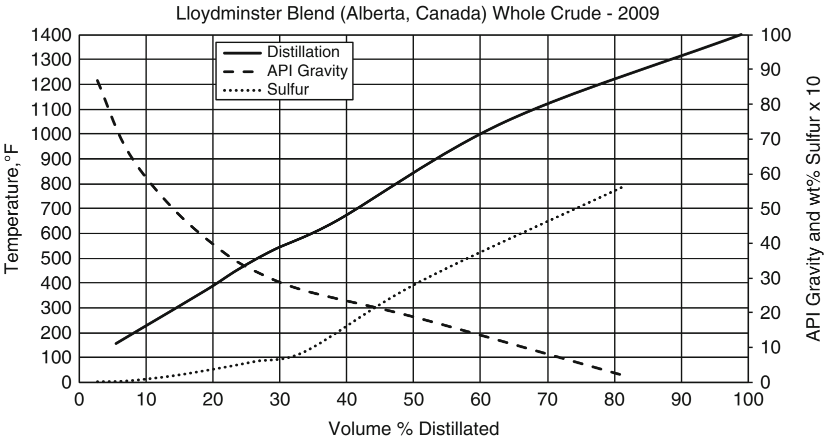
Kuwait Crude (Kuwait) **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light SR	Light Naphtha	Heavy Naphtha	Kerosene	Light Distillate	Vac Gasoil	Vac Residuum
TBP Range, °F	-----	X-60	60-140	140-170	170-310	310-520	520-680	680-1000	680+
Yield, v%	100.0	0.8	5.5	1.9	12.0	18.2	14.1	26.6	47.5
Gravity, °API	31.2		94.6	78.2	62.2	45.9	33.7	21.7	14.0
Sulfur, w%	2.5		0.01	0.02	0.02	0.28	1.66	2.91	4.14
Nitrogen, wppm								950	
CCR, w%	5.3								9.37
Viscosity	58.7 SUS @ 100°F						41.3 SUS @ 100°F	53.9 SUS @ 210°F	267 SUS @ 210°F
Pour Point, °F	0						20	100	70
RVP, psi	5.4								
Salt, ptb	3								
Ni, wppm	9.6							0.1	18
V, wppm	31							0.4	59
Paraffins, v%			98.5	86.2	67.9				
Naphthenes, v%			1.4	12.5	22.1				
Aromatics, v%			0.1	1.3	10	19.5			
RON Clear			78.5	58.8					
Freeze Point, °F						–46			
Aniline Point, °F					133	143		178	
Diesel Index							53.6		
Cetane Index						52.3	55		
Smoke Point, mm						24			



Lloydminster Blend, Alberta, Canada 2009

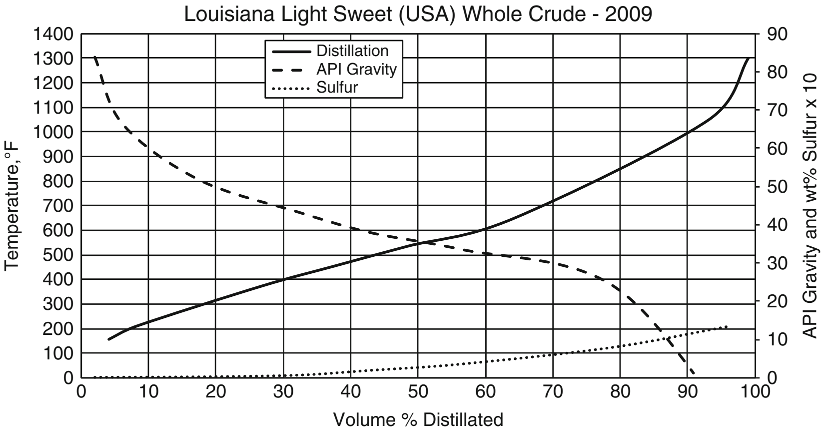
Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	5.6	3.4	10.1	4.7	5.5	9.1	25.3	35.3
Gravity, °API	20.7	86.9	66.7	50.1	37.8	31.9	26.4	18.4	2.1
Sulfur, w%	3.15	0.022	0.046	0.191	0.426	0.61	0.89	2.9	5.620
CCR, w%	9.2							0.5	25.2
Viscosity	101 mm^2/s @ 100°F				1.6 mm2/s @ 100°F	2.9 mm2/s @ 100°F	6.4 mm2/s @ 100°F		
Pour Point, °F	–26				–150	–80	–9		
TAN, mg/g	0.78								
Ni, wppm	52.7							0	123
V, wppm	105							0.1	231
Naphthenes, v%			34.1	38.2					
Aromatics, v%			8.7	16.5	21.7	22.6			
RON Clear		70.5	57.6	55.2					
Freeze Point, °F					–92	–33			
Aniline Point, °F					257	262	273	324	
Cetane Index					36.1	36.1	41.2		
Smoke Point, mm					20.6	17.5			



]

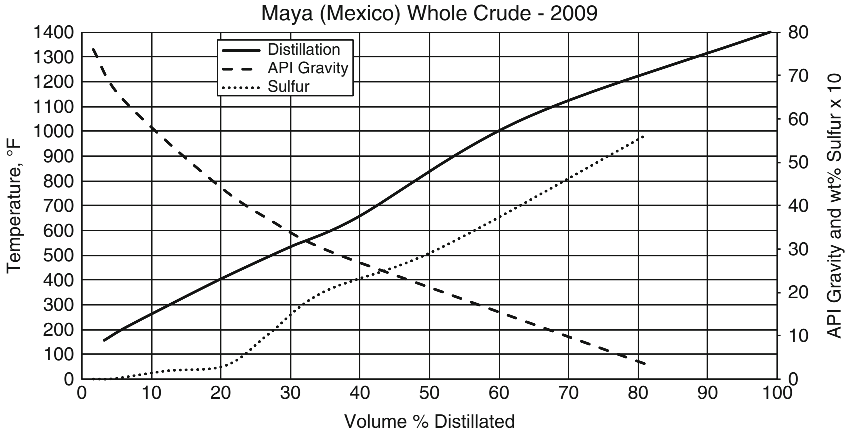
Louisiana Light Sweet (LLS), USA **2009**

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	4.1	4.1	18.5	10.7	10.9	15.8	28.9	5.9
Yield, w%	100.0	3.2	3.5	16.9	10.3	10.8	16.0	31.1	8.2
Gravity, °API	36.1	83.9	66.4	51.8	43.4	38.0	33.6	24.3	–10.4
Sulfur, w%	0.45	0.018	0.022	0.031	0.074	0.2	0.361	0.792	1.343
CCR, w%	1.1							0.3	16.2
Viscosity	4.3 mm^2/s @ 100°F				1.5 mm^2/s @ 100°F	2.9 mm^2/s @ 100°F	5.7 mm^2/s @ 100°F		768 mm^2/s @ 200°F
Pour Point, °F	–35				–89	–17	50		
TAN, mg/g	0.58								
Ni, wppm	7.1							0.1	89
V, wppm	1.2							0	17
Naphthenes, v%			23	36					
Aromatics, v%			7.5	13.4	15.8	17.9			
RON Clear		73.3	66.6	49.8					
Freeze Point, °F					–74	7			
Aniline Point, °F					284	307	327	378	
Cetane Index					46	46.2	52		
Smoke Point, mm					22	17			



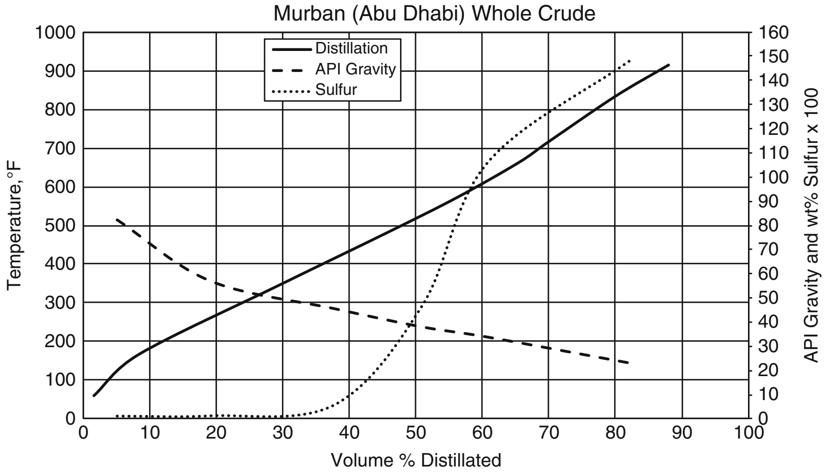
Maya, Mexico **2009**

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	3.2	3.2	11.3	6.0	6.3	9.2	24.1	35.5
Yield, w%	100.0	2.4	2.5	9.3	5.3	5.8	8.8	24.4	40.5
Gravity, °API	22.2	76.0	66.4	54.9	43.2	36.8	30.0	20.3	3.4
Sulfur, w%	3.3	0.01	0.024	0.198	0.327	1.06	2.018	3.023	5.646
CCR, w%	12							0.1	25.2
Viscosity	102 mm^2/s @ 100°F				1.5 mm^2/s @ 100°F	2.6 mm^2/s @ 100°F	5.5 mm^2/s @ 100°F		306862 mm^2/s @ 200°F
Pour Point, °F	-33				–72	0	72		
TAN, mg/g	0.28								
Ni, wppm	52							0.6	122
V, wppm	314							0.1	735
Naphthenes, v%			21.7	27.9					
Aromatics, v%			28.1	29.2	19	21.6			
RON Clear		69.5	57.2	34.9					
Freeze Point, °F					–62	–15			
Aniline Point, °F					270	280	295	325	
Cetane Index					46	45.8	46.4		
Smoke Point, mm					15	10			



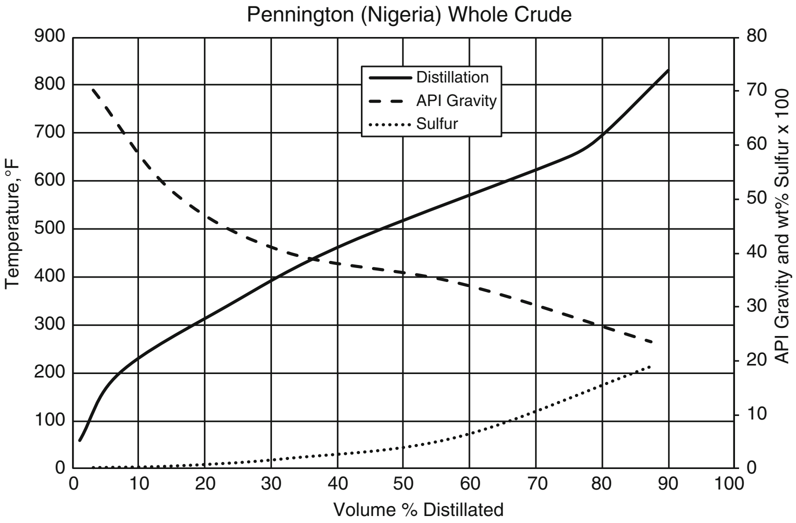
Murban, Abu Dhabi **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light SR	Heavy Naphtha	Kerosene	Light Distillate	Vac Gasoil	Atmos Residuum
TBP Range, °F	-----	X-60	60-167	167-347	347-482	482-572	572-662	662+
Yield, v%	100.0	1.7	6.8	21.2	16.1	10.4	9.2	34.5
Gravity, °API	39.4		82.2	56.9	45.4	37.8	33.6	22.6
Sulfur, w%	0.74		0.012	0.013	0.058	0.47	1.06	1.49
CCR, w%								3.6
Viscosity	5.0 cSt @ 70°F				1.8 cSt @ 68°F	4.2 cSt @ 68°F	9.5 cSt @ 68°F	104 cSt @ 100°F
Pour Point, °F	5					0	39	95
RVP, psi	5		10.1					
Salt, ptb	<5							
Ni, wppm	0.58							2
V, wppm	0.8							2
Wax Content, w%	8.0						17.5	19.5
Paraffins, v%				63				
Naphthenes, v%				20				
Aromatics, v%				17				
RON Clear			69					
Freeze Point, °F					−45			
Aniline Point, °F				124	143			
Diesel Index					65	59	58	
Cetane Index						54		
Smoke Point, mm					24			



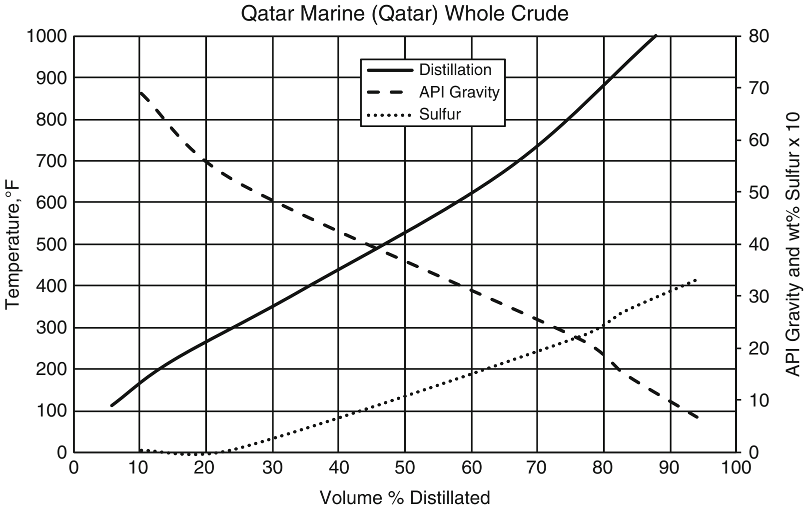
Pennington, Nigeria **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light SR	Heavy Naphtha	Kerosene	Distillate	Atmos Residuum
TBP Range, °F	-----	X-60	60-200	200-340	340-470	470-650	650+
Yield, v%	100.0	1.1	6.0	16.3	18.0	33.5	25.1
Gravity, °API	37.7		70.1	51.2	40.1	34.5	23.6
Sulfur, w%	0.076		0.001	0.004	0.018	0.058	0.19
CCR, w%							1.3
Viscosity	36 SUS @ 100°F						6.9 SUS @ 210°F
Pour Point, °F	37					10	88
Salt, ptb	2.9						
Paraffins, v%			74	32			
Naphthenes, v%			24	56.5			
Aromatics, v%			1.5	11			
Freeze Point, °F					-74		
Smoke Point, mm					21		



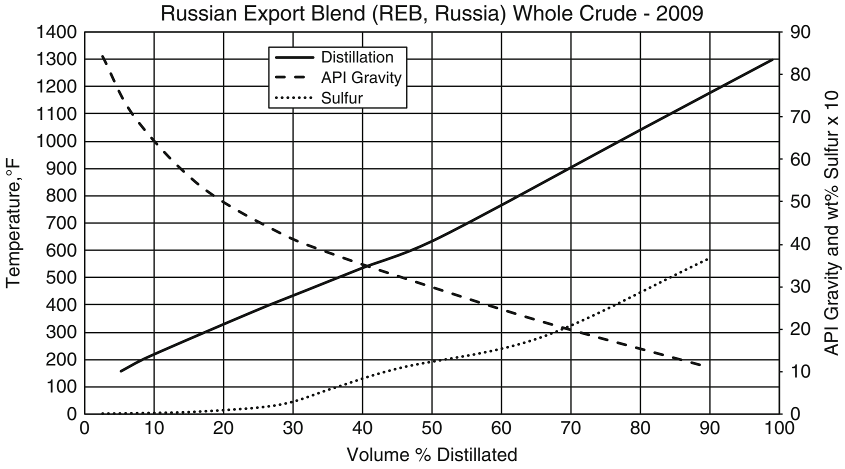
Qatar Marine, Qatar **Source: O&GJ**

Cut	Whole Crude	Light Ends	Light SR	Heavy Naphtha	Distillate	Vac Gasoil	Atmos Residuum	Vac Residuum
TBP Range, °F	-----	X-113	113-220	220-390	390-680	680-1000	680+	1000+
Yield, v%	100.0	5.7	9.1	19.6	31.0	22.5	34.6	12.2
Gravity, °API	37.0		69.0	52.0		21.5	15.3	6.7
Sulfur, w%	1.5		0.04	0.07		2.24	2.69	3.32
Nitrogen, wppm						1400		
CCR, w%							9.27	21.6
Viscosity	42.8 SUS @ 80°F					58.8 SUS @ 210°F	236 SUS @ 210°F	
Penetration, 77°F								36
Pour Point, °F	25					100	85	127
RVP, psi	5.7		3.9					
Salt, ptb	9							
Ni, wppm						0.5	44	107
V, wppm						0.6	110	263
Paraffins, v%			71.3	59.2				
Naphthenes, v%			22.4					
Aromatics, v%			6.3					
Aniline Point, °F						176		



Russian Export Blend (REB), Russia 2009

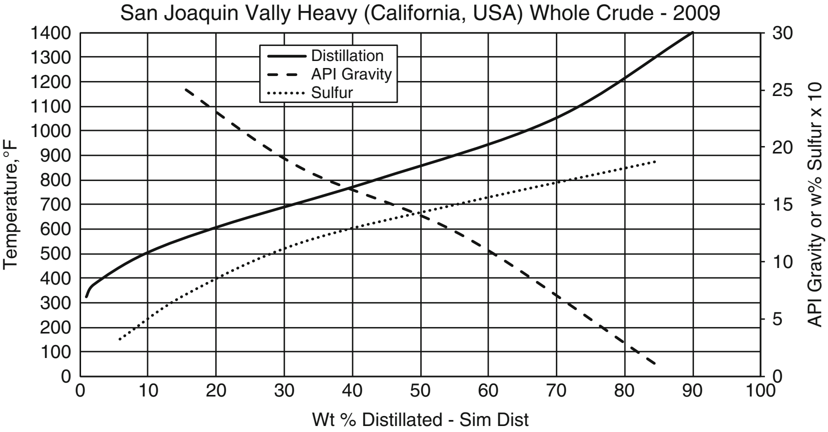
Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	5.3	4.1	14.7	7.9	8.0	11.2	29.3	18.5
Yield, w%	100.0	4.0	3.3	13.0	7.4	7.7	11.2	31.2	21.2
Gravity, °API	31.8	84.2	69.8	53.7	42.8	37.6	32.3	21.8	11.1
Sulfur, w%	1.53	0.005	0.013	0.053	0.211	0.61	1.086	1.809	3.650
CCR, w%	3.9							0.7	18.5
Viscosity	8.3 mm^2/s @ 100°F				1.5 mm^2/s @ 100°F	2.6 mm^2/s @ 100°F	5.5 mm^2/s @ 100°F		1290 mm^2/s @ 200°F
Pour Point, °F	10				–89	–18	84		
TAN, mg/g	0.56								
Ni, wppm	14.7							0.2	73.4
V, wppm	46.7							0.2	230.6
Naphthenes, v%			25.2	37.1					
Aromatics, v%			3.7	11.7	21.8	27.8			
RON Clear		70.9	50.9	39.2					
Freeze Point, °F					–71	0			
Aniline Point, °F					277	288	300	334	
Cetane Index					45	44.9	49.7		
Smoke Point, mm					22	18			



Russian Export Blend (REB, Russia) Whole Crude - 2009

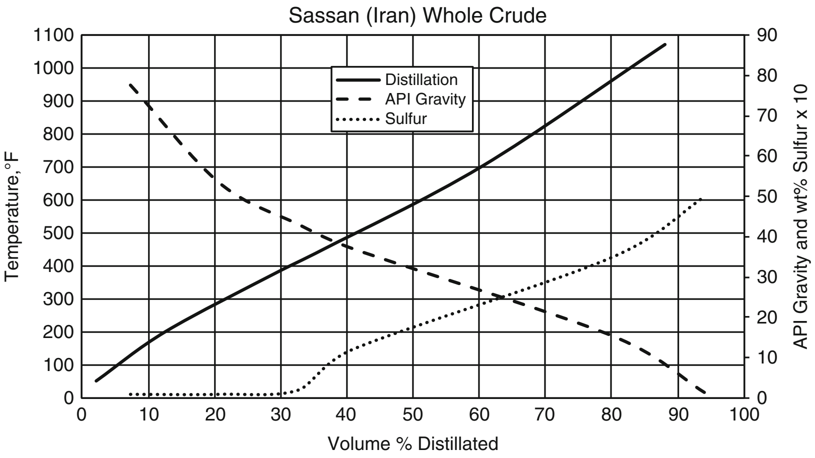
San Joaquin Valley Heavy, USA **2009**

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kerosene	Diesel	Light Gasoil	Heavy Gasoil	Resid
TBP Range, °F	-----	160-250	250-325	325-375	375-500	500-620	620-800	800-1050	1050+
Yield, v%	100.0	0.3	0.7	1.1	7.5	11.9	21.9	26.2	30.5
Yield, w%	100.0	0.2	0.6	0.9	6.5	11.0	21.2	26.5	33.0
Gravity, °API	13.6					25	18.2	12.2	1
Sulfur, w%	1.38				0.33	0.72	1.17	1.52	1.88
CCR, w%									22.3
N+2A		72	82	79					
Cetane Index					33	32			



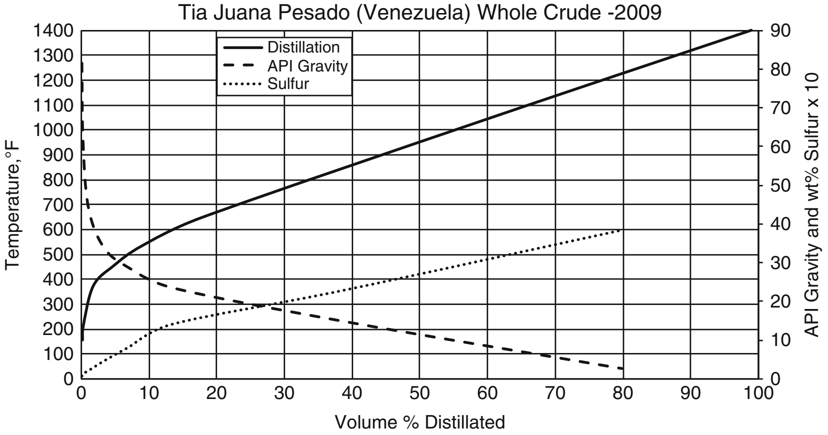
Sassan, Iran **Source: O&GJ**

Cut	Whole Crude	Light Ends	SR Gasoline	Naphtha	Kerosene	Distillate	Atmos Residuum	Vac Residuum
TBP Range, °F	-----	X-50	50-200	200-375	375-450	450-700	700+	1070+
Yield, v%	100.0	2.1	10.5	16.4	7.5	23.8	39.7	12.0
Gravity, °API	33.9		77.6	53.3	43.0	37.0	15.3	1.3
Sulfur, w%	1.91		0.081	0.082	0.19	1.2	3.5	5
RSH Sulfur, wppm			0.067	0.002				
Viscosity	44.2 SUS @ 100°F				2.05 cSt @ 60°F	7.52 cSt @ 60°F	154 SUS @ 210°F	8000 SUS @ 210°F
Pour Point, °F	-5					15	75	
Salt, ptb	1.76							
Ni, wppm							Ni+V 44	Ni+V 127
V, wppm								
Naphthenes, v%				N+A 41				
Aromatics, v%								
RON Clear			61	35.4				
Freeze Point, °F					–50			
Aniline Point, °F				121.5	137.9	153		
Cetane Index						56.3		
Smoke Point, mm					20			
Wax Content, w%	1.9							



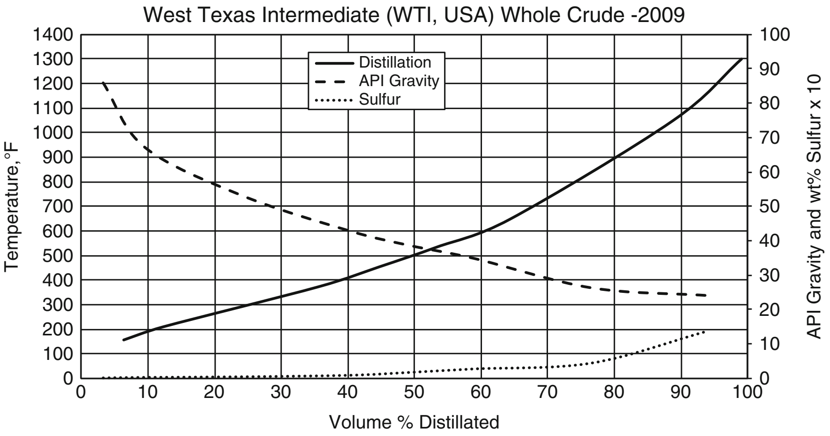
Tia Juana Pesado, Venezuela **2009**

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	0.2	0.1	1.5	3.0	4.2	8.8	42.7	38.5
Yield, w%	100.0	0.2	0.1	1.2	2.6	3.8	8.1	41.9	41.1
Gravity, °API	12.1	81.6	61.8	44.5	34.2	28.9	23.7	14.8	2.8
Sulfur, w%	2.7	0.074	0.14	0.214	0.458	0.81	1.411	2.3	3.831
CCR, w%	11.2							1.2	25.6
Viscosity	3700 mm^2/s @ 100°F				1.9 mm^2/s @ 100°F	3.5 mm^2/s @ 100°F	10.1 mm^2/s @ 100°F		99000 mm^2/s @ 100°F
Pour Point, °F	30				–121	–69	–27		
TAN, mg/g	3.61								
Ni, wppm	38.5								91.4
V, wppm	284								674
Naphthenes, v%			52	72.3					
Aromatics, v%			2.8	11.1	18.1	24.4			
RON Clear		87.7	75.2	69.6					
Freeze Point, °F					–103	–51			
Aniline Point, °F					259	270	282	318	
Cetane Index					31.2	31.2	37.5		
Smoke Point, mm					16.5	10.4			



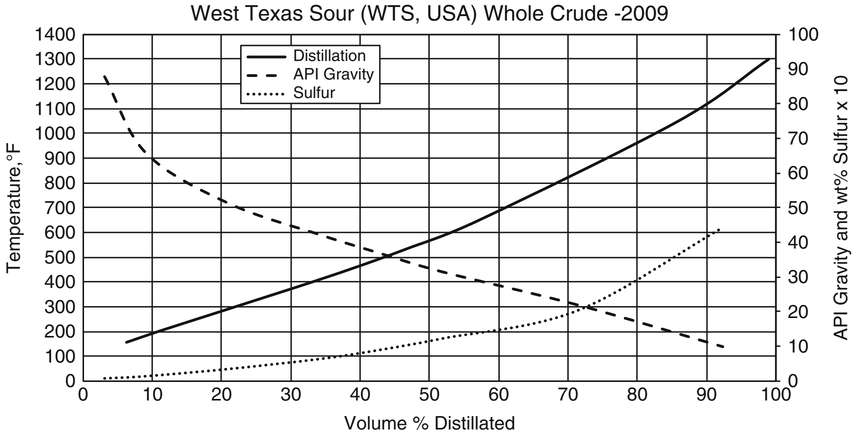
West Texas Intermediate (WTI), USA 2009

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	6.4	6.0	23.2	9.1	8.7	10.9	24.4	10.3
Yield, w%	100.0	5.1	5.2	21.6	9.0	8.8	11.3	26.6	11.4
Gravity, °API	40.8	85.9	67.2	53.2	43.0	38.8	35.0	26.4	24.2
Sulfur, w%	0.34	0.011	0.027	0.044	0.088	0.17	0.274	0.444	1.374
CCR, w%	1.1							0.4	12.6
Viscosity	3.9 mm^2/s @ 100°F				1.5 mm^2/s @ 100°F	2.5 mm^2/s @ 100°F	5.5 mm^2/s @ 100°F		382mm^2/s @ 200°F
Pour Point, °F	–20				–65	10	77		
TAN, mg/g	0.1								
Ni, wppm	1.6							0.1	15.3
V, wppm	1.6							0	15.2
Naphthenes, v%			37.6	38.5					
Aromatics, v%			4.3	13.2	13.7	13.7			
RON Clear		69.8	62.8	50.6					
Freeze Point, °F					–44	16			
Aniline Point, °F					289	316	345	396	
Cetane Index					45	45.1	54		
Smoke Point, mm					24	21			



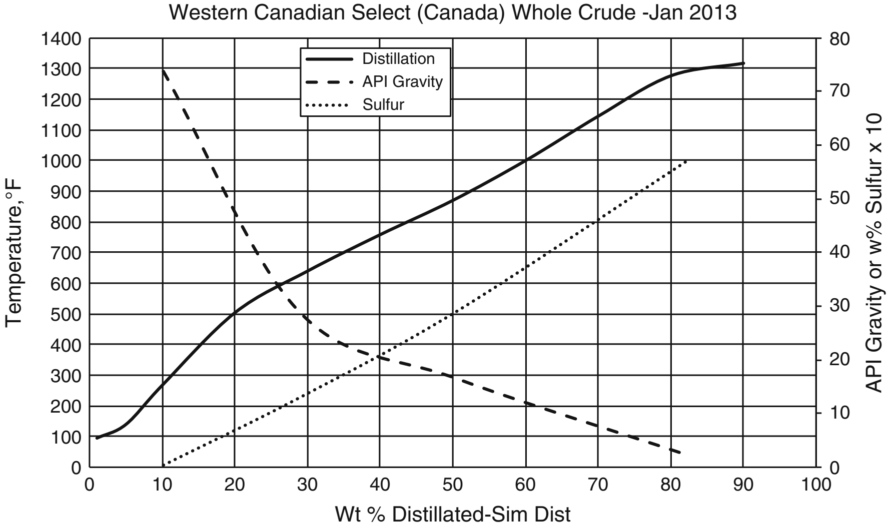
West Texas Sour (WTS), USA 2009

Cut	Whole Crude	Light Naphtha	Medium Naphtha	Heavy Naphtha	Light Kerosene	Kerosene	Diesel	Vacuum Gasoil	Resid
TBP Range, °F	-----	X-158	158-212	212-374	374-455	455-536	536-649	649-1049	1049+
Yield, v%	100.0	6.2	5.7	18.1	8.7	8.0	10.2	28.8	13.2
Yield, w%	100.0	4.7	4.8	16.4	8.3	7.9	10.4	31.1	15.4
Gravity, °API	34.1	87.9	65.9	51.3	42.1	37.0	31.5	22.0	9.9
Sulfur, w%	1.64	0.079	0.143	0.351	0.646	0.9	1.232	2.042	4.441
CCR, w%	3.3							0.7	22.6
Viscosity	4.6 mm^2/s @ 100°F				1.5 mm^2/s @ 100°F	2.5 mm^2/s @ 100°F	5.2 mm^2/s @ 100°F		7440 mm^2/s @ 200°F
Pour Point, °F	–51				–78	–18	54		
TAN, mg/g	0.11								
Ni, wppm	3.7							0.1	31.4
V, wppm	6.4							0.1	54.1
Naphthenes, v%			27.1	38.4					
Aromatics, v%			9	18	21.8	25.2			
RON Clear		69.1	59.3	43.1					
Freeze Point, °F					–63	1			
Aniline Point, °F					273	289	307	354	
Cetane Index					43	43.4	48.7		
Smoke Point, mm					20	16			



Western Candian Select, Canada **Jan-13**

Cut	Whole Crude	Full-Range Naphtha	Full-Range Distillate	Full-Range Gasoil	Residuum
TBP Range, °F	-----	IBP-374	374-649	649-981	981+
Yield, v%	100.0	20.1	17.3	26.6	36.0
Yield, w%	100.0	14.9	16.4	27.4	41.3
Gravity, °API	20.9	73.8	29.1	16.5	2.5
Sulfur, w%	3.48	0.044	1.295	2.924	5.684
Nitrogen, wppm	2481		28	1259	5150
MCR, w%	10.09		0.01	0.18	24.74
Viscosity					72,517 cSt @ 212°F
Salt, ptb	44				
BS&W, wppm	316				
TAN, mg KOH/g	0.76		0.25	1.26	0.61
Ni, wppm	46			0	
V, wppm	115			0	


Western Canadian Select (Canada) Whole Crude -Jan 2013

Conversion Factors Used in Petroleum Processing

Steven A. Treese

Contents

Abstract
This appendix provides general conversion factors, pressure conversions, and viscosity conversions for petroleum processing. These factors are used throughout this handbook.

Keywords
Conversion Factors • Pressure • Viscosity

Steven A. Treese has retired from Phillips 66.

S.A. Treese (✉)
Puget Sound Investments LLC, Katy, TX, USA
e-mail: streese256@aol.com

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7_35

Appendix D: Conversion Factors

D1 General Conversion Factors

To convert from	To	New unit abbreviation	Multiply by
Length			
Feet	Meter	m	0.304
Inch	Millimeter	mm	25.4
Statute mile	Kilometer	km	1.609
Area			
Square inches	Square millimeters	mm^2	645.2
Square inches	Square centimeters	cm^2	6.452
Square inches	Square meters	m^2	0.000645
Square feet	Square meters	m^2	0.0924
Acres	Hectare		0.4047
Volume			
Cubic inches	Cubic millimeter	mm^3	16,387
Cubic inches	Cubic centimeter	cm^3 or cc	16.387
Cubic inches	Cubic meter	m^3	0.00001639
Cubic feet	Cubic meter	m^3	0.0281
Fluid ounces	Milliliter	ml	29.57
Gallons (US)	Liter	l	3.785
Mass			
Pounds	Kilogram	kg	0.4536
Ton (short)	Metric ton	tonne or MT	0.9072
Ton (long)	Metric ton	tonne or MT	1.016
Pressure			
Pounds per square inch	Pascal	Pa	6,895
Pounds per square inch	Kilopascal	kPa	6.895
Kilograms per sq meter	Pascal	Pa	9.807
Bar	Kilopascal	kPa	100
Force			
Pounds force	Newton	N	4.448
Kilogram force	Newton	N	9.807
Work			
British thermal unit	Joule	J	1,055
Foot pound	Joule	J	1.356
Calorie	Joule	J	4.186
Power			
Btu/hour	Watt	w	0.293
Btu/sec	Watt	w	1,055
Horsepower	Kilowatt	kw	0.746
Flow rate			
Cubic feet per minute	Cubic meters/minute	m^3/m	0.0283

(*continued*)

To convert from	To	New unit abbreviation	Multiply by
Gallons (US)/minute	Liter/minute	l/m	3.785
Barrels (US) oil	Gallons oil (US)	gal	42
Specific energy. Latent heat			
Btu/pound	Joule/kilogram	J/kg	2,326
Specific heat, specific			
Entropy	Joule/kilogram – kelvin	J/kg-deg K	4,184
Btu/pound – deg F			
Miscellaneous			
(US) barrels per day	(US) gallons/hour	gph	1.75
(US) gallons	Imperial gallons		0.8326

D2 Pressure Conversion Table

To convert from ↓	Multiply by factor to convert to							
	Atm	psi	in. Hg	Ft H_2O (4 °C)	In. H_2O	mm Hg (torr)	Bar	kg/cm^2
Atm	1.00000	14.696	29.920	33.9000	406.800	760.00	1.0135	1.0333
psi	0.06804	1.000	2.036	2.3070	27.684	51.50	0.0690	0.0703
in. Hg	0.03340	0.491	1.000	1.1330	13.596	25.40	0.0339	0.0345
Ft H_2O (4 °C)	0.02950	0.434	0.883	1.0000	12.000	22.20	0.0299	0.0305
In. H_2O	0.00246	0.036	0.074	0.0833	1.000	1.85	0.0025	0.0025
mm Hg (torr)	0.00132	0.020	0.039	0.0446	0.535	1.00	0.0013	0.0014
Bar	0.98690	14.500	29.521	33.4484	401.381	749.88	1.0000	1.0195
kg/cm^2	0.96780	14.220	28.960	32.8100	393.690	735.51	0.9808	1.0000

Appendix D3 Viscosity Conversion Table

Given units	Multiply the given units by this factor to get					
	g/cm-s (Poise)	kg/m-s	lb$_m$/ft-s	lb$_f$-s/ft^2	Centipoise (cP)	lb$_m$/ft-h
g/cm-s (Poise)	1	10^{-1}	0.0672	2.09×10^{-3}	100	242
kg/m-s	10	1	0.672	0.0209	1,000	2,419
lb$_m$/ft-s	14.88	1.488	1	0.0311	1,488	3,600
lb$_f$-s/ft^2	4,788	47.88	32.17	1	47,880	1.158×10^5
Centipoise (cP)	0.01	0.001	6.72×10^{-4}	2.089×10^{-5}	1	2.4191
lb$_m$/ft-h	4.134×10^{-3}	4.134×10^{-4}	2.78×10^{-4}	8.634×10^{-6}	0.4134	1

Index

S.A. Treese et al. (eds.), *Handbook of Petroleum Processing*,
DOI 10.1007/978-3-319-14529-7