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Fundamentals of Petroleum Refining

M.A. Fahim • T.A. Al-Sahhaf • A.S. Elkilani

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PREFACE

Fundamentals of Petroleum Refining provides a thorough and balanced introduction to refinery engineering topics from basic concepts and unit operations to overall refinery economics. Based on the fundamentals of thermodynamics and kinetics, the text develops the scientific background needed for an understanding of refinery operations. It also provides an in-depth description of major refinery processes and then assimilates an integrated refinery by focusing on the economic and operational aspects necessary for enhancing performance and profitability.

The authors have over two decades of experience teaching and consulting in the field of petroleum refining. Although there are a number of books on petroleum refining, very few of them can be considered suitable for teaching the subject in a manner that integrates engineering fundamentals and petroleum refining technology. Our book has more in-depth coverage and more examples on using computational tools.

Fundamentals of Petroleum Refining serves both professionals and academics. It is mainly directed towards undergraduate and graduate students in Chemical and Petroleum Engineering, Chemistry and Chemical Technology. College graduates new to the field of engineering, who may just be starting their careers in the oil and gas industry, will also find the text useful. Professionals and academics will also benefit from this book. For experienced engineers and managers, *Fundamentals of Petroleum Refining* is ideal for acquiring the necessary background in the field and understanding new applications in the refining industry.

The book includes important subjects which are not commonly considered in refinery textbooks. Topics include clean fuels, gasification, biofuels and the environmental impact of refining. Throughout the book, numerous problem sets and examples are given in order to put the fundamental principles of refining into practice. Many worked examples offer clear understanding of the covered subjects. Excel spreadsheets for property and material balance calculations help in performing detailed and repetitive calculations and these are to be found at http://www.elsevierdirect.com/companions/9780444527851. Examples on using process simulators (UNISIM) are also presented. The text begins with an introduction to the petroleum refining industry then focuses on feedstocks and products in Chapters 1 and 2. Chapter 3 covers the subject of calculating the thermophysical properties of crude oils and petroleum fractions. Atmospheric and vacuum distillations are covered in Chapter 4. Major conversion processes are described in Chapters 5–8. These chapters cover the subjects of catalytic reforming and isomerization, coking, hydroconversion (hydrotreating and hydrocracking) and fluid catalytic cracking. Product blending is covered in Chapter 9, and alkylation is explained in Chapter 10. The subject of hydrogen production, which is of principal importance in a modern refinery, is covered in Chapter 11. Due to the changing energy outlook in terms of pollution regulations on burning fuels, clean fuel production is discussed in Chapter 12.

A great deal of attention has been given in the last few years to residue upgrading in order to improve the economics of refining. Chapter 13 discusses this issue in detail. Refinery safety is also an important topic and is thoroughly reviewed in Chapter 14. Acid gas treatment and removal are discussed in Chapter 15. The factors related to refinery economics are reviewed in Chapter 16. Environmental and effluent treatment methods are discussed in Chapter 17. An overall case study is given in Chapter 18.

Chapters 1–10 can be used as core materials for teaching an undergraduate course in petroleum refining. If time allows, parts of other chapters can also be used. The book also covers more advanced topics, which might be used for an introductory graduate course. Throughout the book, empirical correlations are used to calculate product yields and perform material balances. These correlations are mainly based on regression of published pilot plant data.

The authors would like to thank Dr Souad Al-Radwan and Engineer Hussein Said of Kuwait National Petroleum Company (KNPC) for their valuable comments on some technical issues. We would also like to thank Engineers Mohamed Hamed and Khalid Damiyar for their technical help during the production of this book. Many thanks go to Ms Jennifer Baran for her excellent proofreading and language editing of the book.

CHAPTER ONE

INTRODUCTION

1.1. INTRODUCTION

Petroleum refining plays an important role in our lives. Most transportation vehicles are powered by refined products such as gasoline, diesel, aviation turbine kerosene (ATK) and fuel oil. The recent price rise of crude oil from \$50 to \$150 per bbl over the last 2 years has affected the refining industry in three ways: First is an increased search for fuel products from non-fossil sources such as biodiesel and alcohols from vegetable sources, second is the development of better methods to process tar sand, coal gasification and synthesis of fuels by Fischer–Tropsch (FT) technology and third is the initiation of long-term plans to look for renewable energy sources. However, crude oil prices are still a cheap source for transportation fuels and petrochemicals.

On the other hand, stricter environment regulations have raised the cost of producing clean fuels. This motivated the search for producing clean fuels by non-conventional methods, such as by ambient desulphurization by liquid oxidants. Olefin alkylation and Fischer–Tropsch are other possible methods for producing clean fuels. New technology and better design of refinery equipment are also being developed in order to produce clean and less expense fuels.

In the modern refinery, the refining processes are classified as either physical separation or chemical conversion ones. Examples for each class are given in Table 1.1.

1.2. REFINING PROCESSES

1.2.1. Physical Separation Processes

1.2.1.1. Crude Distillation

Crude oils are first desalted and then introduced with steam to an atmospheric distillation column. The atmospheric residue is then introduced to a vacuum distillation tower operating at about 50 mmHg, where heavier products are obtained. Typical products from both columns and their boiling point ranges are listed in Table 1.2.

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Table 1.1 Major refining processes in modern refineries

	Chemical conversion	
Physical separation	**Catalytic**	**Thermal**
Distillation	Reforming	Delayed coking
Solvent deasphalting	Hydrotreating	Flexicoking
Solvent extraction	Hydrocracking	Visbreaking
Solvent dewaxing	Alkylation	
	Isomerization	

Table 1.2 Crude distillation products (Gary and Handwerk, 2001)

	Yield (wt%)*	True boiling temperature (°C)
Atmospheric distillation		
Refinery gases ($C_1 - C_2$)	0.10	–
Liquid petroleum gases (LPG)	0.69	–
Light straight run (LSR)	3.47	32–82 (90–180 °F)
Heavy straight run (HSR)	10.17	82–193 (180–380 °F)
Kerosene (Kero)	15.32	193–271 (380–520 °F)
Light gas oil (LGO)	12.21	271–321 (520–610 °F)
Heavy gas oil (HGO)	21.10	321–427 (610–800 °F)
Vacuum distillation		
Vacuum gas oil (VGO)	16.80	427–566 (800–1050 °F)
Vacuum residue (VR)	20.30	+566 (+1050 °F)

*The yields quoted here depend on feed composition and properties. In this case feed API was 26.3.

1.2.1.2. Solvent Deasphalting

This is the only physical process where carbon is rejected from heavy petroleum fraction such as vacuum residue. Propane in liquid form (at moderate pressure) is usually used to dissolve the whole oil, leaving asphaltene to precipitate. The deasphalted oil (DAO) has low sulphur and metal contents since these are removed with asphaltene. This oil is also called "Bright Stock" and is used as feedstock for lube oil plant. The DAO can also be sent to cracking units to increase light oil production.

1.2.1.3. Solvent Extraction

In this process, lube oil stock is treated by a solvent, such as *N*-methyl pyrrolidone (NMP), which can dissolve the aromatic components in one phase (extract) and the rest of the oil in another phase (raffinate). The solvent is removed from both phases and the raffinate is dewaxed.

1.2.1.4. Solvent Dewaxing

The raffinate is dissolved in a solvent (methyl ethyl ketone, MEK) and the solution is gradually chilled, during which high molecular weight paraffin (wax) is crystallized, and the remaining solution is filtered. The extracted and dewaxed resulting oil is called ''lube oil''. In some modern refineries removal of aromatics and waxes is carried out by catalytic processes in ''all hydrogenation process''.

1.2.2. Chemical Catalytic Conversion Processes

1.2.2.1. Catalytic Reforming

In this process a special catalyst (platinum metal supported on silica or silica base alumina) is used to restructure naphtha fraction (C_6–C_{10}) into aromatics and isoparaffins. The produced naphtha reformate has a much higher octane number than the feed. This reformate is used in gasoline formulation and as a feedstock for aromatic production (benzene–toluene–xylene, BTX).

1.2.2.2. Hydrotreating

This is one of the major processes for the cleaning of petroleum fractions from impurities such as sulphur, nitrogen, oxy-compounds, chloro-compounds, aromatics, waxes and metals using hydrogen. The catalyst is selected to suit the degree of hydrotreating and type of impurity. Catalysts, such as cobalt and molybdenum oxides on alumina matrix, are commonly used.

1.2.2.3. Catalytic Hydrocracking

For higher molecular weight fractions such as atmospheric residues (AR) and vacuum gas oils (VGOs), cracking in the presence of hydrogen is required to get light products. In this case a dual function catalyst is used. It is composed of a zeolite catalyst for the cracking function and rare earth metals supported on alumina for the hydrogenation function. The main products are kerosene, jet fuel, diesel and fuel oil.

1.2.2.4. Catalytic Cracking

Fluid catalytic cracking (FCC) is the main player for the production of gasoline. The catalyst in this case is a zeolite base for the cracking function. The main feed to FCC is VGO and the product is gasoline, but some gas oil and refinery gases are also produced.

1.2.2.5. Alkylation

Alkylation is the process in which isobutane reacts with olefins such as butylene ($C_4^{=}$) to produce a gasoline range alkylate. The catalyst in this case is either sulphuric acid or hydrofluoric acid. The hydrocarbons and acid react in liquid phase. Isobutane and olefins are collected mainly from FCC and delayed coker.

1.2.2.6. Isomerization

Isomerization of light naphtha is the process in which low octane number hydrocarbons (C_4, C_5, C_6) are transformed to a branched product with the same carbon number. This process produces high octane number products. One main advantage of this process is to separate hexane (C_6) before it enters the reformer, thus preventing the formation of benzene which produces carcinogenic products on combustion with gasoline. The main catalyst in this case is a Pt-zeolite base.

1.2.3. Thermal Chemical Conversion Processes

These processes are considered as upgrading processes for vacuum residue.

1.2.3.1. Delayed Coking

This process is based on the thermal cracking of vacuum residue by carbon rejection forming coke and lighter products such as gases, gasoline and gas oils. Three types of coke can be produced: sponge, shot and needle. The vacuum residue is heated in a furnace and flashed into large drums where coke is deposited on the walls of these drums, and the rest of the products are separated by distillation.

1.2.3.2. Flexicoking

In this thermal process, most of the coke is gasified into fuel gas using steam and air. The burning of coke by air will provide the heat required for thermal cracking. The products are gases, gasoline and gas oils with very little coke.

1.2.3.3. Visbreaking

This is a mild thermal cracking process used to break the high viscosity and pour points of vacuum residue to the level which can be used in further downstream processes. In this case, the residue is either broken in the furnace coil (coil visbreaking) or soaked in a reactor for a few minutes (soaker visbreaker). The products are gases, gasoline, gas oil and the unconverted residue.

A schematic diagram of a modern refinery containing most of the processes described above is given in Figure 1.1 (Gary and Handwerk, 2001).

1.3. REFINERY CONFIGURATION

The refinery configuration can range from single topping for crude distillation to high conversion refinery for petro-refinery. This will depend on the factors indicated in the following sections (Jones and Pufado, 2005):

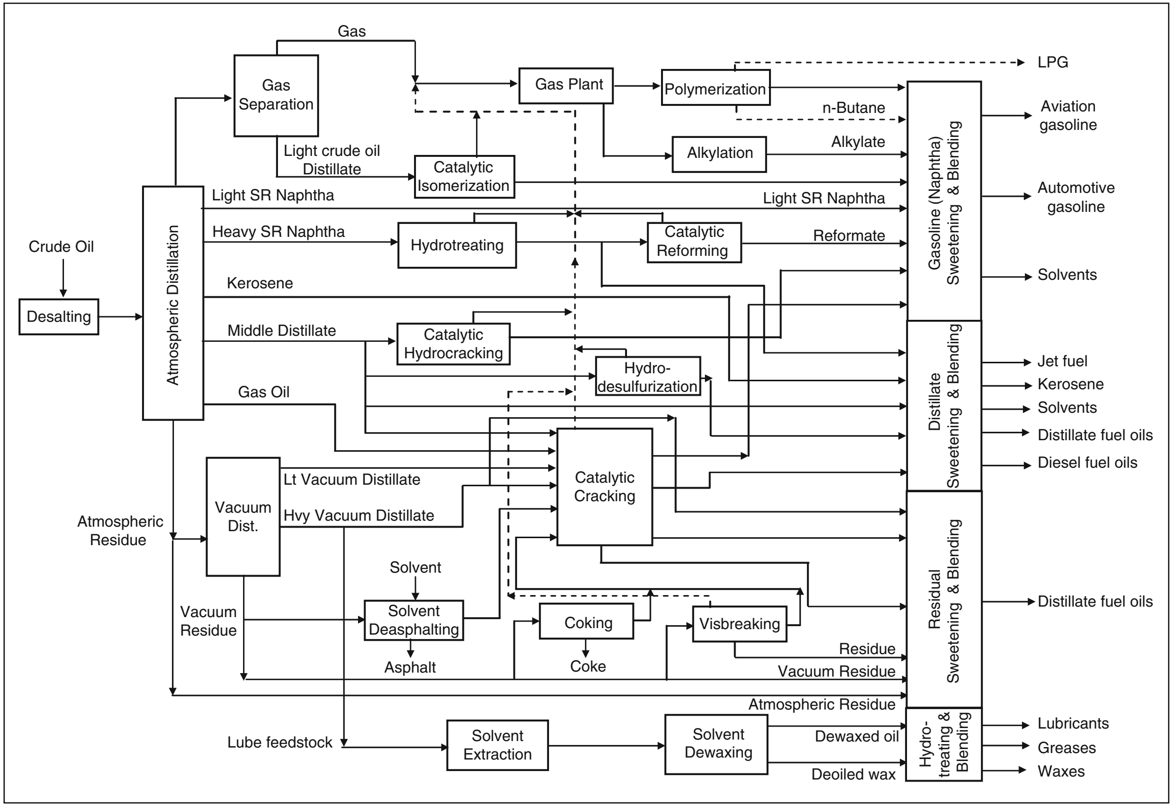

Figure 1.1 The Modern refinery

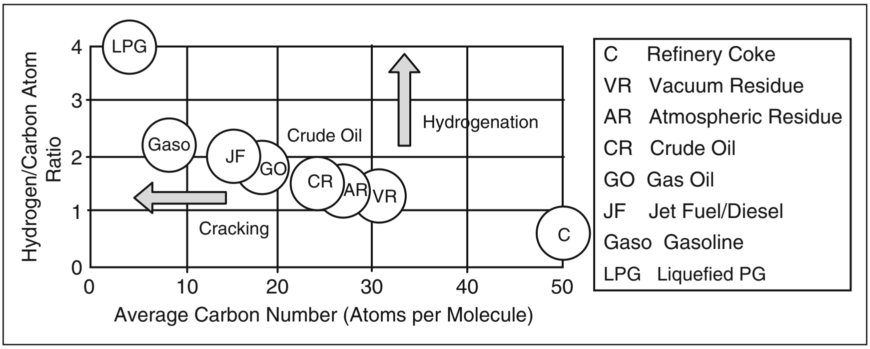

Figure 1.2 Petroleum products (Speight, 1999)

1.3.1. Type of Products

In this case, refining is carried out by increasing the hydrogen/carbon (H/C) ratio. This can be achieved either by hydrogenation processes such as hydrotreating, hydrocracking or by carbon rejection processes such as thermal cracking (coking) and FCC. The products of such processes are shown in Fig. 1.2 (Speight, 1999).

Some products can also be produced by special refining operations, like in catalytic reforming, isomerization and alkylation. In Figure 1.2, the products are classified in terms of average carbon number and H/C ratios.

1.3.2. Environmental Regulation

Modern regulations in many countries require a low level of contaminants like sulphur. This requires the change of severity or design of hydroconversion units which can produce ultra low sulphur products. Clean fuels are gaining great interest, and completely new refinery configurations are now being introduced to produce clean fuels from new refinery feeds and configurations. Additional units have been added to existing refineries to handle untreated gas emissions and refinery waste water due to changes in environmental regulations.

1.3.3. Crude Assay and Quality

Crude quality is getting heavier worldwide. Existing refineries, which are designed to handle normal crudes are being modified to handle heavy crude. New technology for upgrading is used to obtain clean and light products from lower cost feeds. The crude assay will determine the yields of different cuts and consequently, the refinery configuration. A high conversion cracking-coking refinery is shown in Figure 1.3 (Jones and Pufado, 2005).

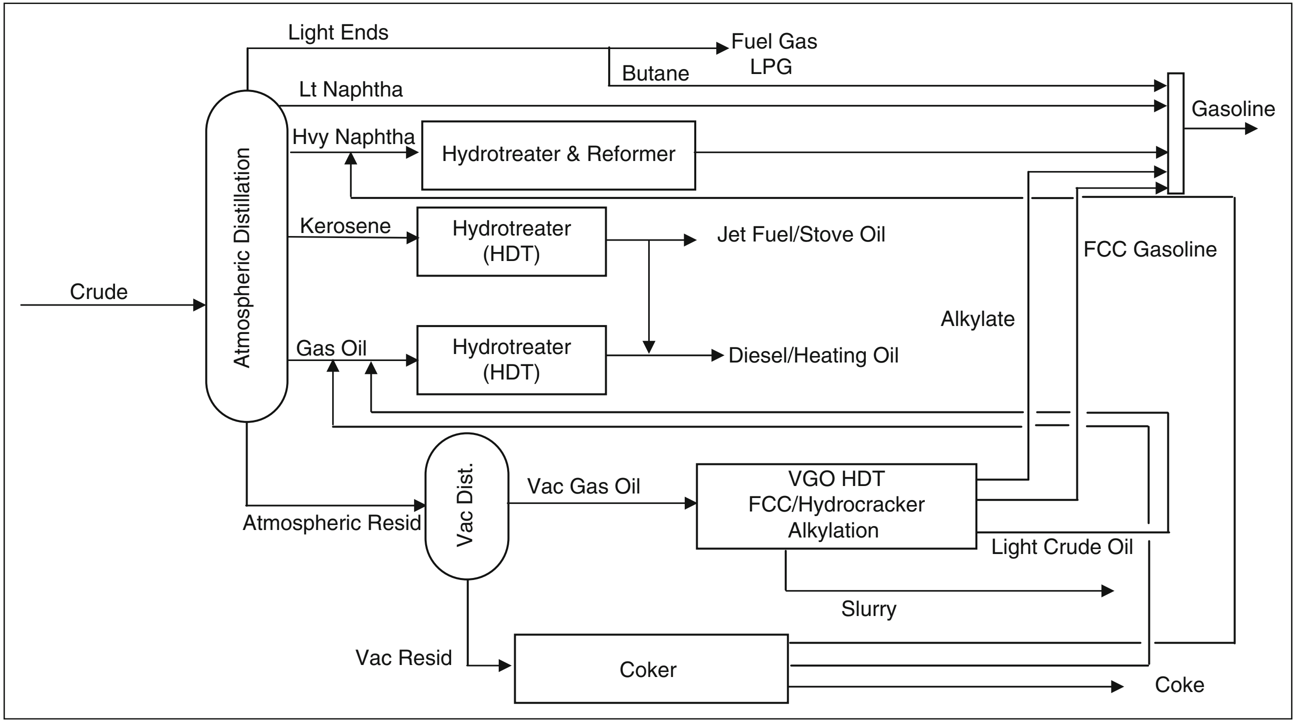

Figure 1.3 A high conversion refinery

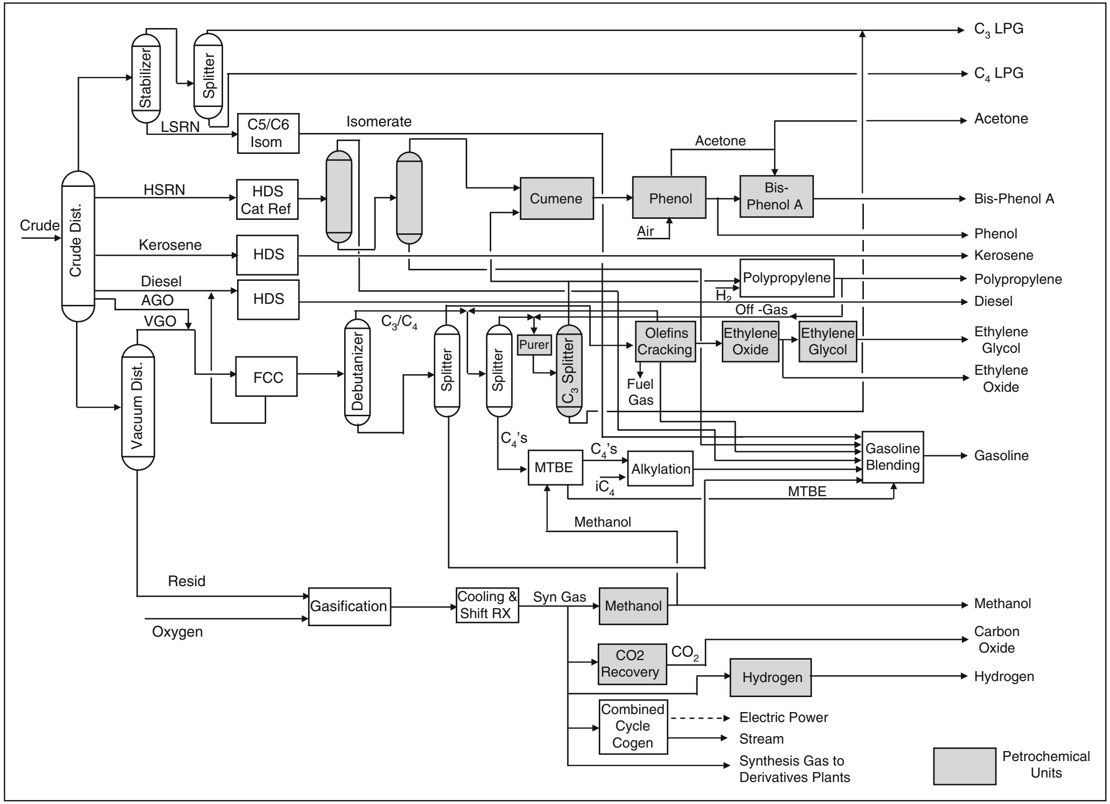

Figure 1.4 Refinery-petrochemical integration

1.3.4. Refinery-petrochemical Integration

The growth of the petrochemical industry has put pressure on refineries to either change their configuration or operating conditions to produce more aromatics and gases. FCC has been developed to petro-FCC which produces high yield of gases. The phasing out of the idea of increasing the octane number by increasing aromatic content has changed the role of the catalytic reformer to produce a high yield of aromatics as BTX feedstock. The addition of gasification units to process vacuum residue has opened the way for the addition of a variety of petrochemicals. Such a refinery-petrochemical configuration is shown in Fig. 1.4 (Crawford *et al.*, 2002).

1.3.5. Development of New Technology

If a new technology is developed to give better yields, save energy, meet environmental regulations and product specifications, then this technology might replace old technology in existing and new refineries, depending on the economics. Other factors, which might influence the refinery configuration, are feedstock availability, product markets and a company's strategic objectives.

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CHAPTER TWO

REFINERY FEEDSTOCKS AND PRODUCTS

2.1. INTRODUCTION

A petroleum refining study starts with describing its feedstock, the crude oil and the range of products that are produced by the various processes. Crude oil comes from different parts of the world and has different physical and chemical characteristics. On the other hand, the products that are produced have to meet market requirements and as such, should comply with certain specifications.

2.2. COMPOSITION OF CRUDE OILS

Crude oil is a complex liquid mixture made up of a vast number of hydrocarbon compounds that consist mainly of carbon and hydrogen in differing proportions. In addition, small amounts of organic compounds containing sulphur, oxygen, nitrogen and metals such as vanadium, nickel, iron and copper are also present. Hydrogen to carbon ratios affect the physical properties of crude oil. As the hydrogen to carbon ratio decreases, the gravity and boiling point of the hydrocarbon compounds increases. Moreover, the higher the hydrogen to carbon ratio of the feedstock, the higher its value is to a refinery because less hydrogen is required.

The composition of crude oil, on an elemental basis, falls within certain ranges regardless of its origin. Table 2.1 shows that carbon and hydrogen contents vary within narrow ranges. For this reason, crude oil is not classified on the basis of carbon content. Despite their low concentrations, impurities such as sulphur, nitrogen, oxygen and metals are undesirable because they cause concerns in the processability of crude feedstock and because they affect the quality of the produced products. Catalyst poisoning and corrosion are the most noticeable effects during refining.

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Table 2.1 Elemental composition of crude oils (Roussel and Boulet, 1995c)

Element	Composition (wt%)
Carbon	83.0–87.0
Hydrogen	10.0–14.0
Sulphur	0.05–6.0
Nitrogen	0.1–0.2
Oxygen	0.05–2.0
Ni	<120 ppm
V	<1200 ppm

There are three main classes of hydrocarbons. These are based on the type of carbon–carbon bonds present (Roussel and Boulet, 1995b). These classes are:

- *Saturated hydrocarbons* contain only carbon–carbon single bonds. They are known as *paraffins* (or *alkanes*) if they are acyclic, or *naphthenes* (or *cycloalkanes*) if they are cyclic.
- *Unsaturated hydrocarbons* contain carbon–carbon multiple bonds (double, triple or both). These are unsaturated because they contain fewer hydrogens per carbon than paraffins. Unsaturated hydrocarbons are known as *olefins*. Those that contain a carbon–carbon double bond are called *alkenes*, while those with carbon–carbon triple bond are *alkyenes*.
- *Aromatic hydrocarbons* are special class of cyclic compounds related in structure to benzene.

2.2.1. Paraffins

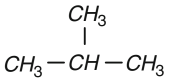
Paraffins, also known as *alkanes*, are saturated compounds that have the general formula C_nH_{2n+2}, where n is the number of carbon atoms. The simplest alkane is methane (CH_4), which is also represented as C_1.

Normal paraffins (n-paraffins or n-alkanes) are unbranched straight-chain molecules. Each member of these paraffins differs from the next higher and the next lower member by a $-CH_2-$ group called a methylene group (Table 2.2). They have similar chemical and physical properties, which change gradually as carbon atoms are added to the chain.

Isoparaffins (or *isoalkanes*) are branched-type hydrocarbons that exhibit structural isomerization. *Structural isomerization* occurs when two molecules have the same atoms but different bonds. In other words, the molecules have the same formulas but different arrangements of atoms, known as *isomers*. Butane and all succeeding alkanes can exist as straight-chain molecules (n-paraffins) or with a branched-chain structure (isoparaffins). For example, butane and pentane have the following structural isomers:

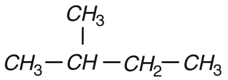
$CH_3-CH_2-CH_2-CH_3$
n-Butane

$CH_3-CH_2-CH_2-CH_2-CH_3$
n-Pentane



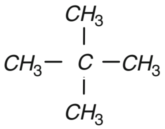
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$

Isobutane
(2-methylpropane)



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$

isopentane
(2-methylbutane)



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$

neopentane
(2,2-dimethylpropane)

Table 2.2 Names and formulas of the first ten parrafins (alkanes)

Name	Number of carbon atoms	Molecular formula	Structural formula	Number of isomers
Methane	1	CH_4	CH_4	1
Ethane	2	C_2H_6	CH_3CH_3	1
Propane	3	C_3H_8	$CH_3CH_2CH_3$	1
Butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
Pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
Hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
Heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
Octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
Nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
Decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

The number of isomers increases geometrically with the carbon number. While there are two isomers for butane and three for pentane, there are 75 isomers for decane ($C_{10}H_{22}$). For paraffins in the range of C_5–C_{12}, there are more than 600 isomers with only 200–400 that are identified in petroleum fractions. Because of their different structures, these isomers have different properties. For instance, the presence of isoparaffins in gasoline is essential for increasing the octane number of gasoline fuels.

2.2.2. Olefins

Olefins, also known as *alkenes*, are unsaturated hydrocarbons containing carbon–carbon double bonds. Compounds containing carbon–carbon triple bonds are known as *acetylenes*, and are also known as *biolefins* or *alkynes*. The general formulas of olefins and acetylenes are $C_nH_{2n}(R–CH=CH–R')$ and $C_nH_{2n-2}(R–CH\equiv C–R')$, respectively. Unsaturated compounds may have more than one double or triple bond. If two double bonds are present, the compounds are called *alkadienes* or, more commonly, *dienes* ($R–CH=CH–CH=R'$). There are also trienes, tetraenes and even polyenes.

Olefins are not naturally present in crude oils but they are formed during the conversion processes. They are more reactive than paraffins. The lightest alkenes are ethylene (C_2H_4) and propylene (C_3H_6), which are important feedstocks for the petrochemical industry. The lightest alkyne is acetylene.

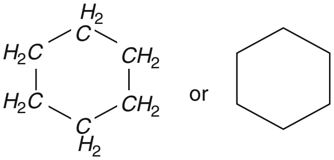
$H_2C=CH_2$
Ethylene
(ethene)

$CH_3-CH=CH_2$
Propylene
(propene)

$HC\equiv CH$
Acetylene
(ethyne)

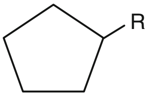
2.2.3. Naphthenes (cycloalkanes)

Naphthenes, also known as *cycloalkanes*, are saturated hydrocarbons that have at least one ring of carbon atoms. They have the general formula C_nH_{2n}. A common example is cyclohexane (C_6H_{12}).

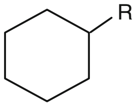


Cyclohexane

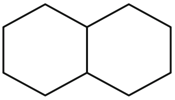
The boiling point and densities of naphthenes are higher than those of alkanes having the same number of carbon atoms. Naphthenes commonly present in crude oil are rings with five or six carbon atoms. These rings usually have alkyl substituents attached to them. Mutli-ring naphthenes are present in the heavier parts of the crude oil. Examples of naphthenes are shown below.



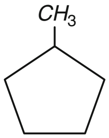
Alkylcyclopentanes



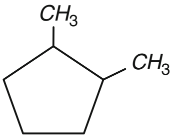
Alkylcyclohexanes



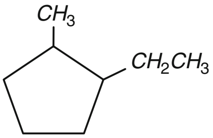
Bicycloalkanes



methylcyclopentane



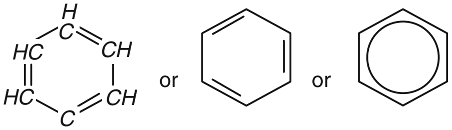
1,2-dimethylcyclopentane



1-ethyl-2-methylcyclopentane

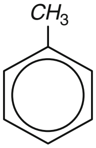
2.2.4. Aromatics

Aromatics are unsaturated cyclic compounds composed of one or more benzene rings. The benzene ring has three double bonds with unique electron arrangements that make it quite stable.

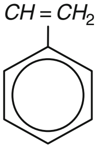


Benzene

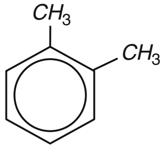
Crude oils from various origins contain different types of aromatic compounds in different concentrations. Light petroleum fractions contain mono-aromatics, which have one benzene ring with one or more of the hydrogen atoms substituted by another atom or alkyl groups. Examples of these compounds are toluene and xylene. Together with benzene, such compounds are important petrochemical feedstocks, and their presence in gasoline increases the octane number.



Toluene
(methylbenzene)

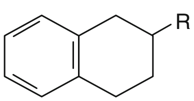


Styrene

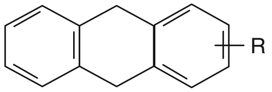


o-xylene
(1,2-Dimethylbenzene)

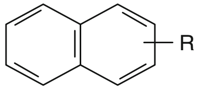
More complex aromatic compounds consist of a number of “fused” benzene rings. These are known as *polynuclear aromatic compounds*. They are found in the heavy petroleum cuts, and their presence is undesirable because they cause catalyst deactivation and coke deposition during processing, besides causing environmental problems when they are present in diesel and fuel oils. The heaviest portion of the crude oil contains asphaltenes, which are condensed polynuclear aromatic compounds of complex structure. Examples of polynuclear aromatic compounds are shown below.



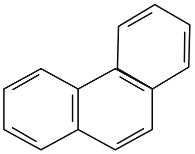
Aromatic-cycloalkanes



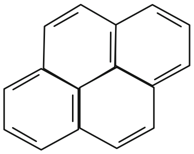
Fluorenes



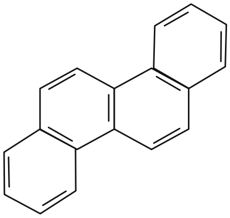
Binuclear aromatics



Phenanthrene



Pyrene



Chrysene

2.2.5. Sulphur Compounds

The Sulphur content of crude oils varies from less than 0.05 to more than 10 wt% but generally falls in the range 1–4 wt%. Crude oil with less than 1 wt % sulphur is referred to as low sulphur or sweet, and that with more than 1 wt% sulphur is referred to as high sulphur or sour.

Crude oils contain sulphur heteroatoms in the form of elemental sulphur S, dissolved hydrogen sulphide H_2S, carbonyl sulphide COS, inorganic forms and most importantly organic forms, in which sulphur atoms are positioned within the organic hydrocarbon molecules.

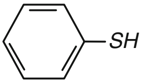
Sulphur containing constituents of crude oils vary from simple mercaptans, also known as thiols, to sulphides and polycyclic sulphides. Mercaptans are made of an alkyl chain with –SH group at the end (R–SH). Examples of mercaptans and sulphides are as follows:

CH_3SH

methyl mercaptan
(methanethiol)

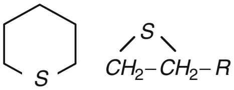
$CH_3CH_2CH_2CH_2SH$

n-butyl mercaptan
(1-butanethiol)

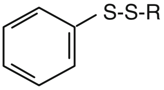


phenyl mercaptan
(thiophenol)

In sulphides and disulphides, the sulphur atom replaces one or two carbon atoms in the chain (R–S–R′ or R–S–S–R′). These compounds are often present in light fractions. Sulphides and disulphides may also be cyclic or aromatic.

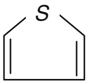


cyclic sulfides

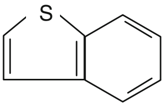


Aromatic disulfide

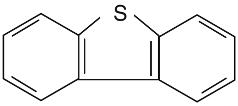
Thiophenes are polynuclear aromatic compounds (Chatila, 1995) in which the sulphur atom replaces one or more carbon atoms in the aromatic ring. They are normally present in heavier fractions. Thiophenes present in crude oils may have the following formulas:



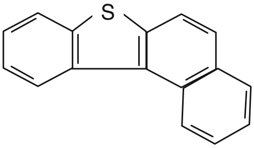
Thiophene



Benzothiophene



Dibenzothiophene



Naphthobenzothiophene

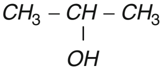
2.2.6. Oxygen Compounds

The oxygen content of crude oil is usually less than 2 wt%. A phenomenally high oxygen content indicates that the oil has suffered prolonged exposure to the atmosphere. Oxygen in crude oil can occur in a variety of forms. These include alcohols, ethers, carboxylic acids, phenolic compounds, ketones, esters and anhydrides. The presence of such compounds causes the crude to be acidic with consequent processing problems such as corrosion.

Alcohols have the general formula R–OH and are structurally similar to water but with one of the hydrogen atoms replaced by an alkyl group. In *phenols*, one of the hydrogen atoms in the aromatic ring is replaced with a hydroxyl group (–OH). *Ethers* have two organic groups connected to a single oxygen atom (R–O–R′). Examples of alcohols, phenols and ethers are:

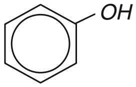
CH_3-OH

methyl alcohol
(methanol)



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

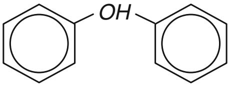
isopropyl alcohol
(2-propanol)



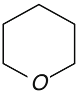
phenyl alcohol
(phenol)

$CH_3CH_2-O-CH_3$

ethyl methyl ether

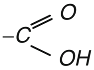


diphenyl ether

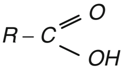


tetrahydropyran
(cyclic ether)
pentamethylene oxide

Carboxylic acids have a carboxyl group as their functional group (–COOH), and their general formula can be written as:



carboxyl group



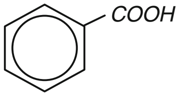
or $R-COOH$

carboxylic acid

Examples of aliphatic and aromatic carboxylic acids are:

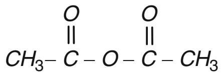
CH_3-COOH

acetic acid
(ethanoic acid)



benzoic acid
(benzenecarboxylic acid)

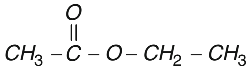
Carboxylic acid anhydrides are formed by removing water from two carboxyl groups and connecting the fragments. The most important aliphatic anhydride is acetic anhydride.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

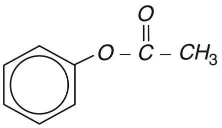
acetic anhydride
(ethanoic anhydride)

Carboxylic acid esters are formed by replacing the –COOH by –COOR group. Examples are:



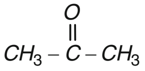
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3$$

ethyl acetate
(ethyl ethanoate)



phenyl acetate

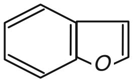
Ketones are compounds with two carbon atoms bounded to the carbon of a carbonyl group $>C=O$. *Furans* are hetroaromatic compounds with five-member oxygenated rings. *Benzofuran* is a furan condensed with an aromatic ring. Examples are:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

dimethyl ketone
(acetone)

furan



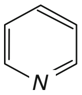
Benzofuran

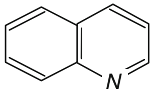
2.2.7. Nitrogen Compounds

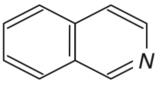
Crude oils contain very low amounts of nitrogen compounds. In general, the more asphaltic the oil, the higher its nitrogen content. Nitrogen compounds are more stable than sulphur compounds and therefore are harder to remove. Even though they are present at very low concentrations, nitrogen compounds have great significance in refinery operations. They can be responsible for the poisoning of a cracking catalyst, and they also contribute to gum formation in finished products.

The nitrogen compounds in crude oils may be classified as basic or non-basic. Basic nitrogen compounds consist of pyridines. The greater part of the nitrogen in crude oils is the non-basic nitrogen compounds, which are generally of pyrrole types.

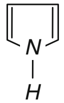
Pyridines are six-membered heteroaromatic compounds containing one nitrogen atom. When fused with benzene rings, pyridines are converted to the polycyclic heteroaromatic compounds *quinolines* and *isoquinolines*.

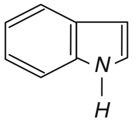

pyridine
(C_2H_5N)

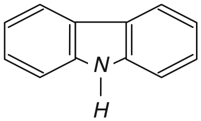

quinoline
(C_9H_7N)


isoquinoline
(C_9H_7N)

In non-basic nitrogen compounds, *pyrroles* are five-membered heteroaromatic compounds containing one nitrogen atom. When fused with benzene ring, pyrrole is converted to the polycyclic heteroaromatic compounds *indole* and *carbazole*.


pyrrole
(C_4H_5N)


indole
(C_8H_7N)


carbazole
($C_{12}H_9N$)

2.2.8. Metallic Compounds

Metallic compounds exist in all crude oil types in very small amounts. Their concentration must be reduced to avoid operational problems and to prevent them from contaminating the products. Metals affect many upgrading processes. They cause poisoning to the catalysts used for hydroprocessing and cracking. Even minute amounts of metals (iron, nickel and vanadium) in the feedstock to the catalytic cracker affect the activity of the catalyst and result in increased gas and coke formation and reduced gasoline yields. For high-temperature power generators, the presence of vanadium in the fuel may lead to ash deposits on turbine blades and cause severe corrosion, and the deterioration of refractory furnace linings.

Part of the metallic constituents of crude oils exist as inorganic water-soluble salts, mainly as chlorides and sulphates of sodium, potassium, magnesium and calcium. These are removed in desalting operations. More important are metals which are present in form of oil-soluble organometallic compounds. Zinc, titanium, calcium and magnesium appear in the form of organometallic soaps. However, vanadium, nickel, copper and iron are present as oil-soluble compounds, capable of complexing with pyrrole compounds.

2.2.9. Asphaltenes and Resins

The physical properties of crude oils, such as the specific gravity (or API), are considerably influenced by high-boiling constituents, in which the heteroatoms (sulphur, nitrogen and metals) concentrate. It is therefore important to characterize the heaviest fractions of crude oils in order to determine their properties and ease of processing. This calls for determining the percentage of two generally defined classes of compounds, namely asphaltenes and resins.

Asphaltenes are dark brown friable solids that have no definite melting point and usually leave carbonaceous residue on heating. They are made up of condensed polynuclear aromatic layers linked by saturated links. These layers are folded, creating a solid structure known as a micelle. Their molecular weights span a wide range, from a few hundred to several million. Asphaltenes are separated from petroleum in the laboratory using non-polar solvents such as pentane and *n*-heptane. Liquefied petroleum fractions (propane and butane) are used commercially in deasphalting residues and lube stock oils.

The presence of high amounts of asphaltenes in crude oil can create tremendous problems in production because they tend to precipitate inside the pores of rock formations, well heads and surface processing equipments. They may also lead to transportation problems because they contribute to gravity and viscosity increases of crude oils. In refinery operations, asphaltenes have markedly adverse effects on the processability of crude oils. They lead to coke formation and metal deposition on the catalyst surface causing catalyst deactivation.

Resins are polar molecules in the molecular weight range of 500–1000, which are insoluble in liquid propane but soluble in *n*-heptane. It is believed that the resins are responsible for dissolving and stabilizing the solid asphaltene molecules in petroleum. The resin molecules surround the asphaltene clusters (micelles) and suspend them in liquid oil. Because each asphaltene is surrounded by a number of resin molecules, the content of resins in crude oils is higher than that of the asphaltenes.

The characterization of crude oils and petroleum fractions involves fractionation techniques, measurement of physical and chemical properties and analytical techniques for compositional measurements.

2.3. PRODUCTS COMPOSITION

There are specifications for over 2000 individual refinery products. Intermediate feed stocks can be routed to various units to produce different blend products depending on market demand. Figure 2.1 shows typical refinery products with their carbon atom contents and boiling ranges. The specifications of each product are discussed in detail in the coming subsections (Roussel and Boulet, 1995a).

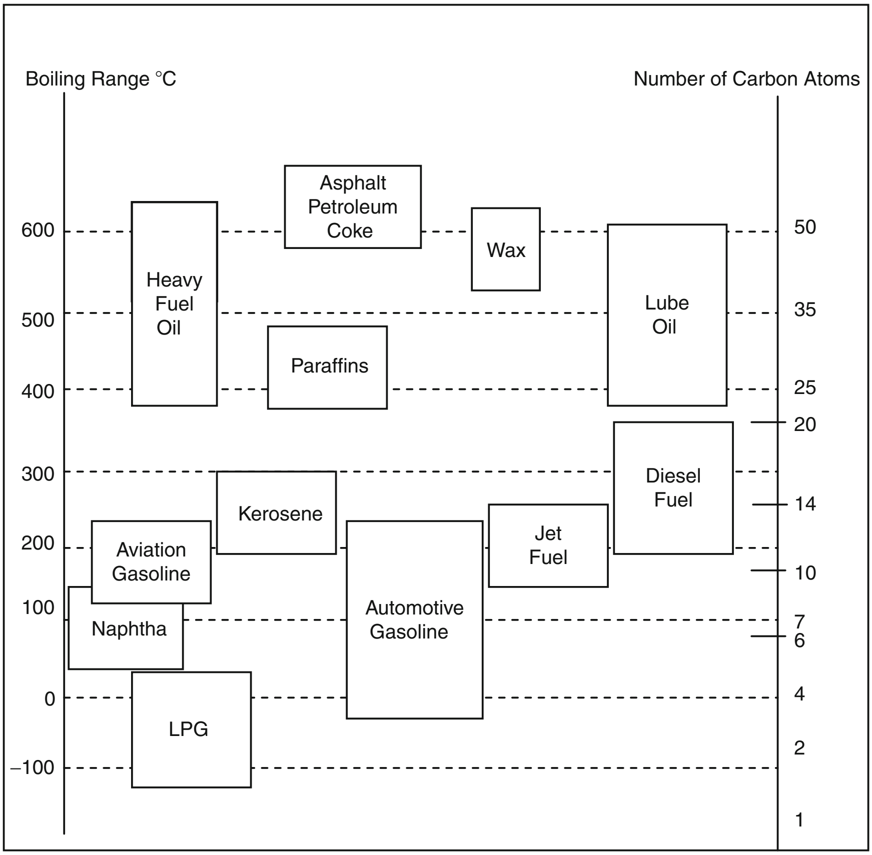


Figure 2.1 Principal petroleum products with carbon numbers and boiling ranges

2.3.1. Liquefied Petroleum Gas (LPG)

Liquified petroleum gas is a group of hydrocarbon-based gases derived from crude oil refining or natural gas fractionation. They include ethane, ethylene, propane, propylene, normal butane, butylene, isobutane and isobutylene. For convenience of transportation, these gases are liquefied through pressurization.

2.3.2. Gasoline

Gasoline is classified by octane ratings (conventional, oxygenated and reformulated) into three grades: Regular, Midgrade and Premium.

- Regular gasoline: Gasoline having an antiknock index, i.e. octane rating, greater than or equal to 85 and less than 88.
- Mid-grade gasoline: Gasoline having octane rating, greater than or equal to 88 and less than or equal to 90.
- Premium gasoline: Gasoline having octane rating greater than 90.

Premium and regular grade motor gasoline are used depending on the octane rating. In addition, aviation gasoline, which is a complex mixture of relatively volatile hydrocarbons, is blended with additives to form suitable fuel for aviation engines.

2.3.3. Kerosene

Kerosene is a light petroleum distillate that is used in space heaters, cook stoves and water heaters and which is suitable for use as a light source. Kerosene has a maximum distillation temperature of 204 °C (400 °F) at the 10% recovery point, a final boiling point of 300 °C (572 °F), and a minimum flash point of 37.8 °C (100 °F). The two grades are recognized by ASTM Specification D3699. A kerosene-type jet fuel-based product is having a maximum distillation temperature of 204 °C (400 °F) at the 10% recovery point and a final maximum boiling point of 300 °C (572 °F) and meeting ASTM Specification D1655.

2.3.4. Jet Fuel

This category comprises both gasoline and kerosene and meets specifications for use in aviation turbine power units.

2.3.5. Diesel Fuel

The quality of diesel fuels can be expressed as cetane number or cetane index. The cetane number (CN) is expressed in terms of the volume percent of cetane ($C_{16}H_{34}$) which has high ignition (CN = 100) in a mixture with alpha-methyl-naphthalene ($C_{11}H_{10}$) which has low ignition quality (CN = 0). Diesel fuel includes No.1 diesel (Super-diesel) which has cetane number of 45 and it is used in high speed engines, trucks and buses. No. 2 diesel has 40 cetane number. Railroad diesel fuels are similar to the heavier automotive diesel fuels, but have higher boiling ranges upto 400 °C (750 °F) and lower cetane numbers (CN = 30).

2.3.6. Fuel Oil

The fuel oils are mainly used in space heating and thus the market is quite high specially in cold climates. No. 1 fuel oil is similar to kerosene and No. 2 fuel oil is very similar to No. 2 diesel fuel. Heavier grades of No. 3 and 4 are also available.

2.3.7. Residual Fuel Oil

It is mainly composed of vacuum residue. Critical specifications are viscosity and sulphur content. Low sulphur residues are in more demand in the market.

2.3.8. Lube Oil

Lubricants are based on the viscosity index. Paraffinic and naphthenic lubricants have a finished viscosity index of more than 75.

2.3.9. Asphalt

Asphalt is an important product in the construction industry and comprises upto 20% of products. It can be produced only from crude containing asphaltenic material.

2.3.10. Petroleum Coke

Carbon compounds formed from thermal conversion of petroleum containing resins and asphaltenes are called petroleum cokes. Fuel grade coke contains about 85% carbon and 4% hydrogen. The balance is made up of sulphur, nitrogen, oxygen, vanadium and nickel.

2.4. PHYSICAL PROPERTY CHARACTERIZATION DATA

2.4.1. Fractionation

Distillation of crude oils determines the yield of the products that can be obtained from this crude oil when it is processed in a refinery. A light crude oil will produce higher amounts of gasoline than a heavier crude oil. Different standard distillation tests can be performed on crude oil or petroleum fractions.

2.4.2. True Boiling Point Distillation

The boiling point distribution of crude oil (boiling point versus volume or mass percent distilled) is obtained through a batch distillation test ASTM 2892. The distillation apparatus has 15–18 theoretical plates with a 5:1 reflux ratio. For boiling points below 340 °C (644 °F) the distillation is performed at atmospheric pressure. The residue is distilled under vacuum (1–10 mm Hg). The boiling points under vacuum are converted to normal boiling points. The distillation continues to a normal boiling point of

535 °C (995 °F). This test allows for the collection of sample cuts at different boiling point ranges. These cuts can be subjected to physical and chemical measurements.

2.4.3. ASTM Distillation

The distillation of petroleum cuts is done in a simple distillation apparatus which does not have a fractionation column. For light cuts (gasoline, kerosene, diesel and heating oil) the distillation is run at atmospheric pressure under ASTM D86 test. For heavier fractions an ASTM D1160 test at reduced pressure is employed.

2.4.4. Simulated Distillation by Gas Chromatography

The boiling point distribution of the whole crude oil can be determined by an injection of the sample in a gas chromatograph which separates the hydrocarbons in boiling point order. The retention time is related to the boiling point through a calibration curve. The results of this test are comparable to the true boiling point tests. In addition, the boiling point distribution of light and heavy petroleum cuts can also be done by gas chromatography. One of the standards methods of measurements is ASTM D5307.

2.4.5. API Gravity

The gravity of crude oil determines its price commercially. It is generally expressed as API gravity defined as:

$$\mathrm{API} = \frac{141.5}{\mathrm{SG}} - 131.5 \tag{2.1}$$

where SG is the specific gravity defined as the density of the crude oil relative to the density of water both at 15.6 °C (60 °F). The API gravity can range from 8.5 for very heavy crudes to 44 for light crudes. Crude oils can generally be classified according to gravity as shown in Table 2.3.

Table 2.3 Classification of crude oils

Crude Category	Gravity
Light crudes	$\mathrm{API} > 38$
Medium crudes	$38 > \mathrm{API} > 29$
Heavy crudes	$29 > \mathrm{API} > 8.5$
Very heavy crudes	$\mathrm{API} < 8.5$

The API gravity is also measured for various petroleum fractions. One of the standard tests is ASTM D1298.

2.4.6. Pour Point

The pour point is defined as the lowest temperature at which the sample will flow. It indicates how easy or difficult it is to pump the oil, especially in cold weather. It also indicates the aromaticity or the paraffinity of the crude oil or the fraction. A lower pour point means that the paraffin content is low. Pour points for the whole crude and fractions boiling above 232 °C (450 °F) are determined by standard tests like ASTM D97.

2.4.7. Viscosity

The resistance to flow or the pumpability of the crude oil or petroleum fraction is indicated by the viscosity. More viscous oils create a greater pressure drop when they flow in pipes. Viscosity measurement is expressed in terms of kinematic viscosity in centiStocks (cSt) and can also be expressed in saybolt seconds. The viscosity is measured at 37.8 °C (100 °F) by ASTM D445 and by ASTM D446 at 99 °C (210 °F).

2.4.8. Refractive Index

The refractive index is the ratio of the velocity of light in a vacuum to the velocity of light in the oil. This parameter is used as a characterization parameter for petroleum fraction composition as will be discussed in Chapter 3. It is measured according to ASTM D1218.

2.4.9. Freezing Point

Petroleum fractions are mostly liquids at ambient conditions. However, heavy oils contain heavy compounds such as waxes or asphaltenes. These compounds tend to solidify at low temperatures, thus restricting flow. The freezing point is the temperature at which the hydrocarbon liquid solidifies at atmospheric pressure. It is one of the important property specifications for kerosene and jet fuels due to the very low temperatures encountered at high altitudes in jet planes. One of the standard tests is ASTM D4790 and ASTM D16.

2.4.10. Aniline Point

The lowest temperature at which an equal volume mixture of the petroleum oil and aniline are miscible is the aniline point. Since aniline is an aromatic compound, a petroleum fractions with high aromatic content will be miscible in aniline at ambient conditions. However, if the oil has more paraffins, it will require a higher temperature and thus higher aniline point in order to be miscible in aniline. This property is important for the specifications of diesel fuels. It is measured by ASTM D611.

2.4.11. Flash Point

The flash point of a liquid hydrocarbon is the lowest temperature at which sufficient vapours are produced above the liquid such that spontaneous ignition will occur if a spark is present. It is an important specification for gasoline and naphtha related to safety in storage and transport in high-temperature environments. Flash point indicates the fire and explosion potential of a fuel. A low flash point fuel is a higher fire hazard. One of the standard tests is ASTM D1711, D09 and D1695.

2.4.12. Octane Number

An octane number is a measure of the knocking tendency of gasoline fuels in spark ignition engines. The ability of a fuel to resist auto-ignition during compression and prior to the spark ignition gives it a high octane number. The octane number of a fuel is determined by measuring its knocking value compared to the knocking of a mixture of *n*-heptane and isooctane (2,2,4-trimethyl pentane). Pure *n*-heptane is assigned a value of zero octane while isooctane is assigned 100 octane. Hence, an 80 vol% isooctane mixture has an octane number of 80. Two octane tests can be performed for gasoline. The motor octane number (MON) indicates engine performance at highway conditions with high speeds (900 rpm). On the other hand, the research octane number is indicative of low-speed city driving (600 rpm). The posted octane number (PON) is the arithmetic average of MON and RON. One of the standard tests is ASTM D2700.

2.4.13. Cetane Number

The cetane number measures the ability for auto ignition and is essentially the opposite of the octane number. The cetane number is the percentage of pure cetane (*n*-hexadecane) in a blend of cetane and alpha methyl naphthalene which matches the ignition quality of a diesel fuel sample. This quality is specified for middle distillate fuels. One of the standard tests is ASTM D976.

2.4.14. Smoke Point

The smoke point is a test measures the burning qualities of kerosene and jet fuel. It is defined as the maximum height in mm, of a smokeless flame of fuel. One of the standard tests is ASTM D1322.

2.4.15. Reid Vapour Pressure

The reid vapour pressure (RVP) of a product is the vapour pressure determined in a volume of air four times the liquid volume at 37.8 °C (100 °F). This property measures the vapour-lock tendency of a motor gasoline in which excessive vapours are produced in the fuel line causing interruption of the supply of liquid fuel to the engine. It also indicates the explosion and evaporation hazards of the fuel. One of the standard tests is ASTM D323.

2.4.16. Water, Salt and Sediment

Crude oil contains small amounts of water, mineral salts and sediments. Most of the salts are dissolved in the water, and the remainder is present in the oil as fine crystals. Chlorides of magnesium, calcium and sodium are the most common salts. The presence of salts causes problems in processing, such as corrosion, erosion and plugging of equipment, and catalyst deactivation. Sediments are solid material that are not soluble in the hydrocarbon or water and can be comprised of sand, drilling mud, rock or minerals coming from erosion of metal pipes, tanks and equipment. One of the standard tests is ASTM D6470.

2.4.17. Molecular Weight

Most crude oils and petroleum fractions have average molecular weights from 100 to 500. Although, there are several methods for measuring the molecular weight, the most suitable method is that based on freezing point depression.

2.5. CHEMICAL ANALYSIS DATA

2.5.1. Elemental Analysis

Carbon, hydrogen and nitrogen content of a petroleum fraction or crude oil can be determined by elemental analysis. The sample is combusted to carbon dioxide, sulphur dioxide, water and nitrogen oxides. The gases are separated and their quantities determined by different methods.

Of utmost importance is the determination of the sulphur content as it determines the processing scheme of the crude oil and thus the market value of the products. The analytical methods for sulphur determination are numerous and depend on the level of sulphur in the sample. The most widely used methods are based on combustion and X-ray fluorescence. Elemental analysis can be estimated by ASTM D5251.

Metal contents such as nickel (Ni), iron (Fe) and vanadium (V) can be also determined by elemental analysis. The methods used are in the category of X-ray fluorescence, atomic absorption and argon plasma. ASTM D5708 can be used for metal determination. Sulphur can be found by the X-ray method by ASTM D2622.

2.5.2. Carbon Residue

The carbon residue of a crude oil, heavy oil or residue is the weight percent of coke that remains after evaporation and cracking of the sample in the absence of air. Depending on the testing procedure used, the result is reported as Conradson or Ramsbottom carbon residue in weight percent. The carbon residue indicates the asphalt content of the oil or the amount of lubricating oils that can be produced from the processing of the oil. It is measured by ASTM D189.

2.5.3. Detailed Hydrocarbon Analysis

Detailed component analyses can be performed on petroleum gases and naphtha fractions by gas chromatography using different columns in a prescribed sequence. An internal standard is used to provide concentrations of the different compounds. A chromatogram can be used to calculate the parafins, isoparrafins, olefins and aromatic (PIONA) content of a sample. ASTM D5445 can be used in this case.

2.5.4. Hydrocarbon Family Analysis

Although gas chromatography can be used for the determination of individual compounds in naphtha fractions, this cannot be said about heavier cuts. Hydrocarbon family analyses by mass spectroscopy (MS) provide information on the relative amounts of different types of saturated and aromatic hydrocarbons. Examples of hydrocarbon families are paraffins, monocycloparaffins, alkylbenzenes, diaromatics, and the sulphur containing family of compounds like thiophenes. The results can be useful in yield calculations, since the correlations for the different processes contain parameters related to hydrocarbon family type. The ASTM D5368 can be used in this case.

2.5.5. Aromatic Carbon Content

The aromaticity of a petroleum cut is defined as the mole fraction of aromatic carbon in the sample as determined by carbon-13 nuclear magnetic resonance (NMR) spectroscopy. The ASTM D5292 can be used in this case.

2.5.6. SARA Analysis

The SARA analysis determines the content of saturate aromatics, resins and asphaltenes in crude oils, heavy cuts and residues. This information is useful in refinery design and operation. The analysis is also preparative, meaning that the test provides enough samples of the above four classes of compounds for further testing and analysis by the chemical analysis testing methods mentioned above (Speight, 1991).

The separation of these four classes of compounds is done in different stages. First, asphaltenes is precipitated by *n*-heptane. The deasphalted oil called maltenes is subjected to liquid chromatography. Liquid chromatography is similar in principles to gas chromatography in that the compounds are eluted from a packed column by a carrier, in this case a liquid instead of a gas. The saturated hydrocarbons are eluted by *n*-heptane, the aromatics by a 2:1 volume mixture of *n*-heptane and toluene and the resins by an equal volume mixture of dichloromethane, toluene and methanol. The ASTM D4124 can be used in this case. In Figure 2.2 a schematic diagram for SARA analysis is shown.

The testing grid for crude oil and different cuts obtained from atmospheric and vacuum distillation is shown in Table 2.4 (Strum and Shay, 2000).

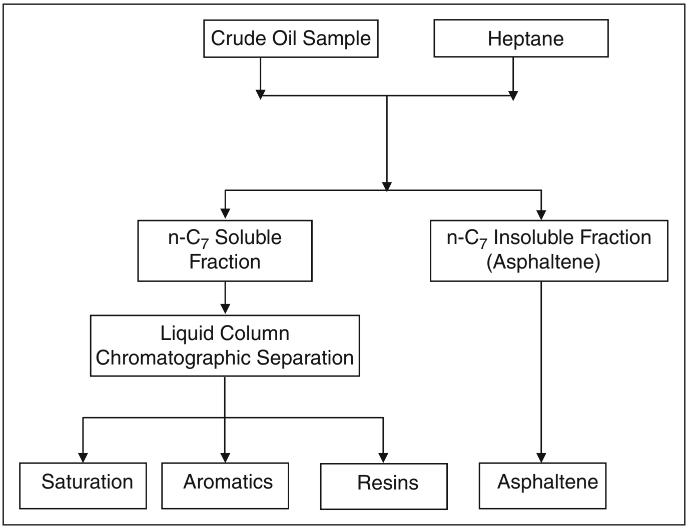


Figure 2.2 Schematic diagram of SARA analysis

Table 2.4 ASTM testing grid for crude oil and petroleum fractions (Strum and Shay, 2000)

	TBP (°F)	ASTM distillation (D86/D1160)	True boiling point (D2892))	Simulate distillation (D5307)	API/SG (D1298)	Total sulphur (D4294)	Mercaptants (D3227)	H_2S (D325)	Total nitrogen D4629	Viscosity (2 Temp) D445 (D446)	Pour point (D97)	Organic chlorides (D4929)	Acid number (D664)	Carbon residue (D189)	Metals (D5708)	Cetane index (D4737)	Aniline point (D611)	Smoke point (D1322)	Octane number (D2700)	Vapour pressure (D323)	Wax and asphaltene	Sediment and water (D473)	Salt content (D6470)	Refractive index (D1218)
Crude		×	×	×	×	×	×	×	×	×	×	×	×	×	×					×	×	×	×	×
LPG		×	×	×	×																			
LSR	90–180	×	×	×	×	×	×	×				×							×					
HSR	180–380	×	×	×	×	×	×	×				×					×		×					×
Kero	380–520	×	×		×	×	×	×	×	×		×	×			×	×	×						×
LGO	520–610	×	×		×	×			×	×	×		×			×	×	×						×
HGO	610–800	×	×		×	×			×	×	×			×	×						×			
VGO	800–1050				×	×			×	×	×			×		×	×				×			×
VR	1050^+				×	×			×	×				×	×						×			

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CHAPTER THREE

THERMOPHYSICAL PROPERTIES OF PETROLEUM FRACTIONS AND CRUDE OILS

3.1. INTRODUCTION

A petroleum refinery is a collection of unit operations, such as fractionation towers, pumps, and heat exchangers. Analysis and design of these units require knowledge of the thermodynamic and physical properties of the petroleum fluids. Designing a crude distillation tower requires knowledge on how hydrocarbons in crude oil are distributed on each tray of the tower, that is vapour–liquid distribution, and the densities of the mixture. Heat exchanger design depends on enthalpies, thermal conductivity and viscosity of the flowing streams. Table 3.1 lists the thermophysical properties required for the design and operation of almost all processing equipment in a refinery.

Due to the complexity of the composition of petroleum fractions and crude oils it is not possible to measure or calculate accurately all of these properties. Furthermore, calculation methods developed for pure hydrocarbons are not always applicable. Therefore, over the years chemical and petroleum refining engineers have developed special methods or correlations to estimate the properties of petroleum fraction from easily measured properties like normal boiling point (NBP) and specific gravity. Such methods and schemes characterize these petroleum fractions. Traditionally these correlations are developed to be simple to use, requiring minimum input data, and are usually presented in graphical form. At this stage, it is instructive to point out that there is a difference between the characterization of crude oils and narrow boiling petroleum fractions. For crude oils, mixture bulk properties cannot directly be used to estimate the properties of the mixture. While for narrow boiling fractions, mixture properties such as the average boiling point, specific gravity, and molecular weight may directly be used to predict many other properties as outlined in the API *Technical Data Book—Petroleum Refining (API-TDB)* (API, 1993).

Fundamentals of Petroleum Refining
DOI: 10.1016/B978-0-444-52785-1.00003-6

Table 3.1 Thermophysical property prediction

Thermodynamic properties
Enthalpy
Heat capacity
Compressibility factors
Equilibrium *K*-values
Flash curves
Transport properties
Viscosity
Thermal conductivity
Diffusivity
Physical properties
Densities
Volumes

3.2. BASIC INPUT DATA

The characterization of petroleum fractions requires several measurable laboratory properties:

- Specific gravity (SG)
- Boiling point curve (ASTM or true boiling point (TBP distillation)
- Kinematic viscosity at 37.8 °C (100 °F) and 98.9 °C (210 °F) (ν_{100}, ν_{210})
- Refractive index (n)
- Molecular weight (M)

With the exception of TBP distillation and molecular weight, these properties can be readily measured in any petroleum characterization laboratory. The meaning of these properties will be explained later.

3.2.1. Specific Gravity

Specific gravity for liquid oils is defined as:

$$\mathrm{SG}_{\mathrm{oil}} = \frac{\rho_{\mathrm{oil}}}{\rho_{\mathrm{water}}} \tag{3.1}$$

where ρ_{oil} is the oil density and ρ_{water} is the water density.

Both densities of oil and water are at the same standard temperature and pressure conditions, which are 1 atm (14.7 psia) and 15.6 °C (60 °F). Since under the same conditions, most petroleum fractions are lighter than water, i.e. $\rho_{\mathrm{oil}} \leq 1$.

Another parameter for oil density is API gravity defined as:

$$\mathrm{API} = \frac{141.5}{\mathrm{SG}} - 131.5 \tag{3.2}$$

Heavy oils have low API and light oils have high API gravities.

The density measurement of petroleum fractions and crude oils are carried out using either a pycnometer or a Mettler/Parr densitometer. The latter method is based on density-dependent frequency changes of an oscillating glass U-tube.

3.2.2. Boiling Point Curves

ASTM distillation or TBP distillations characterize the volatility of petroleum fractions and crude oils. Both are batch distillations which differ mainly in the degree of fractionation obtained during distillation.

3.2.3. ASTM Distillation

ASTM distillation is carried out in a relatively simple apparatus consisting of a flask holding the sample connected to an inclined condenser, which condensed the rising vapours. The fractions distilled are collected in a graduated cylinder. The temperature of the rising vapours is recorded at specific interval of the collected distillates. This is essentially a batch distillation with one equilibrium stage and no reflux and minimum separation of the components of the fractions. For gasoline, kerosene, gas oil and similar light and middle distillates, the ASTM method D86, which is carried out at atmospheric pressure, is used. Heavy petroleum products, which tend to decompose in the ASTM D86 method but can be partially or completely vaporized at a maximum temperature of 400 °C (750 °F) and pressures down to 1 mm Hg, are distilled using the ASTM D1160 method. It is carried out at pressures between 1 and 760 mm Hg.

The temperature at which the first drop of condensate is collected is called the initial boiling point (IBP). The end point (EP) is the maximum vapour temperature when almost the entire sample is distilled (above 95%). Boiling temperatures at subatmospheric pressures (less than 760 mm Hg) can be converted to NBPs (at 760 mm Hg) using procedure 5A1.13 of API-TDB (API, 1993).

Minimum fractionation occurs in ASTM distillation, and components in the mixture do not distil one by one in the order of their boiling points, but rather as mixtures of successively higher boiling points. Nevertheless, because ASTM distillations are quickly conducted and have been successfully automated, require only a small sample, and are quite reproducible, they are widely used.

3.2.4. True Boiling Point Distillation

Data from TBP distillation provides more detailed characterization of the volatility of crude oil or petroleum fraction. It is performed in columns with 15 theoretical plates or equilibrium stages and a reflux ratio of 5. Rising vapours are condensed and collected either at a constant rate of boiling points or constant rate of the sample vaporized. Operation is at 760 mm Hg for boiling points below 400 °C (750 °F). For higher boiling point fractions, the distillation is conducted at reduced pressures as low as 0.5 mm Hg. Results from vacuum operations are extrapolated to atmospheric pressure. The high degree of fractionation in this test gives an accurate component distribution. Because the degree of separation for a TBP distillation test is much higher than that of the ASTM distillation test, its IBP is lower and its EP is higher than those of the ASTM test. The TBP curve (a plot of the NBP versus the percent volume of sample distilled) is usually used as a basis for the characterization of crude oil or a petroleum product for the purpose of design and analysis.

3.2.5. Conversion between ASTM and TBP Distillation

Since TBP distillation is both tedious and time-consuming in comparison with the ASTM method, there has been an incentive to develop correlation to convert ASTM to TBP distillation while at the same time achieving the benefit of the detailed separation of TBP with the little effort of the ASTM distillation. The following equation suggested by Riazi and Daubert (1980) and published by the API (1993) is used for the interconversion, referred to as API method:

$$\mathrm{TBP} = a(\mathrm{ASTM\,D86})^{b} \tag{3.3}$$

where a and b are constants varying with percent of liquid sample distilled as given in Table 3.2. TBP is true boiling point temperatures at 0, 10, 30, 50, 70, 90, and 95 volume percent distilled, in degrees Rankin. ASTM D86 is

Table 3.2 Constants for equation (3.3)

Volume % distilled	*a*	*b*
0	0.9167	1.0019
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.8705	1.0226
90	0.9490	1.0110
95	0.8008	1.0355

Table 3.3 Constants for Daubert's distillation curves interconversion method

Index number i	A_i	B_i
1	7.4012	0.6024
2	4.9004	0.7164
3	3.0305	0.8008
4	0.8718	1.0258
5	2.5282	0.8200
6	3.0419	0.7750
7	0.1180	1.6606

the observed ASTM D86 temperatures at corresponding volume percent distilled, in degrees Rankin. Average error between the calculated and measured TBP is in the range of 5 °C (41 °F).

More recently, Daubert (1994) published a new method for distillation curves interconversion using the following equations:

$$\begin{aligned} &T'_{50} = A_4(T_{50})^{B4}, \quad T'_{30} = T'_{50} - \Delta T'_3, \quad T'_{10} = T'_{30} - \Delta T'_2 \\ &T'_0 = T'_{10} - \Delta T'_1, \quad T'_{70} = T'_{50} + \Delta T'_5, \quad T'_{90} = T'_{70} + \Delta T'_6 \\ &T'_{90} = T'_{95} + \Delta T'_7 \end{aligned} \tag{3.4}$$

where $\Delta T'_i = A_i(\Delta T_i)^{B_i}$, $\Delta T_1 = T_{10} - T_0$, $\Delta T_2 = T_{30} - T_{10}$, $\Delta T_3 = T_{50} - T_{30}$, $\Delta T_5 = T_{70} - T_{50}$, $\Delta T_6 = T_{90} - T_{70}$ and $\Delta T_7 = T_f - T_{90}$.

The symbols T and T' stands for ASTM D86 and TBP temperatures, respectively, both in °F. The subscripts 0 and f stand for the initial and final temperatures, respectively. A_i and B_i are constants given in Table 3.3

The reported average error for this method is about 3 °C (37.4 °F).

Example E3.1

A petroleum cut has the following ASTM D86 Distillation data:

Volume % distilled	0	10	30	50	70	90	95
Temperature (°C)	36.5	54	77	101.5	131	171	186.5

Convert these data to TBP data using the API method of Riazi and Daubert and Daubert's method. Plot the results and compare.

Solution:

Application of the API method is straightforward using equation (3.3) and the constants in Table 3.2. Results are shown in Table E3.1. For the Dauber's method, the constants in Table 3.3 are used to calculate TBP at 50 vol% T'_{50}. The $\triangle T_i$ are calculated from the ASTM data, the $\triangle T'$ for the TBP are then calculated. Then T′ for TBP are calculated using the formulas in equation (3.4). The results are shown in Table E3.1.

Table E3.1 Converted ASTM temperatures

Volume % distilled	D86 T (°C)	TBP (°C) API method equation (3.3)	TBP (°C) Daubert's method equation (3.4)
0	36.5	14.1	−5.3
10	54	33.4	27.5
30	77	69.0	66.7
50	101.5	101.6	101.7
70	131	135.2	138.1
90	171	180.5	184.6
95	186.5	194.1	201.1

As can be seen from Figure E3.1, the TBP distillation curve is below the ASTM curve at volume distilled below 50% and above it for volume distilled above 50%. The API and Duabert's methods give comparable results except for the low range, less than 10% distilled.

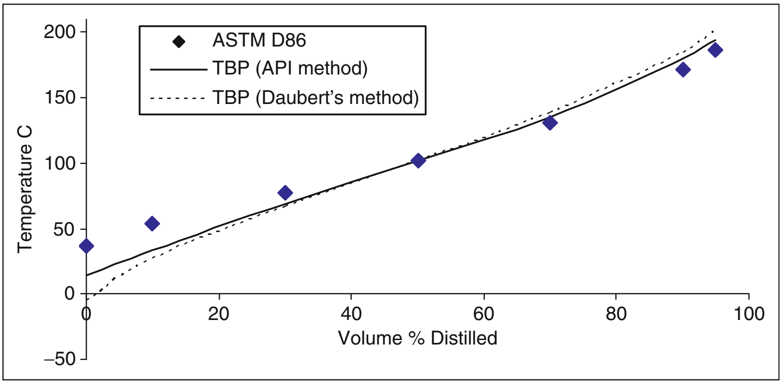

Figure E3.1 Conversion of ASTM D86 into TBP

Based on the distillation curve, five different average boiling points can be estimated. Among these, the volume average boiling point (VABP) and the mean average boiling points (MeABP) are the most widely used in property estimation and design. The MeABP is utilized in the definition of an important parameter, the Watson characterization factor *K* given by:

$$K = \frac{(\mathrm{MeABP})^{1/3}}{\mathrm{SG}} \tag{3.5}$$

where MeABP is in degrees Rankin.

Given the ASTM D86 distillation the VABP can be calculated as the average of the five boiling temperatures at 10, 30, 50, 70 and 90 percent distilled.

$$\mathrm{VABP} = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5} \tag{3.6}$$

where all temperatures are in °F.

The MeABP is calculated using the following equation:

$$\mathrm{MeABP} = \mathrm{VABP} - \mathit{\Delta} \tag{3.7}$$

where $\mathit{\Delta}$ is given by:

$$\ln\ \mathit{\Delta} = -0.94402 - 0.00865(\mathrm{VABP} - 32)^{0.6667} + 2.99791\,\mathrm{SL}^{0.333}$$

$$\mathrm{SL} = \frac{T_{90} - T_{10}}{90 - 10}$$

As mentioned before, ASTM and TBP distillation can be performed on crude oils and petroleum products. The petroleum fractions are “cuts” from the crude oil with specific boiling point range and with special properties such as API gravity and viscosity. Each of these cuts can be further defined by dividing them into narrow boiling fractions, called pseudo- (not real) components. For these pseudo-components, the average boiling point can be estimated as either mid-boiling point or mid-percentage boiling point. The TBP curve is divided into an arbitrary number of pseudo-components or narrow boiling cuts. The mid boiling point is the average between the IBP and the EP of that pseudo-component. The mid percentage boiling point is the temperature at the arithmetic average of the volumes distilled at IBP and EP of that pseudo-component. Since the boiling range is small, both mid points are close to each other and can be considered as the VABP or the MeABP for that pseudo-component.

Example E3.2

Calculate the MeABP of the petroleum fraction of example E3.1. If the API gravity of this fraction is 62, calculate the Watson's characterization factor.

Solution:

The D86 distillation temperatures are converted to °F. The VABP is obtained from equation (3.6)

$$\mathrm{VABP} = \frac{129.2 + 170.6 + 214.7 + 267.8 + 339.8}{5} = 224.4\ ^\circ\mathrm{F}$$

$$\mathrm{SL} = 2.6325$$

$$\Delta = 18.279$$

$$\mathrm{MeBP} = 224.4 - 18.3 = 206.1\ ^\circ\mathrm{F} \quad \text{or} \quad 96.7\ ^\circ\mathrm{C}$$

From equation (3.2) SG can be calculated as:

$$\mathrm{SG} = \frac{141.4}{62 + 131.5} = 0.7313$$

Watson characterization factor from equation (3.5)

$$K = \frac{(206.1 + 460)^{1/3}}{0.7313} = 11.94$$

3.3. PSEUDO-COMPONENTS

Calculations involving crude oil and petroleum fractions require the composition of each process stream. Since most of the actual components are not known, the petroleum fractions are characterized as a mixture of discrete pseudo-components with defined boiling point ranges or cut points on the TBP distillation curve. Each pseudo-component corresponds to several unknown actual compounds (e.g. paraffins, naphthenes and aromatics) which boil in a given temperature range.

Usually each pseudo-component is characterized by an average normal boiling point, specific gravity and molecular weight. The first two properties are obtained experimentally from the TBP curve and gravity versus volume distilled curve. In some cases, only the overall specific gravity of the fraction is measured. The molecular weight is usually calculated through a correlation. Once these parameters are determined, the pseudo-components can be treated as any defined component for the calculation of thermophysical and thermodynamic property like enthalpy, entropy, and transport properties such as viscosity, thermal conductivity and diffusivity. Some properties, like pour point, depend on the chemical nature of the compounds represented in the pseudo-components. Then the information on the chemical compositions in terms of percentage of paraffins, naphthenes and aromatics becomes necessary.

3.3.1. Breakup of TBP Curve into Pseudo-components

The TBP for the crude oil or the petroleum fraction has to be available, either by direct laboratory measurements through ASTM D1160 distillation or through the conversion of ASTM D86 distillation into TBP distillation curve. TBP cut point ranges are used to define pseudo-components with the average temperature of the cut or the mid point NBP. If the petroleum fraction contains components lighter than pentanes, the composition of the lighter ends has to be available experimentally through chromatographic analysis of the vapours. Otherwise the lighter ends are lumped with the lightest pseudo-component. The number of such pseudo-components depends on the boiling point range of the whole petroleum fraction. This number is a trade off between producing a smooth calculated property curve and having too many components which both leads to excessive computation time.

The following cut-point ranges are reasonable for most refining calculations:

TBP range	Number of cuts
< 37.8 °C (100 °F)	Use actual components (pentanes and lighter)
37.8–427 °C (100–800 °F)	28
427–649 °C (800–1200 °F)	8
649–871 °C (1200–1600 °F)	4

A general guideline for determining the number of pseudo-components is as follows:

- 10 °C (50 °F) for light fractions with boiling points less than 200 °C (392 °F)
- 15 °C (59 °F) for fractions with boiling points between 200 and 400 °C (392–752 °F)
- 20 °C (68 °F) for fractions with boiling points between 400 and 600 °C (752–1112 °F)
- 30 °C (86 °F) for fractions with boiling points beyond 600 °C (1112 °F)

The number of pseudo-component depends on the application. In distillation calculations, more NBP cuts might be needed to represent narrow boiling products. Figure 3.1 shows how the TBP curve is cut into several pseudo-components.

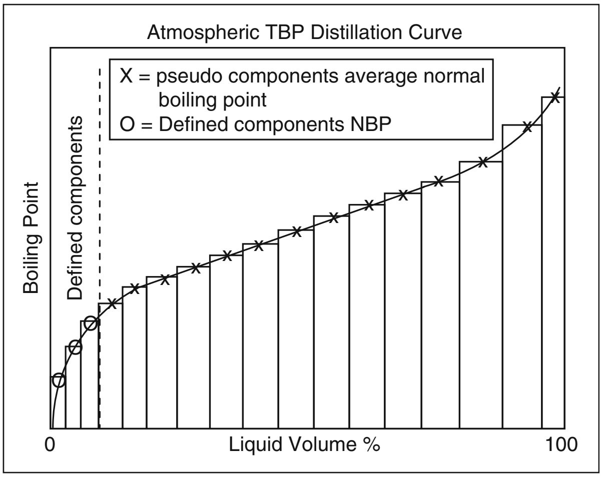

Figure 3.1 Representation of TBP curve by pseudo-components

Example E3.3

Divide the TBP curve of the petroleum cut as calculated from API method in example E3.1 into 20 pseudo-components. Calculate the liquid volume percentage of each pseudo-component.

Solution:

The TBP curve obtained in example E3.1 extends to 95 volume percent distilled only. In order to obtain the average boiling point of the last cuts, the curve is extrapolated to the final point of the distillation (100%) by fitting the curve to a suitable polynomial function and extrapolating the results. An Excel spreadsheet program was used to fit a fifth order polynomial function, as shown Figure E3.3 for TBP temperature versus volume% .

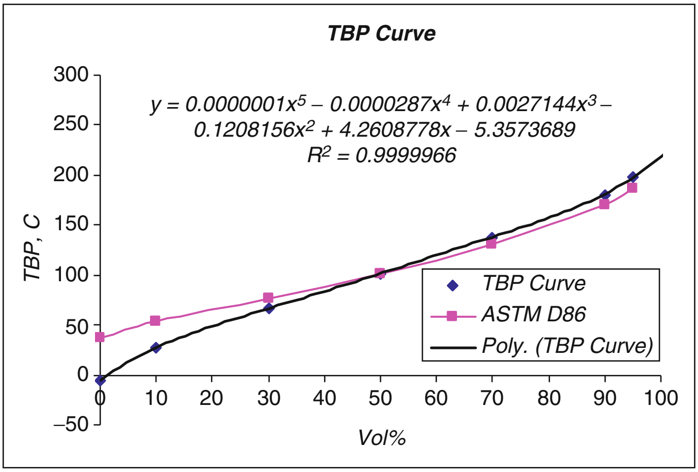

Figure E3.3 Extrapolation of TBP curve

The end point of the cut is 218.2 °C (425 °F) and the IBP is −5.4 °C (22 °F). Therefore each pseudo-component has a temperature interval of (218.2 + 5.4)/20 or 11.2 °C. Then the curve can be cut as follows. The EBP of the first cut is IBP + 11.2 °C or 5.8 °C. The average boiling point for the first pseudo-component is (−5.4 + 5.8)/2 or 0.2 °C. The vol% is 2.84 as read from the TBP curve. The second cut has an end boiling point of 17 °C and an end volume percent of 6.19. Therefore, the vol% of this cut is 6.19 − 2.84 or 3.36 vol%. The average boiling point for the second cut is (17 + 5.8)/2 or 11.4 °C. For the subsequent cut, the results are shown in Table E3.3.

Table E3.3 Pseudo-components

EBP of cut (°C)	NBP of cut (°C)	Volume % at end of cut	Cut vol%
5.8	0.2	2.84	2.84
17.0	11.4	6.19	3.36
28.2	22.6	10.22	4.03
39.4	33.8	15.09	4.87
50.5	44.9	20.82	5.73
61.7	56.1	27.15	6.34
72.9	67.3	33.68	6.52
84.1	78.5	40.10	6.42
95.3	89.7	46.36	6.26
106.4	100.8	52.53	6.17
117.6	112.0	58.69	6.16
128.8	123.2	64.89	6.21
140.0	134.4	71.09	6.20
151.1	145.6	77.07	5.98
162.3	156.7	82.53	5.45
173.5	167.9	87.25	4.73
184.7	179.1	91.25	4.00
195.9	190.3	94.63	3.37
207.0	201.5	97.51	2.88
218.2	212.6	100.00	2.49

3.3.2. Breakup of TBP Curve into Pseudo-components Using Generalized Form

Laboratory crude assay reports provide TBP for the whole crude as explained in Section 3.2.3. The maximum temperature that can be measured with this test is in the range of 496–526 °C (925–975 °F), depending on the crude oil. The actual end point of the crude oil can be as high as 790 °C (1455 °F). This means that a substantial portion of the TBP curve is not defined by laboratory data. Extrapolation of the measured portion of the TBP curve to a volume percent approaching the end point is required. While probability distillation graph paper can be used for extrapolation, a computer method will be used in this section.

The TBP curve can be fitted to the following generalized equation (Riazi, 2005):

$$P^* = \left[\frac{A}{B}\ln\left(\frac{1}{x^*}\right)\right]^{1/B} \tag{3.8}$$

where

$$P^* = \frac{T_b - T_{b0}}{T_{b0}} \quad \text{and} \quad x^* = 1 - x_c$$

The boiling point T_b is in Kelvin. x_c is the cumulative weight, volume or mole fraction. T_{b0} corresponds to the boiling point at $x_c = 0$. Therefore, it should be equal or lower than the IBP given in the assay data. The parameters A and B are obtained by fitting the equation to available assay data. Since in this equation $P^* \to \infty$ as $x^* \to 1$, an arbitrary point can be added to the measured TBP data to limit the actual TBP end point. The same equation can be used to fit data for molecular weight and specific gravity. The above generalized equation can be converted to the following linear form:

$$Y = C_1 + C_2 X \tag{3.9}$$

where

$$Y = \ln P^* \quad \text{and} \quad X = \ln\left[\ln\left(\frac{1}{x^*}\right)\right]$$

From equations (3.8) and (3.9):

$$B = \frac{1}{C_2} \tag{3.10}$$

$$A = B\exp(C_1 B)$$

The fitting procedure is to calculate P^*, knowing T_{b0} and plot Y versus X. This means the correlation parameter R^2 is calculated. If T_{b0} is not known, the value of T_{b0} is assumed and varied until a good fit is obtained ($R^2 = 0.99$). This fitting procedure can be easily done using the linear regression fit of a Microsoft Excel spreadsheet.

T_{b0} represents the initial boiling point. It can be estimated for cases where T_{b0} is not available. Nonlinear regression of equation (3.8) is applied to find T_{b0} as well as A and B.

Example E3.4

The following TBP data for a crude oil sample is available with an IBP of 17 °C. Fit the data to the generalized equation and compare with the polynomial fit.

Volume %	TBP (°C)
5	40
10	85
30	215
50	340
70	495

Repeat the generalized fit if the initial boiling point is not known.

Solution:

Plotting the data of equation (3.9) on a Microsoft Excel spreadsheet with linear fitting, we obtain the following parameters:

$C_1 = 0.452$ and $C_2 = 0.936$, which gives a correlation parameter of $R^2 = 0.998$. The constant A and B for the generalized equation are then calculated to be:

$$A = 1.732 \quad \text{and} \quad B = 1.069$$

A comparison between the experimental and calculated TBP curve is shown in Figure E3.4. The % error calculated for the generalized equation is 3.6%, while the polynomial fit is 2.4%.

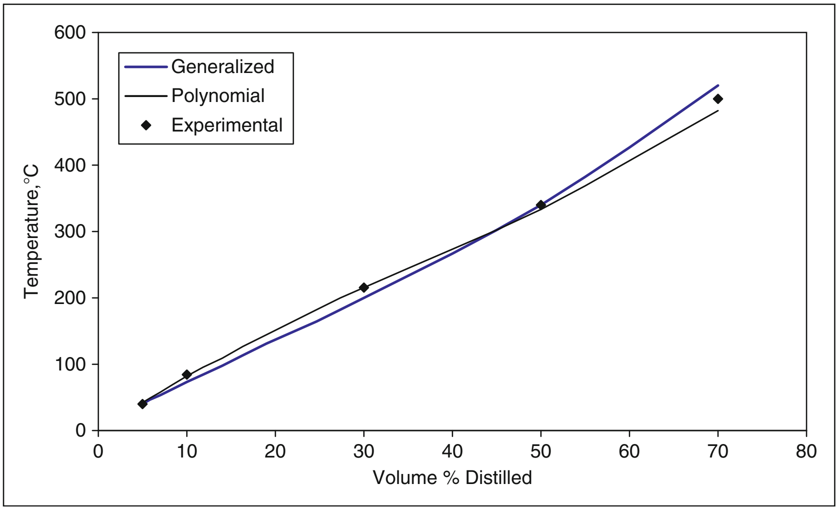

Figure E3.4 TBP curve for Kuwait export crude sample

This example can be solved again to estimate the value of IBP, T_{b0}. C_1 and C_2 are calculated using linear regression as follows:

$$Y = \ln P^* = \ln\left[\frac{T_b - T_{b0}}{T_{b0}}\right] \quad \text{and} \quad X = \ln\left[\ln\left(\frac{1}{x^*}\right)\right]$$

$$Y = C_1 + C_2X$$

$$R^2 = \left[\frac{n\Sigma(XiYi) - \Sigma Xi\Sigma Yi}{\sqrt{n\Sigma X_i^2 - (\Sigma Xi)^2}\sqrt{n\Sigma Y_i^2 - (\Sigma Yi)^2}}\right]^2$$

$$C_2 = \left[\frac{n\Sigma(XiYi) - \Sigma Xi\Sigma Yi}{n\Sigma X_i^2 - (\Sigma Xi)^2}\right]$$

$$C_1 = \frac{\Sigma Yi}{n} - C_2\frac{\Sigma Xi}{n}$$

Excel solver is used to determine the value of T_{b0}. The target is to set the value of R^2 close to 1.0 by changing the value of T_{b0}. The solution is shown in the table below which shows the values of C_1 and C_2 that result in T_{b0} = 8.03 °C (281.03K).

n	xc cum vol%	T_b (°C)	Y	$x^\star = 1 - xc$	$X = \ln(\ln(1/x^\star))$	XY	x^2	y^2
1	5	40	−2.1738	0.9500	−2.9702	6.4567	8.8221	4.7256
2	10	85	−1.2951	0.9000	−2.2504	2.9145	5.0642	1.6774
3	30	215	−0.3059	0.7000	−1.0309	0.3154	1.0628	0.0936
4	50	340	0.1666	0.5000	−0.3665	−0.0610	0.1343	0.0277
5	70	500	0.5599	0.3000	0.1856	0.1039	0.0345	0.3135
sum			−3.0484		−6.4324	9.7295	15.1178	6.8378
			C_2	0.8488				
			C_1	0.4822				
			R	0.9950				
			R^2	0.9900				
			T_{b0} = 8.0349 °C					

3.3.3. Calculation of Pseudo-components Specific Gravities

As pointed out earlier, the distillation test might include the measurement of gravity versus volume distilled. Sometimes this is not available and only the average gravity of the whole petroleum fraction is measured. In this case, the following procedure is used to obtain the gravity for each pseudo-component. This step is necessary to calculate the molecular weight of the pseudo-component and hence to convert volume fractions into mass fractions or mole fractions.

Any petroleum fraction or NBP cut can be characterized by the *Watson* Characterization (K) factor defined in equation (3.5). For the petroleum cut comprising the pseudo-components, the K factor for the pseudo-components is assumed constant and equal to its value for the whole petroleum cut. Hence the definition of the K factor is used to calculate the gravity of each pseudo-component given its average NBP.

Example E3.5

Calculate the specific gravity of each pseudo-components of the crude assay attached, knowing that $K = 11.94$.

Volume %	TBP (°C)
5	40
10	85
30	215
50	340
70	495

Plot the API gravity versus vol% and fit it to the proper polynomial.

Solution:

The K factor for this cut is 11.94. Using this value for each of the pseudo-components and the TBP of each cut, the specific gravity of the pseudo-components is generated and then the API is calculated.

TBP is calculated at the extended vol% up to 95% from the generalized equation from Example E3.4.

The polynomial fit of the API versus vol% is

$$\text{API} = -0.0002\ \text{vol\%}^3 + 0.0238\ \text{vol\%}^2 - 1.7637\ \text{vol\%} + 80.471 \text{ with } R^2 = 0.9994$$

Figure E3.5 shows the API-TBP versus vol% curves.

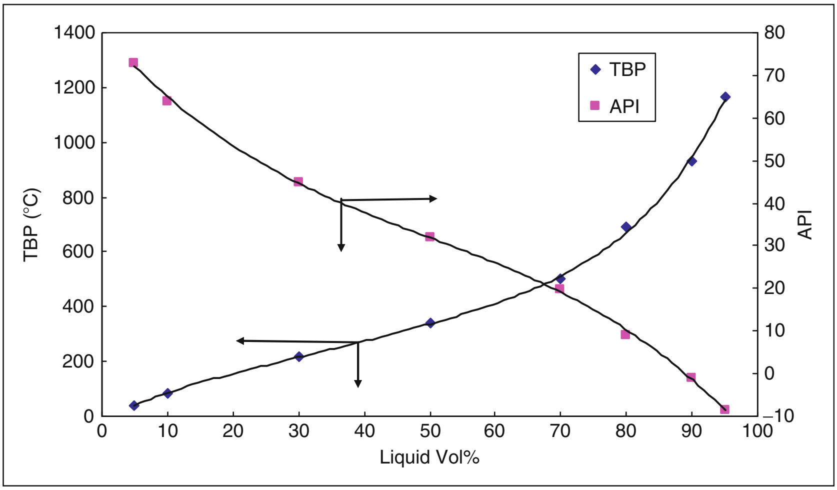

Figure E3.5 TBP and API versus vol%

3.4. Thermophysical Properties Calculation

3.4.1. Molecular Weight

Any material or energy balance calculations would certainly require the estimation of molecular weight of a petroleum fraction. Experimentally, the average molecular weight can be determined by several methods, such as freezing point depression osmometry, or gel permeation chromatography. Most oil fractions have molecular weights in the range of 100–700. The method most suitable for determining molecular weights within this range is that based on freezing point depression.

Prediction of the molecular weight of petroleum fractions is achieved through the following equation (Pedersen *et al.*, 1989):

$$M = 42.965[\exp(2.097 \times 10^{-4} T_b - 7.78712\ \mathrm{SG} + 2.08476 \times 10^{-3} T_b \mathrm{SG})]\, T_b^{1.26007} \mathrm{SG}^{4.98308} \tag{3.11}$$

where M is the molecular weight of the petroleum fraction, T_b is the mean average boiling point of the petroleum fraction in K, and SG is the specific gravity, 60 °F/60 °F.

Example E3.6

Calculate the molecular weight for the cut with NBP of 216.4 °C and K = 11.94.

Solution:

This cut has a NBP of 216.4 °C or 489.55 K and a specific gravity of 0.8029 from equation (3.5) knowing that $K = 11.94$. Using equation (3.11), the molecular weight is calculated to be 170.8.

3.4.2. Viscosity

The following equations can be used to calculate the liquid viscosities of petroleum fractions at atmospheric pressure and at temperatures of 37.8 °C (100 °F) and 98.9 °C (210 °F) (Pedersen *et al.*, 1989):

$$\begin{aligned}\log \nu_{210} = {} & -0.463634 - 0.166532(\mathrm{API}) + 5.13447 \times 10^{-4}(\mathrm{API})^2 \\ & - 8.48995 \times 10^{-3} K(\mathrm{API}) \\ & + \frac{8.0325 \times 10^{-2} K + 1.24899(\mathrm{API}) + 0.197680(\mathrm{API})^2}{\mathrm{API} + 26.786 - 2.6296K}\end{aligned} \tag{3.12}$$

$$\begin{aligned}\log \nu_{100} = {} & 4.39371 - 1.94733K + 0.127690K^2 + 3.2629 \times 10^{-4}(\mathrm{API})^2 \\ & - 1.18246 \times 10^{-2} K(\mathrm{API}) \\ & + \frac{0.17161K^2 + 10.9943(\mathrm{API}) + 9.50663 \times 10^{-2}(\mathrm{API})^2 - 0.860218K(\mathrm{API})}{\mathrm{API} + 50.3642 - 4.78231K}\end{aligned} \tag{3.13}$$

where ν_{100} and ν_{210} are the kinematic viscosities at 100 and 210 °F, in centistokes.

3.4.3. Refractive Index

The refractive index is a readily measured property that can be used as an input parameter for other correlations. It is defined as the speed of light in vacuum with respect to the speed of light in the medium. Since refractive indices of petroleum fractions are not always known, it is important to predict the refractive index. The following equation may be used:

$$n = \left(\frac{1 + 2I}{1 - I}\right)^{1/2} \tag{3.14}$$

Values of I may be calculated from:

$$I = a \exp(bT_\mathrm{b} + c\mathrm{SG} + dT_\mathrm{b}\mathrm{SG})\, T_\mathrm{b}^{e}\mathrm{SG}^{f} \tag{3.15}$$

where a, b, c, d, e, and f are the constants varying with molecular weight range (Table 3.4), n is the refractive index at 20 °C (68 °F), I is the Huang characterization parameter at 20 °C (68 °F), T_b is the mean average boiling point, in degrees Rankin, M is the molecular weight of petroleum fractions, and SG is the specific gravity of petroleum fraction, 60 °F/60 °F.

Table 3.4 Constants for equation (3.15)

Constants	Light fractions	Heavy fractions
Molecular weight range	70–300	300–600
Boiling point range (°F)	90–650	650–1000
a	2.266×10^{-2}	2.341×10^{-2}
b	3.905×10^{-4}	6.464×10^{-4}
c	2.468	5.144
d	-5.704×10^{-4}	-3.289×10^{-4}
e	0.0572	−0.407
f	−0.720	−3.333

Example E3.7

Calculate the kinematic viscosities and the refractive index for oil which has a MeABP of 320 °C and API gravity of 34.

Solution:

The boiling point is 593.15 K or 1067.7 R. Using equations (3.2) and (3.5), the specific gravity is 0.855 and the Watson K factor is 11.95. From equations (3.12) and (3.13)

$$\nu_{100} = 5.777 \text{ cSt} \quad \text{and} \quad \nu_{210} = 1.906 \text{ cSt}.$$

From equations (3.14) and (3.15), the refractive index n is calculated to be 1.481 (M is 257.1 as calculated from equation (3.11)).

3.4.4. Molecular Type Composition of Petroleum Fractions

The following equations are used to predict the fractional composition of paraffins, naphthenes and aromatics (PNA) contained in both light and heavy petroleum fractions. The viscosity, specific gravity and refractive index of the desired fraction are used as input parameters. For heavy fractions ($M > 200$):

$$\begin{aligned} x_p &= a + b(R_i) + c(\text{VGC}) \\ x_n &= d + e(R_i) + f(\text{VGC}) \\ x_a &= g + h(R_i) + i(\text{VGC}) \end{aligned} \tag{3.16}$$

Table 3.5 Constants for equation (3.16) and (3.24)

Constants	Light fraction	Heavy fractions
Molecular weight range	70–200	200–600
a	−13.359	2.5737
b	+14.4591	+1.0133
c	−1.41344	−3.573
d	+23.9825	+2.464
e	−23.333	−3.6701
f	+0.81517	+1.96312
g	−9.6235	−4.0377
h	+8.8739	+2.6568
i	+0.59827	+1.60988

where a, b, c, d, e, f, g, h, and i are the constants varying with molecular weight range as given in Table 3.5; x_p, x_n, and x_a are the mole fraction of paraffins, naphthenes, and aromatics, respectively; R_i is the refractivity intercept as given by the equation below

$$R_i = n - \frac{d}{2} \tag{3.17}$$

where n = refractive index at 20 °C (68 °F) and 1 atmosphere, d is the liquid density at 20 °C (68 °F) and 1 atmosphere in grams per cubic centimetre, VGC is the viscosity gravity constant as given by equations below.

$$\mathrm{VGC} = \frac{10\ \mathrm{SG} - 1.0752\log(V_{100} - 38)}{10 - \log(V_{100} - 38)} \tag{3.18}$$

or

$$\mathrm{VGC} = \frac{\mathrm{SG} - 0.24 - 0.022\log(V_{210} - 35.5)}{0.755} \tag{3.19}$$

where SG is the specific gravity at 15.6 °C (60 °F) and V is the Saybolt universal viscosity at 37.8 or 98.9 °C (100 or 210 °F), in Saybolt universal seconds.

The Saybolt (SUS) universal viscosity (V) is related to the kinematics viscosity (ν) in cSt by the relation:

$$V_{100}(\mathrm{SUS}) = 4.6324\upsilon_{100} + \frac{1 + 0.03264\upsilon_{100}}{(3930.2 + 262.7\upsilon_{100}^2 + 1.646\upsilon_{100}^3) \times 10^{-5}} \tag{3.20}$$

$$V_{210}(\mathrm{SUS}) = 1.0066856\,V_{100}(\mathrm{SUS}) \tag{3.21}$$

For light fractions, $M \leq 200$, The viscosity gravity function (VGF) can be calculated as:

$$\mathrm{VGF} = -1.816 + 3.484\,\mathrm{SG} - 0.1156 \ln \nu_{100} \tag{3.22}$$

or

$$\mathrm{VGF} = -1.948 + 3.535\,\mathrm{SG} - 0.1613 \ln \nu_{210} \tag{3.23}$$

In this case:

$$\begin{aligned} x_\mathrm{p} &= a + b(R_\mathrm{i}) + c(\mathrm{VGF}) \\ x_\mathrm{n} &= d + e(R_\mathrm{i}) + f(\mathrm{VGF}) \\ x_a &= g + h(R_\mathrm{i}) + i(\mathrm{VGF}) \end{aligned} \tag{3.24}$$

In both cases note that: $\mathrm{x_p} + \mathrm{x_n} + \mathrm{x_a} = 1$

Example E3.8

Calculate the paraffins, naphthenes and aromatic mole fraction for the crude having the properties listed in example E3.7.

Solution:

From example E3.7, $\mathrm{SG} = 0.855$ then $d = 0.855\ \mathrm{g/cm^3}$
$n = 1.481$ then $R_\mathrm{i} = 1.0535$ from equation (3.17)
$M = 257.1$ which can be considered heavy fraction
$\nu_{100} = 5.777$ cSt then $\mathrm{VGC} = 0.8348$ from equation (3.18)
By substituting the constants for the heavy fraction, R_i and VGC in equation (3.16)

$$x_\mathrm{p} = 0.789,\ x_\mathrm{n} = 0.164 \quad \text{and} \quad x_\mathrm{a} = 0.046$$

3.4.5. Pseudo-critical Constants and Acentric Factors

Almost all the methods which are used to calculate the thermodynamic properties and transport properties rely on the principle of corresponding states and an equation of state. To use these methods the critical temperature and pressure and the acentric factor are required as input constants. While these constants are tabulated for defined components, these have to be estimated for narrow boiling petroleum cuts or pseudo-components. The general adopted method in this regard is to calculate these constants from two characteristic properties; the average boiling point and the specific gravity or API gravity. While there are several equations available such as those of Riazi and Daubert (1980), Lee and Kessler (1976), we will use those of Lee and Kessler because they are used as default methods in process simulators.

3.4.5.1. Pseudo-critical Temperature

$$T_c = 189.8 + 450.6\ \mathrm{SG} + (0.422 + 0.1174\ \mathrm{SG})T_b + \frac{(14,410 - 100,688\ \mathrm{SG})}{T_b} \tag{3.25}$$

where pseudo-critical temperature T_c and the average boiling point T_b are in K.

3.4.5.2. Pseudo-critical Pressure

$$\begin{aligned}\ln P_c = {} & 5.689\ \mathrm{SG} - \frac{0.0566}{\mathrm{SG}} - 10^{-3}T_b\left(0.436392 + \frac{4.12164}{\mathrm{SG}} + \frac{0.213426}{\mathrm{SG}^2}\right) \\ & + 10^{-7}T_b^2\left(4.75794 + \frac{11.819}{\mathrm{SG}} + \frac{1.53015}{\mathrm{SG}^2}\right) - 10^{-10}T_b^3\left(2.45055 + \frac{9.901}{\mathrm{SG}^2}\right)\end{aligned} \tag{3.26}$$

where P_c is in bars.

3.4.5.3. Acentric Factor

The equation for calculating the acentric factor depends on the value of the reduced average NBP $T_{br} = T_b/T_c$ as follows:

For $T_{br} < 0.8$

$$\omega = \frac{\ln P_{br} - 5.92714 + 6.09648/T_{br} + 1.28862\ln T_{br} - 0.169347T_{br}^6}{15.2518 - 15.6875/T_{br} - 13.4721\ln T_{br} + 0.43577T_{br}^6} \tag{3.27}$$

where $P_{br} = P_b/P_c$ and P_b is the pressure at which T_b is measured which is atmospheric pressure.

For $T_{br} > 0.8$ the equation to use is:

$$\omega = -7.904 + 0.1352K - 0.007465K^2 + 8.359T_{br} + (1.408 - 0.01063K)/T_{br} \tag{3.28}$$

where K is the Watson characterization factor.

Example E3.9

Calculate the critical temperature and pressure and the acentric factor for an oil which has a MeABP of 320 °C and 34 API gravity.

Solution:

The boiling point is 593.15 K and the specific gravity is 0.855. Using equations (3.25) and (3.26), $T_c = 764.17\mathrm{K}$ and $P_c = 15.26$ bar.

The acentric factor is 0.777.

3.4.6. Generalized Equation for Thermophysical Properties

Riazi and Al-Sahhaf (1996) presented a method for the calculation of different properties such as the NBP, density, refractive index, critical temperature, pressure and density, acentric factor, solubility parameter and surface tension given only the molecular weight and using the following general equation

$$\theta = \theta_\infty - \exp(a - bM^C) \tag{3.29}$$

where θ can be any one of the properties mentioned above. M is the molecular weight and θ_∞ is the limiting value for any property as $M \rightarrow \infty$. This generalized equation can be used to calculate the following properties knowing the molecular weight.

- T_b, the mean average boiling point, K
- SG, the specific gravity
- d_{20}, the liquid density at 20 °C or 68 °F
- I, the Huang characterization parameter
- $T_{br} = T_b/T_c$, the reduced boiling point which is used to calculate the critical temperature in K
- P_c, the critical pressure in bars
- d_c, the critical density in g/cm^3
- ω, the acentric factor
- σ, the surface tension in dynes/cm
- δ, the solubility parameter, in $(\text{cal/cm}^3)^2$

The constants a, b and c for each property are given in Table 3.6.

The application of this correlation is simple. You only need to know the average NBP of the petroleum fraction. First, the molecular weight is calculated from the correlation using the constants for the boiling

Table 3.6 Constants for the Riazi–Al-Sahhaf equation

Θ	θ_∞	a	b	c
T_b	1080	6.97996	0.01964	0.67
SG	1.07	3.56073	2.93886	0.1
d_{20}	1.05	3.80258	3.12287	0.1
I	0.34	2.30884	2.96508	0.1
T_{br}	1.20	−0.34742	0.02327	0.55
$-P_c$	0	6.34492	0.72390	0.3
$-d_c$	−0.22	−3.2201	0.00090	1
$-\omega$	0.30	−6.2520	−3.64457	0.1
Σ	30.3	17.45018	9.70188	0.1
Δ	8.60	2.29195	0.54907	0.3

point. Once the molecular weight is known, other properties can be calculated using equation (3.29) with the appropriate constants from Table 3.6.

Example E3.10

Use the Riazi and Al-Sahhaf (1996) equation to calculate the properties for an oil which has a MeABP of 320 °C and 34 API gravity.

Solution:

The molecular weight is calculated as 256 from equation (3.29) using the boiling point. Using this value, other properties are calculated, and the values are shown below.

SG	0.859	d_c	0.252
d_{20}	0.855	ω	0.798
I	0.2824	σ	28.55
T_c	773	δ	8.055
P_c	12.5		

3.5. CALCULATION OF ENTHALPY OF PETROLEUM FRACTIONS

The design of process equipment, such as heat exchangers and compressors requires the calculation of enthalpy and entropy. While there are different methods for the calculation of thermodynamic properties, we will concentrate in this section on Lee–Kessler method which is suitable for hand calculation. Equations of state, such as the Soave–Redlich–Kwong and the Peng–Robinson, are widely used in process simulation programs.

The Lee–Kessler generalized correlation (Kessler and Lee, 1976) has the following expression for the compressibility factor:

$$Z = Z^0 + \omega Z^1 \qquad (3.30)$$

Equation (3.30) can be used to calculate the molar volume as: $V = RT/P$ or the mass density as $\rho = M/V$.

The departure functions $H - H^{\mathrm{ig}}$ is given by

$$\left(\frac{H - H^{\mathrm{ig}}}{RT_c}\right) = \left(\frac{H - H^{\mathrm{ig}}}{RT_c}\right)^0 + \omega\left(\frac{H - H^{\mathrm{ig}}}{RT_c}\right)^1 \qquad (3.31)$$

The superscripts ^{0} and ^{1} denote the value for the simple fluid and the correction terms, respectively. These values are obtained from published tables which can be found in standard chemical engineering thermodynamics textbooks as functions of the reduced temperature and pressure (Smith *et al.*, 1999). The critical temperature, critical pressure and the acentric factor for the petroleum fraction can be obtained from the equations in Section 3.4.5. If the fraction is treated as being made up of pseudo-components, the critical temperature, critical pressure and acentric factor can be calculated using the following simple mixing rule equations:

$$\begin{aligned} T_c &= \sum_i y_i T_{ci} \\ P_c &= \sum_i y_i P_{ci} \\ \omega &= \sum_i y_i \omega_i \end{aligned} \tag{3.32}$$

Where y_i is the mole fraction of each pseudo-component.

The enthalpy change of a fluid from state 1 at T_1 and P_1 to state 2 at T_2 and P_2 is given by:

$$H_2 - H_1 = (H_2 - H_2^{\mathrm{ig}}) + (H_2^{\mathrm{ig}} - H_1^{\mathrm{ig}}) - (H_1 - H_1^{\mathrm{ig}}) \tag{3.33}$$

To calculate the enthalpy with respect to a reference state set, $H_1 = H_{\mathrm{ref}} = 0$. If the reference state is at low pressure (ideal gas), then $(H_1 - H_1^{\mathrm{ig}}) = 0$. The enthalpy equation becomes

$$H = (H - H^{\mathrm{ig}}) + (H^{\mathrm{ig}} - H_{\mathrm{ref}}^{\mathrm{ig}}) \tag{3.34}$$

The ideal gas enthalpy change is calculated from the integration of the ideal gas heat capacity with temperature:

$$H_2^{\mathrm{ig}} - H_1^{\mathrm{ig}} = \int_{T_1}^{T_2} C_{\mathrm{p}}^{\mathrm{ig}} \mathrm{d}T \tag{3.35}$$

The ideal gas heat capacity for petroleum fractions is given by

$$C_{\mathrm{p}}^{\mathrm{ig}} = A + BT + CT^2 \tag{3.36}$$

Integration of equation (3.36) yields:

$$H_2^{\mathrm{ig}} - H_1^{\mathrm{ig}} = A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) + \frac{C}{3}(T_2^3 - T_1^3) \tag{3.37}$$

The constants A, B, and C can be estimated from the following relations proposed by Lee and Kessler as:

$$A = 4.1843M(-0.33886 + 0.02827K - 0.26105\ \mathrm{CF} + 0.59332\omega\ \mathrm{CF}) \tag{3.38}$$

$$B = -7.5318M\Big((0.9291 - 1.1543K + 0.0368K^2)10^{-4} + \mathrm{CF}(4.56 - 9.48\omega)10^{-4}\Big) \tag{3.39}$$

$$C = 13.5573M\Big(-1.6658 \times 10^{-7} + \mathrm{CF}(0.536 - 0.6828\omega)10^{-7}\Big) \tag{3.40}$$

where

$$\mathrm{CF} = \left(\frac{(12.8 - K)(10 - K)}{10\omega}\right)^2 \tag{3.41}$$

K is the Watson characterization factor and M is the molecular weight. The calculated heat capacity in equation (3.36) with T in K is in kJ/(kg mol K). To convert the value to kJ/(kg K), divide by M.

Example E3.11

Calculate the molar volume and enthalpy of an oil at 450 °C and 3.45 bar. The oil has a MeABP of 320 °C and 34 API gravity. The reference state is ideal gas at 298 K.

Solution:

The specific gravity is 0.855 and the K factor is 11.95. Using equations (3.25) and (3.26): $T_c = 765.5$ K and $P_c = 15.26$ bar. The acentric factor is 0.777. The molecular weight from equation (3.11) is 257.12.

$$T_r = 0.9447 \quad \text{and} \quad P_r = 0.2261.$$

From the Lee–Kessler tables:

$$Z^0 = 0.9029, \quad Z^1 = -0.0325$$

$$Z = 0.9029 + (0.777)(-0.0325) = 0.8776$$

$$V = \frac{ZRT}{P} = \frac{(0.8776)(8.3143)(450 + 273.15)}{0.345} = 15294.5\ \mathrm{cm^3/mol}$$

From the Lee–Kessler tables:

$$\left(\frac{H - H^{\mathrm{ig}}}{RT_c}\right)^0 = -0.1487, \quad \left(\frac{H - H^{\mathrm{ig}}}{RT_c}\right)^1 = -0.2882$$

From equation (3.31),

$$\left(\frac{H - H^{\mathrm{ig}}}{RT_{\mathrm{c}}}\right) = -0.1487 + (0.777)(-0.2882) = -0.3727$$

$$(H - H^{\mathrm{ig}}) = -2371.9\,\mathrm{kJ/kg\,mol}$$

For the ideal heat capacity and from equations (3.38) to (3.41)

$$A = 8.74721, \quad B = 1.44929 \quad \text{and} \quad C = 0.000581$$

From equation (3.37) and for temperatures between 298 and 723.15 K;

$$H_2^{\mathrm{ig}} - H_1^{\mathrm{ig}} = A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) + \frac{C}{3}(T_2^3 - T_1^3)$$

$$(H^{\mathrm{ig}} - H_{\mathrm{ref}}^{\mathrm{ig}}) = 312,088.8\ \mathrm{kJ/kg\,mol}$$

Therefore,

From equation (3.34)

$$H = (H - H^{\mathrm{ig}}) + (H^{\mathrm{ig}} - H_{\mathrm{ref}}^{\mathrm{ig}}) = -2371.9 + 312,088.8$$

$$H = 309,717\ \mathrm{kJ/kg\,mol} \quad \text{or} \quad 1223\ \mathrm{kJ/kg}$$

3.6. ESTIMATION OF PROPERTIES RELATED TO PHASE CHANGES

In petroleum refining, crude oil and petroleum fractions are separated into narrower fractions by unit operations that utilize the phase equilibrium between the hydrocarbons in the liquid and vapour phases such as distillation, adsorption, condensation and evaporation. When water is present, such as the case in the atmospheric distillation column, liquid–liquid–vapour equilibrium is encountered.

Equilibrium K_{eq} values, that is (y_i/x_i) are the fundamental building blocks of all unit operations involving phase change. Traditional older methods for calculations of K_{eq} values rely on methods or charts which are based on temperature and pressure only with no composition dependence.

3.6.1. Cubic Equations of State

With the development of more accurate equations of state and with the widespread use of computer simulation in process design, these methods are replaced with computer packages which rely on equations of state for phase equilibria calculations. Equations based on the Redlich–Kwong equation have proven to be the most successful for petroleum systems. The most widely used modifications of the Redlich–Kwong equations are the modifications of Soave and Peng–Robinson. In this section, we will concentrate on the latter equation.

The Peng–Robinson (PR) equation is a cubic equation in volume with the form:

$$Z = \frac{V}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{3.42}$$

where Z is the compressibility factor defined as PV/RT, and V is the molar volume. The equation is characterized by the energy parameter which is a function of temperature and the size parameter which is constant for a specific fluid. The equations for calculating these constants given the critical temperature and pressure and the acentric factor can be found in many standard chemical engineering thermodynamics books (Smith *et al.*, 1999).

This equation can be applied to mixtures by applying the mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad \text{and} \quad b = \sum_i x_i b_i \tag{3.43}$$

The combining rule for a_{ij} is given by

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$$

where k_{ij} is the binary interaction parameters. Values of k_{ij} between hydrocarbons are usually equal to zero. For non-hydrocarbon–hydrocarbon interactions, the values of these parameters are tabulated.

3.6.2. Vapour–liquid Equilibrium

The equilibrium K_{eq} value for a component in a vapour–liquid equilibrium system is given by

$$K_{\text{eq}} = {}^{\varphi_i^{\text{l}}}\!\big/_{\varphi_i^{\text{v}}} \tag{3.44}$$

φ_i^l and φ_i^v are called the fugacity coefficients of component i in the liquid and vapour phase, respectively. These coefficients are functions of temperature, pressure and composition and are calculated directly from the equation of state. The expressions for these coefficients for the PR equation of state can also be found in standard thermodynamics textbooks. These K_{eq} values are utilized in distillation or flashing in the well-known bubble, dew and flash calculation.

Example E3.12

A petroleum cut has the following ASTM D86 Distillation data:

Volume % distilled	0	10	30	50	70	90	95
Temperature (°C)	36.5	54	77	101.5	131	171	186.5

Convert these data to TBP data using the API method of Riazi and Daubert and Daubert's method. Plot the results and compare.

Solution:

The results for the API method of Riazi and Daubert are shown in Table E3.12.1 and plotted in Figure E3.12.1.

Table E3.12.1 Method of Riazi and Daubert

Volume % distilled	a	b	D86 T, °C	D86 T, °F	TBP, °F	TBP, °C
0	0.9167	1.0019	36.5	97.7	57.4	14.1
10	0.5277	1.0900	54.0	129.2	92.0	33.4
30	0.7429	1.0425	77.0	170.6	156.1	69.0
50	0.8920	1.0176	101.5	214.7	214.9	101.6
70	0.8705	1.0226	131.0	267.8	275.3	135.2
90	0.9490	1.0110	171.0	339.8	356.9	180.5
95	0.8008	1.0355	186.5	367.7	381.4	194.1

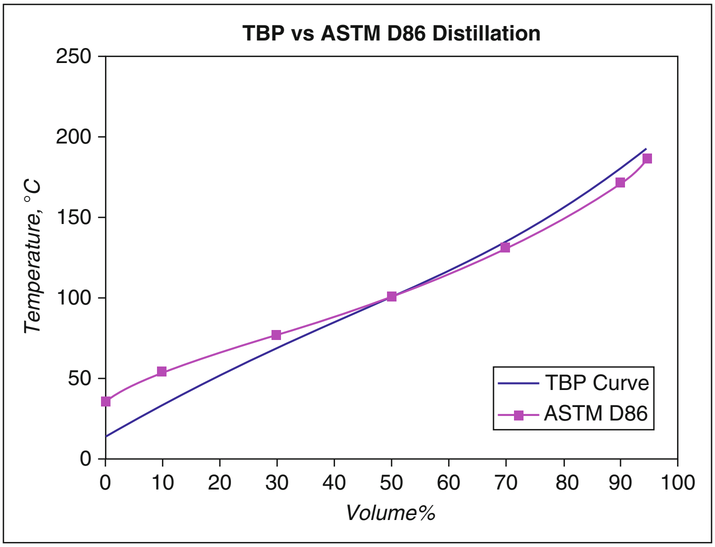

Figure E3.12.1 API method

The results for the Daubert's method are shown in Table E3.12.2 and plotted in Figure E3.12.2.

Table E3.12.2 Method of Daubert

Volume % distilled	Index i	A_i	B_i	ΔT_i	$\Delta T_i'$, F	TBP, °F	TBP, °C
0	1	7.4012	0.6024	31.5	59.14	22.4	−5.3
10	2	4.9004	0.7164	41.4	70.57	81.6	27.5
30	3	3.0305	0.8008	44.1	62.86	152.1	66.7
50	4	0.8718	1.0258		0.00	215.0	101.7
70	5	2.5282	0.820	53.1	65.67	280.7	138.1
90	6	3.0419	0.755	72	76.81	357.5	180.8
	7	0.1180	1.6606				
		224.42 °F					
VABP		106.9 °C					
		206.14 °F					
MeABP		96.75 °C					

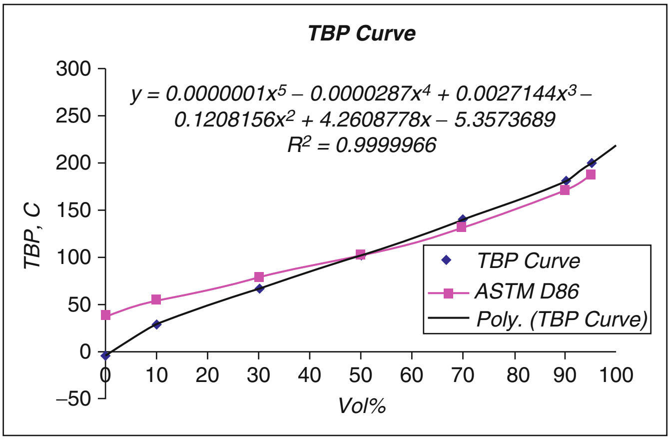

Figure E3.12.2 Daubert's method

Example E3.13

A petroleum crude has an API of 34 and a TBP of 320 °C. Calculate all properties such as critical, refractive index, viscosity and molecular type composition.

Solution:

The calculated properties are shown in Table E3.13. Listed in details in Table E3.13.

Table E3.13 Calculations of properties

The following calculations require the API gravity and the mean average boiling point and other variable.

Calculation of Watson Characterization factor and Molecular weight

API gravity =	34.00				
Specific gravity =	0.8550				
MeABP, C =	320.00	593.15	K	494.59	R
Watson K Factor =	11.95				
Mol. Weight	257.12				

Calculation of Kinematic viscosity

Kinematic viscosity at 100 F, cSt	5.823
Kinematic viscosity at 210 F, cSt	1.916

Calculation of Critical Properties and Acentric factor

Critical Temperature, T_c		Critical Pressure, P_c	T_{br}	ω
K	R	bar		
765.49	1377.87	15.26	0.774867	0.7770

Refractive Index

Light Fractions MW = 70–300

Huang Characterization parameter,	I =	0.284			
Refrective index	n =	1.481	Constants for I		
Density at 68 F, g/cm^3	d =	0.8514	a	0.02266	0.02341
Refractivity intercept	RI =	1.055	b	0.000391	0.000646
			c	2.468	5.144
			d	−0.00057	−0.00033

Heavy Fractions MW = 300–600			e	0.0572	−0.407
	I =	0.308	f	−0.72	−3.333
	n =	1.528			
Density at 68 F, g/cm^3	d =	0.8514			
Refractivity intercept	RI =	1.102			
Molecular type composition					
Light fractions MW = 70–200			a	−13.359	
Viscosity gravity constant			b	14.4591	
Paraffins, mol pct.	VGF =	0.9591	c	−1.41344	
Naphthenes, mol pct.		53.83	d	23.9825	
Aromatics, mol pct.		15.03	e	−23.333	
TOTAL		31.14	f	0.81517	
		100.00	g	−9.6235	
			h	8.7739	
			I	0.59827	
Heavy fractions MW = 200–600					
Kinematic viscosity at 100 F in Sybolt seconds		45.01			
Viscosity gravity constant	VGC =	0.8346			
Paraffins, mol pct.		70.80			
Naphthenes, mol pct.		5.86			
Aromatics, mol pct.		23.33			
TOTAL		100.00			

3.7. CALCULATING PROPERTIES UTILIZING UNISIM SOFTWARE

Process simulators are used to characterize crude oil and determine the thermophysical properties of crude oil and fractions. UNISIM simulator (UNISIM, 2007) can be utilized in defining pseudo-components of a crude oil, given its crude assay. It provides the option of selecting the thermodynamic model for vapour–liquid equilibrium and thermodynamic properties calculations. It is recommended to use Peng–Robinson equation of state to model hydrocarbon and petroleum mixtures in UNISIM. Detailed information about UNISIM simulator is given in Appendix C.

Example E3.14

Consider the following crude assay which has API = 29:

Volume %	TBP (°C)	Volume %	TBP (°C)
0.00	−9.44	40.00	273.33
4.50	32.22	50.00	326.67
9.00	73.89	60.00	393.33
14.50	115.56	70.00	473.89
20.00	154.44	76.00	520.56
30.00	223.89	80.00	546.11
40.00	273.33	85.00	565.56

Use UNISIM to divide the crude into 10 pseudo-components and calculate all cut properties. Compare the results with those obtained from the correlations in this chapter.

(UNISIM Design Tutorial and Applications, Honey Well, 2007)

Solution:

The crude assay (vol% versus TBP) is entered the oil environment and oil manager data entry of UNISIM, and the number of pseudo-components (10 cuts) is entered in the Blend calculation. The properties calculated by UNISIM are listed in Table E3.14.1.

The corresponding properties calculated using the correlations described in this chapter are listed in Table E3.14.2.

Comparing the results included in Tables E3.14.1 and E3.14.2 shows that values of the properties calculated using UNISIM and the correlations are in good agreement.

Table E3.14.1 Cut property results from UNISIM simulator

Cut	NBP (°C)	MW	Density (kg/m^3)	ω	P_c (kPa)	T_c (°C)	Viscosity (cP)
NBP_29	28.64	64.60	703.31	0.218	3544.42	202.21	0.16
NBP_81	81.13	86.71	743.36	0.299	3459.30	262.09	0.20
NBP_133	133.30	110.54	775.15	0.388	2932.88	318.84	0.28
NBP_187	187.03	141.39	808.52	0.468	2479.23	374.36	0.42
NBP_242	242.17	181.05	841.61	0.615	2111.10	429.01	0.69
NBP_292	292.25	222.75	868.27	0.716	1824.02	476.34	1.11
NBP_346	345.58	272.21	894.35	0.853	1563.23	524.94	1.89
NBP_399	399.12	322.66	919.05	0.990	1342.14	572.40	3.51
NBP_482	481.97	422.22	955.54	1.131	1065.91	644.06	11.85
NBP_585	585.11	556.72	1000.19	1.383	809.38	731.80	124.42

Table E3.14.2 Cut property results from correlations

Cut	NBP (°C)	MW	Density (kg/m^3)	ω	P_c (kPa)	T_c (°C)	Viscosity (cP)
NBP_29	28.64	68.15	738.41	0.257	3044.42	252.27	0.128
NBP_81	81.13	89.67	778.95	0.312	2959.30	288.45	0.160
NBP_133	133.30	114.41	815.45	0.425	2432.88	319.06	0.224
NBP_187	187.03	144.00	849.91	0.497	1979.23	346.49	0.336
NBP_242	242.17	179.53	882.58	0.655	1611.10	371.38	0.552
NBP_292	292.25	217.19	910.29	0.786	1324.02	441.74	0.888
NBP_346	345.58	264.03	938.06	0.871	1063.23	511.51	1.512
NBP_399	399.12	319.38	964.37	1.015	842.14	579.73	2.808
NBP_482	481.97	425.45	1002.46	1.220	565.91	655.31	9.480
NBP_585	585.11	603.15	1046.17	1.413	309.38	683.66	99.536

QUESTIONS AND PROBLEMS

3.1. A naphtha fraction has the following ASTM D86 distillation data:

Volume %	Temperature (°C)
0.0	138.8
10.0	149.6
30.0	158.8
50.0	165.8
70.0	169.9
90.0	178.1
95.0	180.4

Obtain the TBP curve using the API method. Extrapolate the curve to 100% volume distilled.

3.2. Plot the volume percent versus specific gravity, for the naphtha fraction given in problem 3.1, knowing that its specific gravity is 0.801.

3.3. Use the following crude assay data with crude API of 36 to estimate cut vol%, critical properties and molecular weight for Light Naphtha (90–190 °F) and Kerosene (380–520 °F). In addition, calculate the fractions of paraffins, naphthenes and aromatics in the two cuts.

ASTM D86 (°F)	Volume %	Cum vol%	SG
86	0.0	0.0	
122	0.5	0.5	0.6700
167	1.2	1.7	0.6750
212	1.6	3.3	0.7220
257	2.7	6.0	0.7480
302	3.1	9.1	0.7650
347	3.9	13.0	0.7780
392	4.7	17.7	0.7890
437	5.7	23.4	0.8010
482	8.0	31.4	0.8140
527	10.7	42.1	0.8250
584	5.0	47.1	0.8450
636	10.0	57.1	0.8540
689	7.8	64.9	0.8630
742	7.0	71.9	0.8640
794	6.5	78.4	0.8890
–	20.8	99.2	0.9310

3.4. A gas oil has the following TBP distillation data

Volume %	TBP (°C)
0	216
10	243
30	268
50	284
70	304
90	318
95	327
100	334

It also has an average boiling point of 280 °C and an average density of 0.850 g/cm^3.

(a) Split this gas oil fraction into five pseudo-components. Calculate T_c, P_c and ω for each pseudo-component.

(b) Calculate T_c, P_c and ω for the whole gas oil fraction.

(c) Calculate the enthalpy of this gas oil fraction at 400 °C using the Lee–Kessler correlation with a reference state of ideal gas at 273.15 K.

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CHAPTER FOUR

CRUDE DISTILLATION

4.1. INTRODUCTION

Crude distillation unit (CDU) is at the front-end of the refinery, also known as topping unit, or atmospheric distillation unit. It receives high flow rates hence its size and operating cost are the largest in the refinery. Many crude distillation units are designed to handle a variety of crude oil types. The design of the unit is based on a light crude scenario and a heavy crude scenario. The unit should run satisfactorily at about 60% of the design feed rate. Seasonal temperature variation should be incorporated in the design because changes in the cut point of gasoline can vary by 20 °C (36 °F) between summer and winter.

The capacity of the CDU ranges from 10,000 barrels per stream day (BPSD) or 1400 metric tons per day (tpd) to 400,000 BPSD (56,000 metric tpd). The economics of refining favours larger units. A good size CDU can process about 200,000 BPSD. The unit produces raw products which have to be processed in downstream unit to produce products of certain specifications. This involves the removal of undesirable components like sulphur, nitrogen and metal compounds, and limiting the aromatic contents.

Typical products from the unit are:

- Gases
- Light straight run naphtha (also called light gasoline or light naphtha)
- Heavy gasoline (also called military jet fuel)
- Kerosene (also called light distillate or jet fuel)
- Middle distillates called diesel or light gas oil (LGO)
- Heavy distillates called atmospheric gas oil (AGO) or heavy gas oil (HGO)
- Crude column bottoms called atmospheric residue or topped crude.

Fundamentals of Petroleum Refining
DOI: 10.1016/B978-0-444-52785-1.00004-8

4.2. PROCESS DESCRIPTION

The process flow diagram of a typical crude distillation unit is shown in Figure 4.1. Crude oil is pumped from storage tanks where it is freed from sediments and free water by gravity. It goes through a series of heat exchangers where it is heated with hot products coming out from the distillation column and by the exchange with heat from the pumparound liquid streams. The temperature of the crude feed can reach 120–150 °C (248–302 °F).

The crude oil contains salt in the form of dissolved salt in the tiny droplet of water which forms a water-in oil emulsion. This water cannot be separated by gravity or through mechanical means. It is separated through electrostatic water separation. This process is called desalting. In the electrostatic desalter, the salty water droplets are caused to coalesce and migrate to the aqueous phase by gravity. It involves mixing the crude with dilution water (5–6 vol%) through a mixing valve.

The crude is further heated in product heat exchangers. The preheating of the crude using the hot products cools down the products to the desired temperature for pumping to the storage tanks. This is essential for the economics of the unit in terms of energy conservation and utilization. Of course, preheating is not enough, as the crude has to be partially vaporized to the extent that all products, except for the atmospheric residue have to be in the vapour phase when the crude enters the atmospheric distillation column. Thus a furnace is required to boost the temperature to

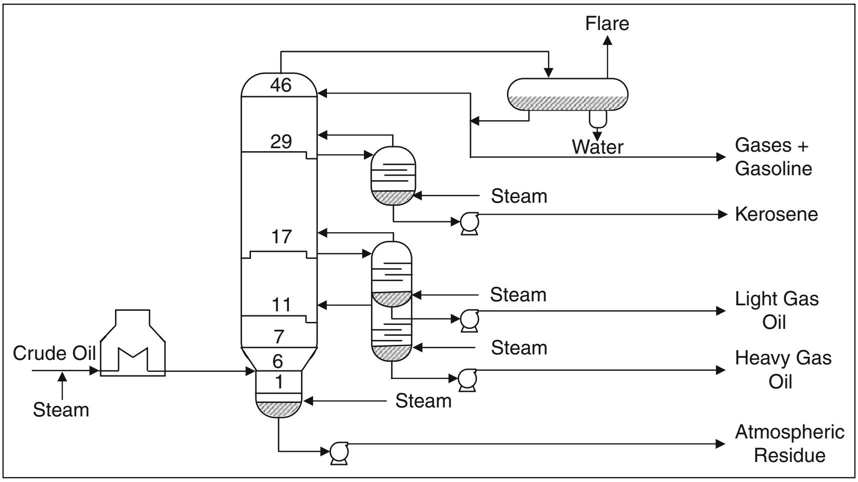

Figure 4.1 Process flow diagram of an atmospheric distillation unit

between 330 and 385 °C (626 and 725 °F) depending on the crude composition.

The partially vaporized crude is transferred to the flash zone of the column located at a point lower down the column and above what is called the stripping section. The main column is typically 50 m (164 ft) high and is equipped with about 30–50 valve trays. The vapour goes up in tremendous amounts and at a high flow rate, necessitating a large diameter column above the flash zone. At the bottom of the stripping section, steam is injected into the column to strip the atmospheric residue of any light hydrocarbon and to lower the partial pressure of the hydrocarbon vapours in the flash zone. This has the effect of lowering the boiling point of the hydrocarbons and causing more hydrocarbons to boil and go up the column to be eventually condensed and withdrawn as side streams. As the hot vapours from the flash zone rise through the trays up the column, they are contacted by the colder reflux down the column. In the overhead condenser, the vapours are condensed and part of the light naphtha is returned to the column as reflux. Further reflux is provided by several pumparound streams along the column.

In the distillation tower, heat required for separation is provided by the enthalpy of the feed. For effective separation heat has to be removed from the tower, in this case, by the overhead condenser and several pumparound streams along the tower length. The pumparound stream is a liquid withdrawn at a point below a side stream tray that is cooled by the cold crude feed as part of the preheat exchangers train. It is then returned to the column a few trays above the draw tray. This pumparound cooling accomplishes a number of tasks. First, the cold liquid condenses more of the rising vapours thus providing more reflux to compensate for the withdrawal of products from the column. Second, heat is removed from the column at higher temperatures. This is in addition to the heat removal from the condenser which takes place at relatively lower temperatures, thus the thermal efficiency of the column is improved and the required furnace duty is reduced. Third, pumparound streams reduce the vapour flow rate throughout the column. Therefore, the required column is smaller than what would otherwise be required if pumparound streams where not there. The drawback to using more pumparound streams is that they tend to reduce the fractionation because a more fractionated liquid is mixed after cooling with a less fractionated liquid a few trays above.

The side draw products are usually stripped to control their initial boiling point. The strippers contain several trays and the stripping is done using steam at the bottom of the stripper or reboiler type side stream strippers. The end boiling point of the side stream is controlled by the flow rate of the side stream product.

The overhead vapour is condensed at the top of the tower by heat exchange with the cool crude coming into the unit and by air and cooling water. The liquid product is called light straight run naphtha. Part of this product is returned to the column as an external reflux. Down the column,

Table 4.1 Tray distribution in a crude distillation unit

Zone	Number of trays
Overhead product to kerosene	10
Kerosene to light gas oil	8
Light gas oil to heavy gas oil	6
Heavy gas oil to flash zone	6
Flash zone to atmospheric residue	6
Pumparounds	3–4

other products are withdrawn, such as heavy straight run naphtha, kerosene or jet fuel, LGO and HGO. All of these products are withdrawn above the feed tray. The atmospheric residue is withdrawn from the bottom of the column.

The main column is equipped with between 30 and 50 valve trays. Typical designs have the trays distribution between products as shown in Table 4.1.

4.3. OPERATION OF CRUDE DISTILLATION UNITS

The CDU can be looked at from the point of view of a process engineering as a multicomponent distillation column. Indeed, the commercial process simulation program models CDU as a case of multicomponent distillation with undefined pseudo-components instead of the normally encountered defined components. However, because we are dealing with a mixture of thousands of compounds and due to the limitation of any distillation column in terms of its capacity to fractionate these components, there are specific operational aspects which characterize the CDU operation. In addition, there are some practical aspects in meeting the required specifications and boiling range of the required transportation fuels. In this section, the factors which affect the design and operation of the unit are explored.

4.3.1. Fractionation

The degree of fractionation in a crude unit is determined by the gap or overlap between two adjacent side stream products. Hence we can talk about the gap or overlap in the boiling point range between kerosene and LGO for example. In the ideal case there would be no overlap between these products and the end boiling point of kerosene would be the initial boiling point of the LGO. However, if we compare the ASTM distillation boiling points, and since ASTM distillation does not give perfect fractionation, the ASTM end point of kerosene is higher than the initial ASTM boiling point of LGO. This is called fractionation overlap.

Since determining the initial and end point on the laboratory test is not always possible or accurate, the fractionation gap is defined as the difference between the ASTM 5% boiling point of the product and the 95% point of the lighter product. When this difference is positive, we have a gap indicating good fractionation. A negative difference is called an overlap indication that some of the light product is still in the heavier product and vice versa. Figure 4.2 shows the gap and overlap concept. By controlling the cut point of any two consecutive products we can affect the degree of fractionation.

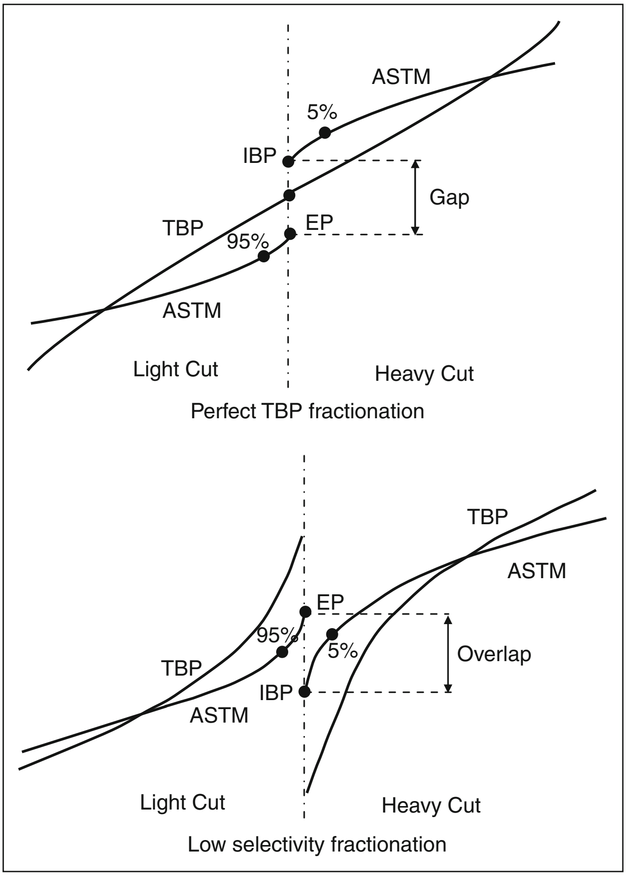

Figure 4.2 Gap and overlap (Ptak *et al.*, 2000)

4.3.1.1. Cut Points

The cut points in the CDU are controlled by the overhead vapour temperature which determines how much vapour goes to the condensers to produce light naphtha and by the flow rate of the various products straight from the column or the side stream strippers. The atmospheric residue level control inside the column determines its flow rate and thus its initial cut point.

The amount of light naphtha is determined by the dew point of the naphtha at its partial pressure, which is close to the overhead temperature. Changing the drawoff rate of any product affects the cut points of the heavier product below it. For example, lowering the kerosene flow rate will lower its end point (make it lighter), but will also modify the initial cut points of the LGO and HGO and the initial cut point of the atmospheric residue. The residue flow rate, the internal reflux rate, the drawoff temperatures and the pumparounds are also affected.

Therefore, if the cut point of one stream is changed through a change in its withdrawal rate, the flow rate of the heavier product next to it should be changed in the reverse and by the same amount in order to make the changes in the desired stream only. For example, if the end point of kerosene is lowered by decreasing the kerosene flow rate by a certain amount, the flow rate of LGO has to be increased by the same amount. If this action is taken, only the cut point of kerosene is affected and the cut points of the other products remain unchanged.

The side stream rate also affects the temperature at the withdrawal tray and lowers the internal reflux coming out of that tray. The internal reflux rate affects the degree of fractionation. It can be increased by increasing the heater outlet temperature, and by lowering the pumparound duty in the lower section of the column. When less heat is removed by the lower pumparound, more vapours will be available up the column and more internal reflux is produced as the vapours are condensed.

4.3.1.2. Degree of Fractionation

The fractionation quality between two consecutive streams is affected by several factors such as the vapour and liquid flow rates in the column zone between these two streams, the number of trays, and the heat extracted by the pumparound. Fractionation quality is formulated in terms of gap or overlap of the products. For perfect fractionation, zero gap and overlap are required. This means that the EBP of the light cut would be the IBP of the heavier cut and so on.

4.3.2. Overflash

In order to fractionate the crude oil into the various products, it has to be heated to a temperature between 330 and 385 °C (626 and 725 °F), depending on the crude composition. The partially vaporized crude is transferred to the flash zone of the column located at a point lower down the column. The furnace outlet temperature should be enough to vaporize all products withdrawn above the flash zone plus about 3–5 vol% of the bottom product. This overflash has the function of providing liquid wash to the vapours going up the column from the flash zone, and improving fractionation on the trays above the flash zone, thereby improving the quality of the HGO and reducing the overlap with the bottom products below the flash zone. This necessitates that there must be few trays in the region between the flash zone and the HGO drawoff. The overflash provides heat input to the column in excess to that needed to distill the overhead products. It also prevents coke deposition on the trays in the wash zone.

The furnace outlet temperature is controlled to keep coking inside the furnace tubes and in the column flash zone to a minimum. However, the composition of the crude plays a part in determining the maximum temperature allowed. Paraffinic crude oils cracks more readily than an aromatic or asphalt-base crude. Therefore, the furnace outlet temperature for paraffinic crude oils is lower than that for other crude types.

4.3.3. Column Pressure

The pressure inside the CDU column is controlled by the back pressure of the overhead reflux drum at about 0.2–0.34 bar gauge (3–5 psig). The top tray pressure is 0.4–0.7 bar gauge (6–10 psig) higher than the reflux drum. The flash zone pressure is usually 0.34–0.54 bar (5–8 psi) higher than the top tray.

4.3.4. Overhead Temperature

The overhead temperature must be controlled to be 14–17 °C (25–31 °F) higher than the dew point temperature for the water at the column overhead pressure so that no liquid water is condensed in the column. This is to prevent corrosion due to the hydrogen chloride dissolved in liquid water (hydrochloric acid).

Example E4.1

If the overhead stream contains 8.5 mol% water at a pressure of 34.7 psia (2.36 bars), calculate the overhead temperature for safe operation.

Solution:

The saturation temperature of water at the partial pressure of water in the overhead vapour.
Water partial pressure $= 0.085 \times 2.36 = 0.2$ bars
From the steam tables:
Saturated steam temperature at 0.2 bars = 61 °C
Safe overhead operating temperature $= 61 + 17 = 78$ °C

4.3.5. Pre-flash Columns and Crude Column Capacity

The crude flow rate to the CDU determines the capacity of the whole refinery. A crude column is typically designed for 80% loading, which means that the unit can be operated at 20% throughput more than the design value. The capacity of the column is limited by the vapour flow rate with a velocity between 2.5 and 3.5 ft/s (0.76 and 1.07 m/s). The vapour flow rate increases as the vapours rise from the flash zone to the overhead. To keep the vapour velocity within the limits mentioned above, the pumparounds, which are installed at several points along the column, extract heat from the column. This results in condensing the rising vapours and reducing the vapour velocity.

To expand crude capacity, the most used technique is to introduce a pre-flash column before the crude heater. The crude oil after preheating in the hot products and pumparound heat exchangers is flashed into a column where the lightest products are removed. The bottoms from the pre-flash column are introduced into the crude heater and then to the crude column. The amounts of the light ends in the crude are now less, and this reduces the vapour loading up the column. Although the unit throughput is increased, the furnace duty is not increased, since the crude rate going to the furnace is not affected due to the removal of the light ends. Pre-flash columns are also introduced in the original design of the CDU when the crude oil is light, and when it contains a lot of light ends in the naphtha range.

4.4. CRUDE OIL DESALTING

When the crude oil enters the unit, it carries with it some brine in the form of very fine water droplets emulsified in the crude oil. The salt content of the crude measured in pounds per thousand barrels (PTB) can be as high as 2000. Desalting of crude oil is an essential part of the refinery operation. The salt content should be lowered to between 5.7 and 14.3 kg/1000 m^3 (2 and 5 PTB). Poor desalting has the following effects:

- Salts deposit inside the tubes of furnaces and on the tube bundles of heat exchangers creating fouling, thus reducing the heat transfer efficiency;
- Corrosion of overhead equipment; and,
- The salts carried with the products act as catalyst poisons in catalytic cracking units.

4.4.1. Types of Salts in Crude Oil

Salts in the crude oil are mostly in the form of dissolved salts in fine water droplets emulsified in the crude oil. This is called a water-in-oil emulsion, where the continuous phase is the oil and the dispersed phase is the water.

The water droplets are so small that they cannot settle by gravity. Furthermore, these fine droplets have on their surfaces the big asphaltene molecules with the fine solid particles coming from sediments, sands or corrosion products. The presence of these molecules on the surface of the droplets acts as a shield that prevents the droplets from uniting with each other in what is called coalescence. The salts can also be present in the form of salts crystals suspended in the crude oil. Salt removal requires that these salts be ionized in the water. Hence, wash water is added to the crude to facilitate the desalting process as will be explained later.

Going back to the subject of salt types, these are mostly magnesium, calcium and sodium chlorides with sodium chloride being the abundant type. These chlorides, except for NaCl, hydrolyze at high temperatures to hydrogen chloride:

$$\mathrm{CaCl_2 + 2H_2O \rightarrow Ca(OH)_2 + 2HCl} \tag{4.1}$$

$$\mathrm{MgCl_2 + 2H_2O \rightarrow Mg(OH)_2 + 2HCl} \tag{4.2}$$

On the other hand, NaCl does not hydrolyze. Hydrogen chloride dissolves in the overhead system water, producing hydrochloric acid, an extremely corrosive acid.

4.4.2. Desalting Process

To remove the salts from the crude oil, the water-in oil emulsion has to be broken, thus producing a continuous water phase that can be readily separated as a simple decanting process. The process is accomplished through the following steps (Abdel-Aal *et al.*, 2003):

- *Water washing*: Water is mixed with the incoming crude oil through a mixing valve. The water dissolves salt crystals and the mixing distributes the salts into the water, uniformly producing very tiny droplets. Demulsifying agents are added at this stage to aide in breaking the emulsion by removing the asphaltenes from the surface of the droplets.
- *Heating*: The crude oil temperature should be in the range of 48.9–54.4 °C (120–130 °F) since the water–oil separation is affected by the viscosity and density of the oil.
- *Coalescence*: The water droplets are so fine in diameter in the range of 1–10 μm that they do not settle by gravity. Coalescence produces larger drops that can be settled by gravity. This is accomplished through an electrostatic electric field between two electrodes. The electric field ionizes the water droplets and orients them so that they are attracted to each other. Agitation is also produced and aides in coalescence. The force of attraction between the water droplets is given by:

$$F = KE^2 d^2 \left(\frac{d}{s}\right)^4 \tag{4.3}$$

where E is the electric field, d is the drop diameter and s is the distance between drops centres and K is a constant.

- *Settling*: According to Stock's law the settling rate of the water droplets after coalescence is given by

$$\text{Settling rate} = \frac{k(\rho_{H_2O} - \rho_{oil})d^2}{\mu_{oil}} \tag{4.4}$$

where ρ is the density μ is the viscosity, d is the droplet diameter and k is a constant.

4.4.3. Description of Desalter

A typical desalter contains two metal electrodes as shown in Figure 4.3. A high voltage is applied between these two electrodes. For effective desalting the electric fields are applied as follows:

- A high voltage field called the "secondary field" of about 1000 V/cm between the two electrodes is applied. The ionization of the water droplets and coalescence takes place here

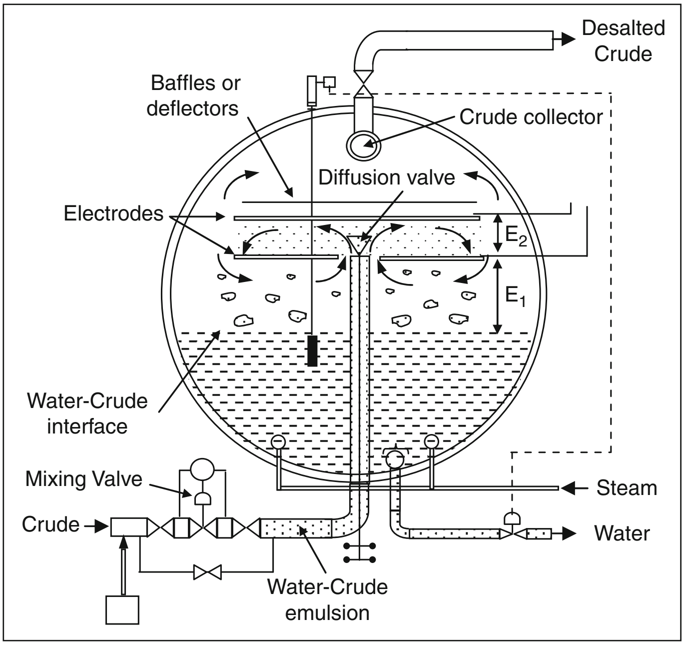

Figure 4.3 Simplified flow diagram of an electrostatic desalter (Ptak *et al.*, 2000)

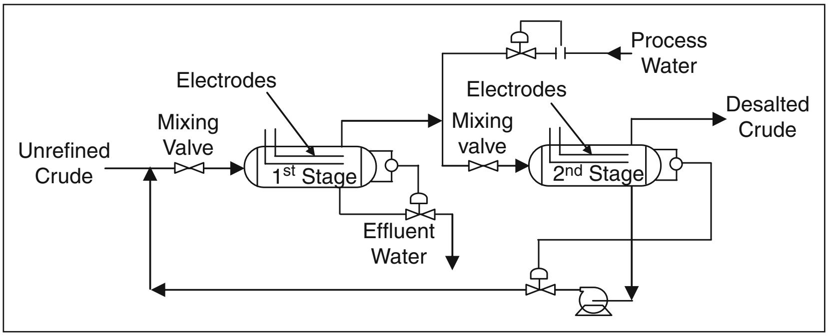

Figure 4.4 Two-stage desalting

- A primary field of about 600 V/cm between the water–crude interface and the lower electrode is applied. This field helps the water droplets settle faster.

The desalter of this design achieves 90% salt removal. However 99% salt removal is possible with two-stage desalters as shown in Figure 4.4. A second stage is also essential since desalter maintenance requires a lengthy amount of time to remove the dirt and sediment which settle at the bottom. Therefore, the crude unit can be operated with a one stage desalter while the other is cleaned.

4.4.4. Desalter Operating Variables

For an efficient desalter operation, the following variables are controlled:

- *Desalting temperature*: The settling rate depends on the density and viscosity of the crude. Since increasing the temperature lowers the density and viscosity, the settling rate is increased with temperature based on the crude gravity, typical desalting temperature can vary between 50 and 150 °C (122 and 302 °F).
- *Washing water ratio*: Adding water to the crude oil helps in salt removal. Hence, increasing the wash water rate increases the coalescence rate. Depending on the desalting temperature, a minimum value should be use. For example, Kuwait crude (31.2 API) requires 7–8 vol% water addition relative to the crude rate.
- *Water level*: Raising the water level reduces the settling time for the water droplets in the crude oil, thus improving the desalting efficiency. However, if the water level gets too high and reaches the lower electrode, it shorts out the desalter. Since the primary electric field depends on the distance between the lower electrode and the water–crude interface, it is always better to keep the level constant for stable operation.
- *Washing water injection point*: Usually the washing water is injected at the mixing valve. However, if it is feared that salt deposition may occur in

the preheat exchangers, part or all of the washing water is injected right after the crude feed pump.

- *Demulsifier injection rate*: Demulsifiers are basic copolymers with one end being hydrophilic (loves water and attaches to the surface of the water droplet), and the other end being hydrophobic (loves the oil and is directed to the oil side). When these compounds are adsorbed on the droplet surface, they stabilize the droplet. The demulsifier is added to the crude after the feed pump or before the mixing valve at levels between 3 and 10 ppm of the crude.
- *Type of washing water*: Process water in addition of fresh water is used for desalting. The water should be relatively soft in order to prevent scaling. It should be slightly acidic with a pH in the range of 6. It should be free from hydrogen sulphide and ammonia so as to not create more corrosion problems. Therefore, distillation overhead condensates and process water from other units can be used after stripping.
- *Pressure drop in the mixing valve*: Mixing the washing water with crude oil is necessary in order to distribute the water and dissolve any suspended salts crystals. The pressure drop across the mixing valve determines the mixing efficiency. On the other hand, the mixing process produces finer (smaller diameter) droplets which tend to stabilize the emulsion and make water separation more difficult. Therefore, there is a compromise in selection of the appropriate pressure drop across the mixing valve. A pressure drop between 0.5 and 1.5 bar (7.4 and 22 psi) is used.

One variable which is not mentioned above is the desalter pressure. The operation of the desalter requires that the crude be in the liquid phase during desalting. A typical pressure of 12 bar (176 psia) is necessary to achieve this purpose. When the process control variables are properly adjusted, a 90% salt rejection (2–5 PTB of salts in the desalted crude relative to the raw crude) can be achieved. With a two stage operation the salt rejection can reach 99%. Any remaining salts are neutralized by the injection of sodium hydroxide which reacts with the calcium and magnesium chloride to produce sodium chloride.

$$\mathrm{CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl} \tag{4.5}$$

NaCl does not hydrolyze to the corrosive hydrogen chloride.

4.5. VACUUM DISTILLATION

To extract more distillates from the atmospheric residue, the bottom from the atmospheric CDU is sent to the vacuum distillation unit. The vacuum unit distillates are classified as light vacuum gas oil (LVGO), medium vacuum gas oil (MVGO), and heavy vacuum gas oil (HVGO). In addition a vacuum residue is produced. If the distillates are feed to down stream conversion process, their the sulphur, metal and asphaltene content should be reduced by hydrotreating or hydroprocessing. In some refineries the whole atmospheric residue is hydroprocessed before vacuum distillation. The vacuum unit can also be used to produce lubrication oil grade feed stocks. This depends on the quality of the crude oil feed to the refinery as only special types of crude can produce lube grade feed stocks.

4.5.1. Process Description

Figure 4.5 shows the flow diagram of the vacuum distillation unit. The atmospheric residue can be sent directly to the vacuum unit after heat extraction in the crude preheat exchangers train. If it is sent to storage, the temperature should not be below 150 °C (300 °F) to control the viscosity necessary for proper flow. It is then heated in several exchangers by the hot products and pumparounds of the vacuum unit. Final heating to 380–415 °C (716–779 °F) is done in a fired heater. To minimize thermal cracking and coking, steam is injected in the heater tube passes. The feed enters the vacuum tower at the lower part of the column. As in the case of atmospheric distillation, a 3–5 vol% overflash is maintained (i.e., 3–5 vol% vapours are produced more than the total products withdrawn above the flash zone). This is to provide some fractionation between the HVGO

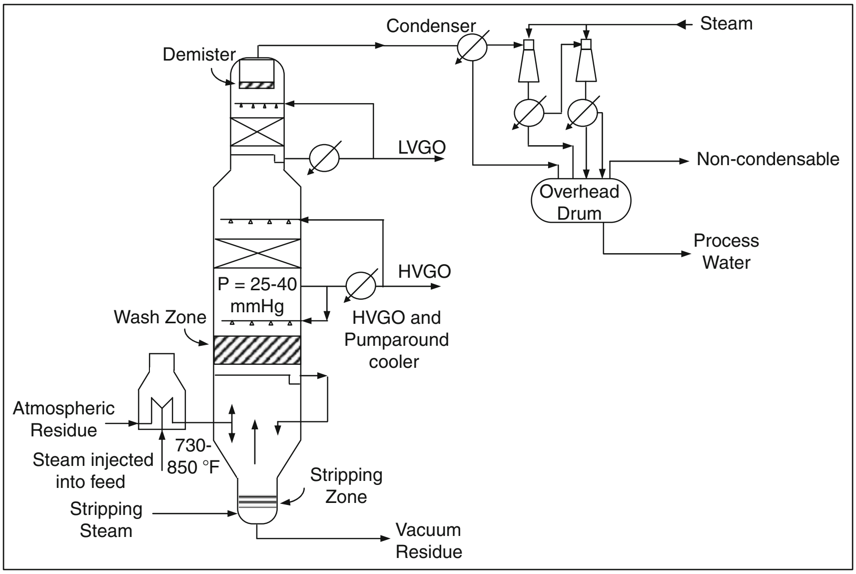

Figure 4.5 Process flow diagram of the vacuum distillation unit

drawoff tray and the flash zone, thereby controlling its end point. The distillate is withdrawn as LVGO and two other cuts, MVGO and HVGO. The two cuts of MVGO and HVGO are necessary to extract heat from the tower at a more advantageous level from the HVGO pumparound.

Vacuum distillation columns are equipped with packing for fractionation and heat exchange zones. This is in order to reduce the pressure drop in the column which is necessary for creating a low vacuum in the lower section of the column. The bottom zone is equipped with valve trays. The vapours from the flash zone go through a wash and fractionation zone where the heavy ends are condensed with HVGO reflux. Further up, the column sections (consisting of a heat exchange and fractionation zone) are separated by sprays of liquid from the pumparound or the internal reflux.

Vacuum distillation units have a system to create the vacuum that uses either ejectors or a combination of ejectors and liquid ring pumps. Ejectors recompress the gases through a nozzle where vapours from the column are sucked into the venturi section of the nozzle by a stream of medium or low pressure steam. The vapour phase at the ejector exit is partially condensed in an exchanger with cooling water. The liquid phase is then sent to the overhead drum. The vapour phase goes from the condenser to another ejector-condenser stage.

Liquid ring pumps are similar to rotor gas compressors. One pump can replace two or three stages of ejectors in dry or wet type vacuum distillation. They do not use steam and can significantly reduce hydrocarbon-rich aqueous condensates in a system using ejectors. Systems with ejectors are much more flexible and rapid to put into operation. The higher investments required by liquid ring pumps are offset by reduced steam consumption and lower installation costs.

4.6. CRUDE DISTILLATION MATERIAL BALANCE

In this section, we will consider the product slate from the crude distillation unit (atmospheric and vacuum distillation). For a given crude oil feed rate, the flow rates and the properties of the various products are calculated. Furthermore, the properties of the various cuts are estimated. For this purpose, crude assay data have to be provided. In addition, the desired products from the atmospheric and vacuum distillation towers are assigned along with their respective boiling point ranges.

4.6.1. Crude Assay Data

Laboratory crude assay reports provide TBP for the whole crude as explained in Section 3.2.3. The maximum temperature that can be measured with this test is in the range of 496–526 °C (925–975 °F), depending on the crude oil. The actual end point of the crude oil can be as high as 790 °C (1454 °F). Extrapolation of the measured portion of the TBP curve to a volume percent approaching the end point is discussed in Sections 3.3.1 and 3.3.2.

The products from the crude distillation unit (atmospheric and vacuum distillation) are then chosen. Typical products with their end points are shown in example E4.2. The volume percent of each cut is determined by calculating the cumulative volume percent for each fraction at its end boiling point from any of the fit procedures explained earlier in Section 3.3 and then calculating the difference. The volume fraction of the vacuum residue is obtained as 100 minus the cumulative volume percent at the end boiling point of the vacuum distillate.

Example E4.2

Consider the Kuwait export crude with the following TBP-vol% data:

Volume %	TBP (°C)
5	40
10	85
30	215
50	340
70	495

Determine the volumetric yield, average boiling point, molecular weight and specific gravity for the products shown in Table E4.2.1.

Table E4.2.1 Typical CDU products and their end boiling points

Cut #	Product	End point (°C)
1	Off gas	10
2	Light straight run naphtha	70
3	Naphtha	180
4	Kerosene	240.0
5	Light diesel	290.0
6	Heavy diesel	340.0
7	Atm. gas oil	370.0
8	Vacuum gas oil	390.0
9	Vac. distillate	550.0
9	Vac. residue	–

Solution:

From the fifth order polynomial fit of TBP data versus vol% (Section 3.3.1) and given the end point of each cut, we can calculate the cumulative volume percent. For example, the cumulative volume percent for the off gas and the light straight run naphtha is 1.33 and 8.6%, respectively. Therefore, the volume percent of the light straight run naphtha is 8.6–1.33 or 7.27%. The average normal boiling point for each cut is calculated at the mid percent of each cut. This means that we can use polynomial fit again but this time, at a cumulative volume percent of the cut (in this case the light straight run naphtha) 1.33 + 7.27/2 or 4.965%. The average boiling point is then calculated to be 43.6 °C. From equation (3.29) with this average boiling point, the molecular weight is 71.2. The specific gravity is calculated, from the molecular weight and average boiling point using equation (3.11), to be 0.680. The calculations for the other cuts are shown below. These calculations can be done using the Excel spreadsheet Crude Unit. Table E4.2.2 shows the results.

Table E4.2.2 Volumetric yield of cuts and their properties

Cut #	Product	Vol% of cut	End point °C	Average NBP, °C	Molecular weight	Specific gravity
1	Off gas	1.33	10	2.5	55.6	0.635
2	Lt. St. Run Naph	7.27	70	43.6	71.2	0.680
3	Naphtha	16.56	180	131.5	112.4	0.754
4	Kerosene	10.05	240.0	209.9	159.8	0.803
5	Light Diesel	7.83	290.0	264.4	200.1	0.831
6	Heavy Diesel	6.99	340.0	314.3	243.6	0.854
7	Atm. Gas Oil	3.84	370.0	354.8	284.7	0.870
8	Vacuum Gas Oil	2.43	390.0	379.9	313.2	0.880
9	Vac. Distillate	18.34	550.0	466.6	434.7	0.910
9	Vac. Residue	26.70	–	688.6	1150.3	0.969

The TBP curve for each product can also be obtained from the volume percent of each cut as shown in the example E4.3.

Example E4.3

Plot the true boiling point curve for the kerosene product from Table E4.2.2.

Solution:

Volume percent of kerosene = 9.51%

The cumulative vol% at the IBP of kerosene = 1.33 + 7.27 + 16.56 = 25.16%

The cumulative vol% at the EBP of kerosene = 25.16 + 10.05 = 35.21%

The cumulative vol% at the 10% of kerosene cut = 0.1(10.05) + 25.16 = 26.17%. At vol% of 26.17% the estimated TBP is 186.73 °C using the same polynomial fit that was used in E4.2. The procedure is repeated at 20% of kerosene volume which yield 27.17% and TBP of 189.26 °C. Figure E4.3.1 shows the TBP curve for kerosene which starts at IBP of 180 °C and ends at EBP of 240 °C.

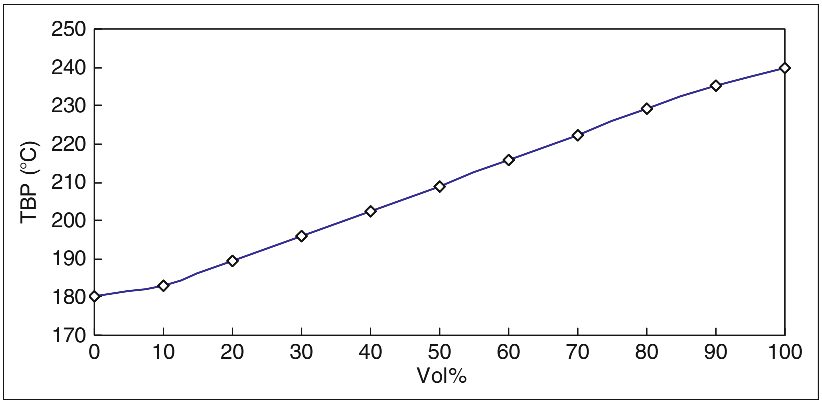

Figure E4.3.1 TBP curve for kerosene cut

4.6.2. Material Balance

For a given feed flow rate in barrels per calendar day (BPCD), and given the specific gravity of the feed, the mass flow rate of the feed can be calculated. Then the volumetric throughput of each product cut in BPCD and in kg/h (lb/h) is calculated. The mass flow rate of the vacuum residue is calculated as the difference between the feed mass flow rate and the total mass flow rate of all products lighter than the vacuum residue. Similarly from the mass flow rate of the residue and its gravity, its volumetric flow rate can be calculated. The sum of the volumetric flow rates of the products may become higher than the feed. This is expected, since the volume change of mixing is negative for petroleum fractions. When the fractions are mixed, the total volume of the mixture is less than the sum of the volumes of the fractions. Example E4.4 illustrates the material balance calculations.

Example E4.4

For Kuwait export crude (API = 31.5) given in the example E4.2, perform a material balance CDU calculations for a feed rate of 100,000 BPCD.

Solution:

Mass flow rate of feed is 573,844 kg/h. The volumetric product yield is converted to mass flow rates. The mass flow rate of the residue is the difference between the feed rate and the sum of product lighter than the vacuum residue. The results are shown in Table E4.4.1

Table E4.4.1 Crude unit material balance

	EBP, °C	Vol%	BPCD	SG	kg/h
Feed					
Crude oil		100	100,000.0	0.8685	573,844
Products					
Off gas	10	1.33	1330	0.635	5,580
Lt. St. Run	70	7.27	7270	0.680	32,664
Naphtha	180	16.56	16560	0.754	82,500
Kerosene	240.0	10.05	10050	0.803	53,322
Light diesel	290.0	7.83	7830	0.831	42,992
Heavy Diesel	340.0	6.99	6990	0.854	39,442
Atm. Gasoil	370.0	3.84	3840	0.870	22,074
Vac. Gasoil	390.0	2.43	2430	0.880	14,129
Vac. Distil	550.0	18.34	18340	0.910	110,272
Vac. Residue	–	26.70	26700	0.969	170,869
		101.33	101330		573,844

4.6.3. Sulphur Material Balance

For crude oil containing significant amounts of sulphur, it is necessary to make a sulphur balance around the crude unit. The sulphur content of the crude oil should be given. The sulphur content of the products should also be known. If these data are not available the estimation of the sulphur content of petroleum fractions can be calculated using the following equations in the two ranges of molecular weight M (Riazi *et al.*, 1999):

For fractions with $M < 200$

$$\mathrm{wt}\%S = 177.448 - 170.946R_\mathrm{i} + 0.2258m + 4.054\mathrm{SG} \tag{4.6}$$

And for fractions with $M \geq 200$

$$\text{wt\%}S = -58.02 + 38.463R_{\text{i}} - 0.023m + 22.4\text{SG} \tag{4.7}$$

where SG is the specific gravity, R_i is the refractivity intercept defined as

$$R_{\text{i}} = n - \frac{d}{2} \tag{4.8}$$

where n and d are the refractive index and density of liquid hydrocarbon at 68 °F (20 °C) in g/cm^3. Refer to Chapter 3, Sections 3.4.3 and 3.4.4 on how to calculate these parameters. The parameter m is defined as

$$m = M(n - 1.475) \tag{4.9}$$

After calculating the wt% S in each product except the vacuum residue, the amount of sulphur is calculated by multiplying this percentage by the mass rate of each product. The sulphur in the vacuum residue is calculated from the difference of the total sulphur in the crude feed and the total sulphur in the products.

Example E4.5

Perform a sulphur balance on the crude unit of example E4.4, knowing that the sulphur content of Kuwait export is 2.52 wt%.

Solution:

The wt% S in each product except the vacuum residue is calculated using equations (4.6) and (4.7) in Table E4.5.1.

Table E4.5.1 Calculation of sulphur content of the products

	T_b, K	SG	d, 20 °C	I	n, 20 °C	R_i	MW	m	S, wt%
Off gas	275.7	0.635	0.6298	0.2188	1.3565	1.0416	55.6	-6.5890	0.479
Lt. St. Run	316.8	0.680	0.6754	0.2324	1.3814	1.0437	71.2	-6.6710	0.287
Naphtha	404.7	0.754	0.7496	0.2540	1.4219	1.0471	112.4	-5.9731	0.161
Kerosene	483.1	0.803	0.7989	0.2681	1.4488	1.0493	159.8	-4.1919	0.379
Light diesel	537.5	0.831	0.8271	0.2760	1.4642	1.0506	200.1	-2.1700	1.054
Heavy Diesel	587.4	0.854	0.8499	0.2823	1.4766	1.0516	243.6	0.3786	1.541
Atm. Gasoil	627.9	0.870	0.8666	0.2869	1.4857	1.0523	284.7	3.0372	1.880
Vac. Gasoil	653.1	0.880	0.8764	0.2896	1.4910	1.0528	313.2	5.0039	2.069
Vac. Distil	739.7	0.910	0.9070	0.2979	1.5077	1.0541	434.7	14.1990	2.591

The Sulphur material balance is shown in Table E4.5.2.

Table E4.5.2 Sulphur material balance

	Mass (kg/hr)	wt% S	kg/hr S
Feed	573,844	2.52	14,461
Products			
Off gas	5,580	0.479	26.7
Lt. St. Naphtha	32,664	0.287	93.8
Naphtha	82,500	0.161	132.8
Kerosene	53,322	0.379	202.1
Light diesel	42,992	1.054	453.1
Heavy diesel	39,442	1.541	607.8
Atm. Gas Oil	22,074	1.880	415.0
Vac. Gas Oil	14,129	2.069	292.3
Vac. Distillate	110,272	2.591	2857.1
Vac. Residue	170,869	5.490	9380.3
Total	573,844	2.52	14,461

4.7. DESIGN OF CRUDE DISTILLATION UNITS USING PROCESS SIMULATORS

Although the CDU contains many pieces of equipment with different unit operations, the most important one is the distillation column. The design and simulation of the atmospheric and vacuum distillation columns is the most important part of the whole unit design. It determines the quality of the product and since it is energy intensive, it can have a substantial effect on the economics of the unit. Thus, improving the design or operation of the distillation columns can increase the profitability of the refinery. The simulation or design of the distillation columns involves dividing the crude oil into pseudo-components as outlined in Chapter 3. Then a thermodynamic model is chosen for vapour liquid equilibrium and thermodynamic properties calculations. A good model is the cubic equations of state, and the Peng–Robinson equation is one of the most widely used models for hydrocarbon and petroleum mixtures. Next, the unit operations stage-wise or “tray to tray” distillation calculations are performed. The mass, energy balance and vapour liquid equilibrium relations for each tray are written and solved together, subject to certain specification for the products. Computer simulation programs such as UNISIM are used for quick simulation of CDU units.

Example E4.6

Perform a material balance for a CDU using UNISIM for 100,000 BPCD of 29 API crude with the following assay.

vol%	TBP (°C)	vol%	TBP (°C)
0.0	−9.44	40.0	273.33
4.5	32.22	50.0	326.67
9.0	73.89	60.0	393.33
14.5	115.56	70.0	473.89
20.0	154.44	76.0	520.56
30.0	223.89	80.0	546.11

The crude is fed to a pre-flash separator operating at 450 °F and 75 psia. The vapour from this separator bypasses the crude furnace and is remixed with the hot (650 °F) liquid leaving the furnace. The combined stream is then fed to the distillation column (Figure E4.6.1). The column operates with a total condenser, three side strippers and three pumparounds (Figure E4.6.2). (UNISIM 2007).

Solution:

In the oil environment and oil manager data entry of the UNISIM software, the crude assay is entered as vol% and TBP. The yield distribution of the products is shown in Figure E4.6.3.

The distillation column has three inlet steam streams, with pressures and flow rates listed in Table E4.6.1. The main distillation column contains 29 stages (see Figure E4.6.2). The overhead condenser operates at 19.7 psia and the bottoms at 32.7 psia. The side stripper connections are also shown in Figure E4.6.2.

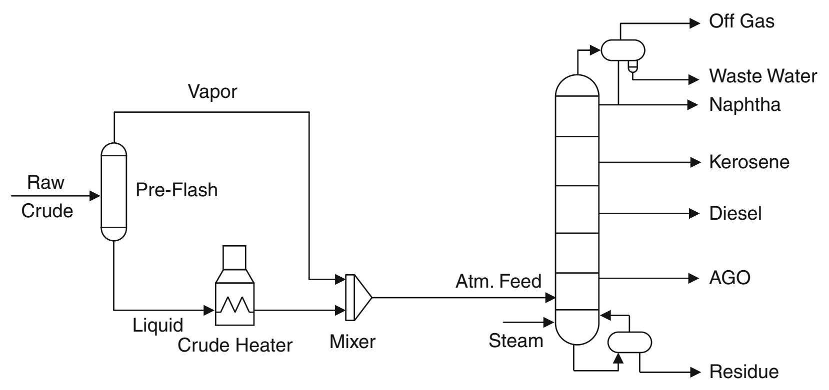

Figure E4.6.1 Crude distillation flowsheet

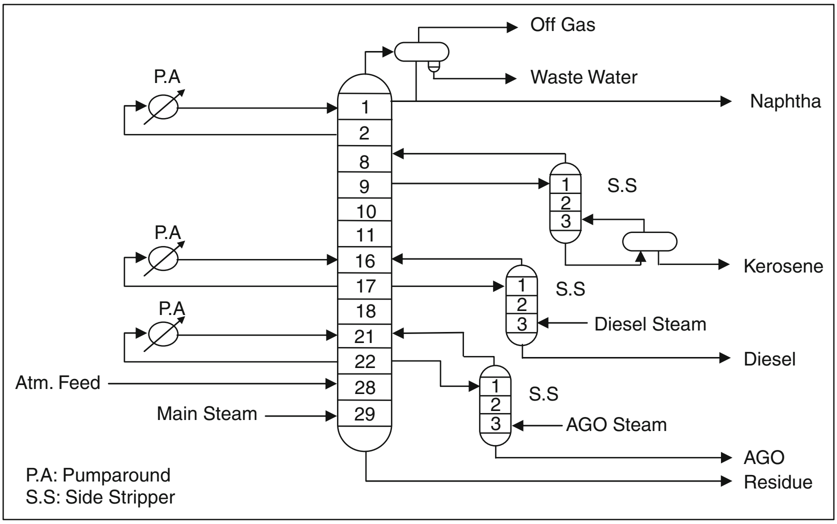

Figure E4.6.2 Distillation column

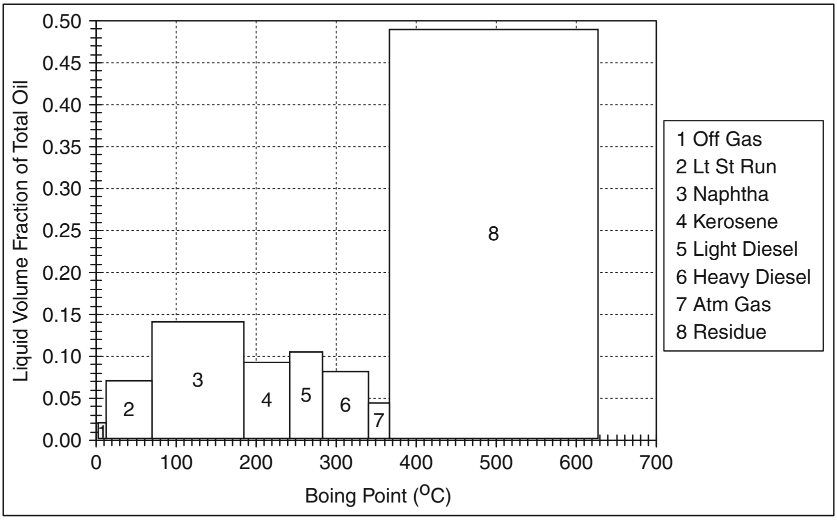

Figure E4.6.3 Crude distribution curve

The distillation column specifications are listed in Table E4.6.1.

Table E4.6.1 Column specifications

Item	Specification
Kero-SS product flow	61.61 m^3/h
Diesel-SS product flow	127.5 m^3/h
AGO-SS product flow	29.81 m^3/h
Pumparound 1 rate	331.2 m^3/h
Pumparound 1 duty	-5.8×10^7 kJ/h
Pumparound 2 rate	198.7 m^3/h
Pumparound 2 duty	-3.7×10^7 kJ/h
Pumparound 3 rate	198.7 m^3/h
Pumparound 3 duty	-3.7×10^7 kJ/h
Naphtha product rate	152.4 m^3/h
Liquid flow	23.19 m^3/h
Kero reboiler duty	7.913×10^6 kJ/h
Vapour product flow	0.0
Reflux ratio	1

The solved material and energy balance is shown in Table E4.6.2.

Table E4.6.2 Material and energy balance

Name	Vapour fraction	T (°C)	P (kPa)	Molar flow (kg mol/h)	Mass flow (kg/h)	Molar enthalpy (kJ/kg mol)
Hot crude	0.6447	343.3	448.2	2843	5.829×10^5	-2.673×10^5
Main steam	1.0	190.6	1034	188.8	3402	-2.359×10^5
Diesel steam	1.0	148.9	344.7	75.54	1361	-2.370×10^5
AGO steam	1.0	148.9	344.7	62.95	1134	-2.370×10^5
Off gas	1.0	41.92	135.8	0	0	–
Naphtha	0.0	41.92	135.8	1283	1.124×10^5	-1.921×10^5
Waste water	0.0	41.92	135.8	316.8	5707	-2.841×10^5
Kerosene	0.0	236.5	205.8	320.9	5.079×10^4	-2.678×10^5
Diesel	0.0	253.0	213.6	509.8	1.106×10^5	-3.583×10^5
AGO	0.0	300.4	218.6	91.7	2.708×10^4	-4.493×10^5
Residue	0.0	355.1	225.5	647.8	2.822×10^5	-5.953×10^5

QUESTIONS AND PROBLEMS

4.1. With 100,000 BPD of the following crude (API = 36), estimate the products of the atmospheric distillation column. If the atmospheric residue of the crude is taken at 650+ °F. It enters in a vacuum distillation tower to give three products: light vacuum gas oil (650–850 °F), heavy vacuum gas oil (850–1050 °F) and vacuum residue (1050+ °F). Calculate the mass flow rate of these products. Then calculate the sulphur content (lb/hr) for each product.

ASTM D86 (°F)	vol%	Cum vol%	SG
86	0.0	0.0	
122	0.5	0.5	0.6700
167	1.2	1.7	0.6750
212	1.6	3.3	0.7220
257	2.7	6.0	0.7480
302	3.1	9.1	0.7650
347	3.9	13.0	0.7780
392	4.7	17.7	0.7890
437	5.7	23.4	0.8010
482	8.0	31.4	0.8140
527	10.7	42.1	0.8250
584	5.0	47.1	0.8450
636	10.0	57.1	0.8540
689	7.8	64.9	0.8630
742	7.0	71.9	0.8640
794	6.5	78.4	0.8890
–	20.8	99.2	0.9310

4.2. What is the concentration of salt in the washed solution for a desalted oil containing 1 lb of NaCl/1000 bbl of oil, if the inlet oil contains 20 lb of NaCl/1000 bbl of oil? Assume the amount of water in oil before and after desalting is the same and the wash water used is 10 vol % of oil.

4.3. Sketch a combined atmospheric and vacuum distillation for a crude oil feed.

4.4. Sketch a side view for the desalter.

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CHAPTER FIVE

CATALYTIC REFORMING AND ISOMERIZATION

5.1. INTRODUCTION

Catalytic reforming of heavy naphtha and isomerization of light naphtha constitute a very important source of products having high octane numbers which are key components in the production of gasoline. Environmental regulations limit on the benzene content in gasoline. If benzene is present in the final gasoline it produces carcinogenic material on combustion. Elimination of benzene forming hydrocarbons, such as, hexane will prevent the formation of benzene, and this can be achieved by increasing the initial point of heavy naphtha. These light paraffinic hydrocarbons can be used in an isomerization unit to produce high octane number isomers.

5.2. CATALYTIC REFORMING

Catalytic reforming is the process of transforming C_7–C_{10} hydrocarbons with low octane numbers to aromatics and iso-paraffins which have high octane numbers. It is a highly endothermic process requiring large amounts of energy. A schematic presentation of the feedstock, products and process condition is shown in Figure 5.1. The process can be operated in two modes: a high severity mode to produce mainly aromatics (80–90 vol%) and a middle severity mode to produce high octane gasoline (70% aromatics content).

5.2.1. Reformer Feed Characterization

Feeds are characterized by the Watson characterization factor (K), naphthenes (N) vol% and aromatics (A) vol% in which ($N + 2A$) must be defined. In addition, initial boiling points (IBP) and end points (EP) for feeds must be characterized. Feeds can be also characterized by the hydrocarbon family and their number of carbon atoms. Naphthenic feeds give a much higher yield than paraffinic feeds. The main feed comes from hydrotreated heavy naphtha, and some feed comes from hydrotreated coker naphtha.

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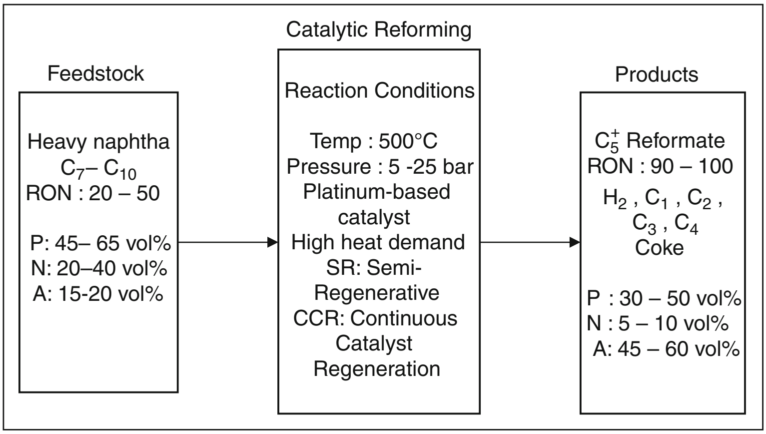


Figure 5.1 Catalytic reforming process

5.2.2. Role of Reformer in the Refinery and Feed Preparation

The catalytic reformer is one of the major units for gasoline production in refineries. It can produce 37 wt% of the total gasoline pool. Other units such as the fluid catalytic cracker (FCC), the methyl ter-butyl ether (MTBE) production unit, alkylation unit and isomerization unit, also contribute to this pool. These units will be covered in other chapters of the book.

The straight run naphtha from the crude distillation unit is hydrotreated to remove sulphur, nitrogen and oxygen which can all deactivate the reforming catalyst. The hydrotreated naphtha (HTN) is fractionated into light naphtha (LN), which is mainly C_5–C_6, and heavy naphtha (HN) which is mainly C_7–C_{10} hydrocarbons. It is important to remove C_6 from the reformer feed because it will form benzene which is considered carcinogenic upon combustion. Light naphtha (LN) is isomerized in the isomerization unit (I). Light naphtha can be cracked if introduced to the reformer. The role of the heavy naphtha (HN) reformer in the refinery is shown in Figure 5.2. Hydrogen, produced in the reformer can be recycled to the naphtha hydrotreater, and the rest is sent to other units demanding hydrogen.

5.2.3. Research Octane Number

The research octane number (RON) is defined as the percentage by volume of iso-octane in a mixture of iso-octane and *n*-heptane that knocks with some intensity as the fuel is being tested. A list of the RON of pure hydrocarbon is given in Appendix D. It is seen from this appendix that the RON of paraffins, iso-paraffins and naphthenes decrease as the carbon number of the molecule increases. Aromatics have the opposite trend. This is shown in Figure 5.3.

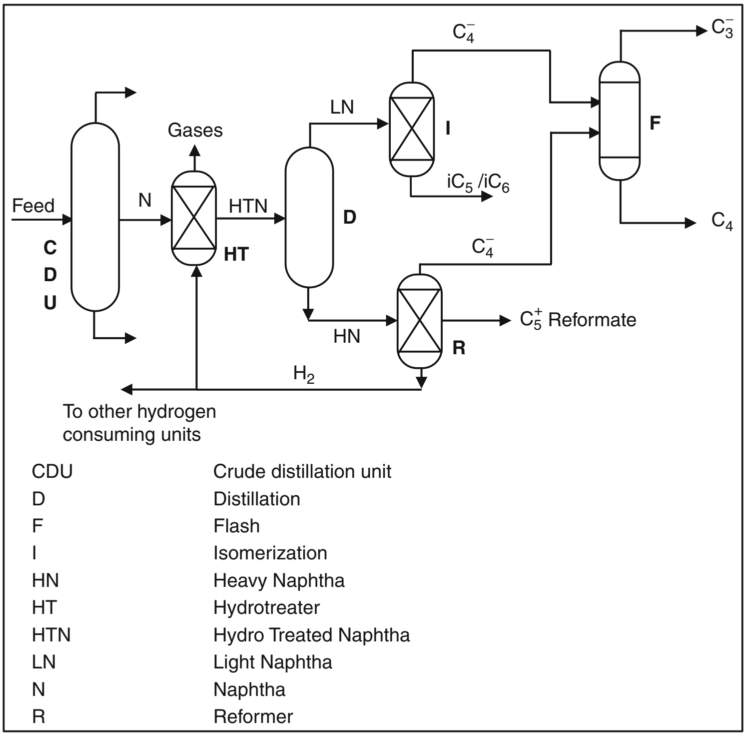


Figure 5.2 Role of reformer in the refinery

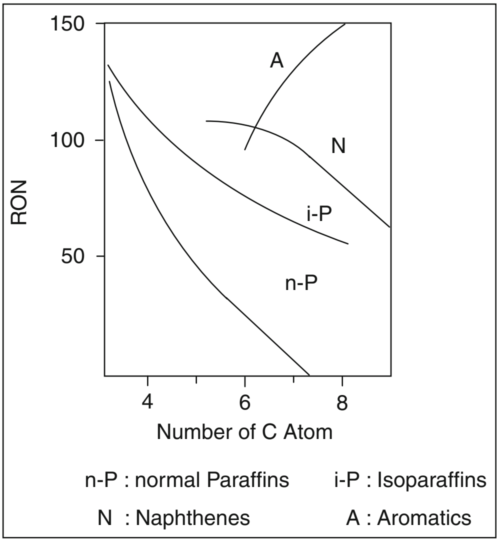
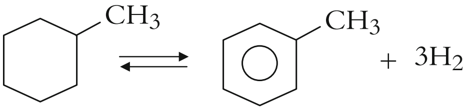


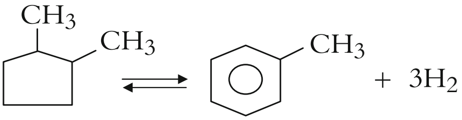
Figure 5.3 Variation of research octane number (RON) (Antos *et al.*, 1995)

5.2.4. Reforming Reactions

5.2.4.1. Naphthene Dehydrogenation of Cyclohexanes


(5.1)

Methyl Cyclohexane Toluene

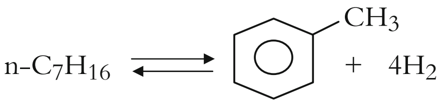

(5.2)

Dimethyl-Cyclopentane Toluene

5.2.4.2. Paraffin Dehydrogenation

$$\underset{\text{n-heptane}}{\text{n-}C_7H_{16}} \rightleftarrows \underset{\text{n-heptene}}{\text{n-}C_7H_{14}} + H_2 \quad (5.3)$$

5.2.4.3. Dehydrocyclization


(5.4)

n-heptane Toluene

All the above reactions are highly endothermic.

5.2.4.4. Isomerization

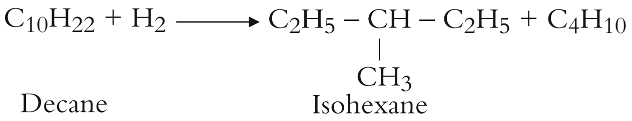
$$\underset{\text{n-heptane}}{\text{n-}C_7H_{16}} \rightleftarrows \underset{\text{isoheptane}}{iC_7H_{16}} \quad (5.5)$$

Isomerization is a mildly exothermic reaction and leads to the increase of an octane number.

5.2.4.5. Hydrocracking Reactions

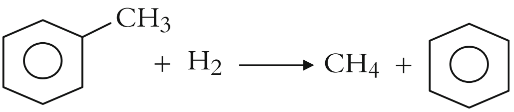
Hydrocracking reactions are the main sources of C_4^- hydrocarbons (C_1, C_2, C_3 and C_4). The reactions are highly exothermic and consume high amounts of hydrogen. Cracking results in the loss of the reformate yield.

Paraffin hydrocracking:



$$\underset{\text{Decane}}{C_{10}H_{22}} + H_2 \longrightarrow \underset{\text{Isohexane}}{C_2H_5-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C_2H_5} + C_4H_{10} \qquad (5.6)$$

Hydrocracking of aromatics



(5.7)

Other paraffins can crack to give C_1–C_4 products.

5.2.4.6. Coke Deposition

Coke can also deposit during hydrocracking resulting in the deactivation of the catalyst. The catalyst in this case has to be re-activated by burning off the deposited coke. The catalyst is selected to produce a slow hydrocracking reaction. Coke formation is favoured at low partial pressures of hydrogen. Hydrocracking is controlled by operating the reaction at low pressure between 5–25 atm (74–368 psia), not too low for coke deposition and not too high in order to avoid cracking and loss of reformate yield.

A summary of reformer reactions and interactions is shown by the reaction network in Figure 5.4.

5.2.5. Thermodynamics of Reforming Reactions

The dehydrogenation reactions are the main source of reformate product and are considered to be the most important reactions in reforming. These are highly endothermic reactions and require a great amount of heat to keep the reaction going. For this reason three reactors are usually used in the reforming process with heating the product from each reactor before entering the other.

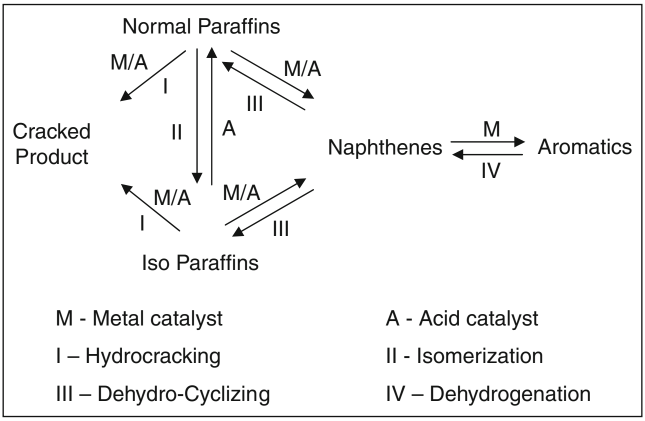
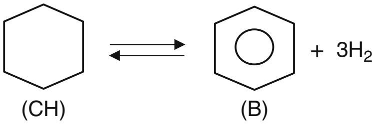


Figure 5.4 Network of reforming reaction

The dehydrogenation reactions are reversible and equilibrium is established based on temperature and pressure. It is usually important to calculate the equilibrium conversion for each reaction. In reforming, a high temperature around 500 °C (932°F) and a low hydrogen pressure are required. The minimum partial pressure of hydrogen is determined by the amount of the desired aromatics conversion.

Example E5.1

The Gibbs free energy of the following reaction at 500 °C and 20 atm is calculated to be −20.570 kcal/mol



Calculate the reaction equilibrium conversion and barrels of benzene formed per one barrel of cyclohexane.

The hydrogen feed rate to the reactor is 10,000 SCF/bbl of cyclohexane.

Solution:

The Gibbs free energy of a reaction is defined as:

$$\Delta G = -RT\ln(K)$$

Using this equation, the equilibrium constant can be evaluated as

$$-20,570 = -(1.987)(773)\ \ln(K), K = 6.55 \times 10^5$$

The equilibrium conversion is calculated as follows

$$\text{moles of cyclohexane} = 1\ \text{bbl}\left(\frac{42\ \text{gal}}{1\ \text{bbl}}\right)\left(\frac{10^6\ \text{cm}^3}{264.17\ \text{gal}}\right)\left(\frac{0.779\ \text{g}}{\text{cm}^3}\right)\left(\frac{1\ \text{mol}}{84.16\ \text{g}}\right)$$
$$= 1471.63\ \text{mol}$$

$$\text{moles of hydrogen} = \left(\frac{10{,}000\ \text{SCF}}{1\ \text{bbl}}\right)\left(\frac{1\ \text{mol}}{379\ \text{SCF}}\right)(1\,\text{bbl of CH}) = 26.39\,\text{mol}$$

We will assume X moles is transformed to benzene (B) and $3X$ to hydrogen (H_2). The equilibrium constant can be expressed as:

$$K = \frac{P_B P_{H_2}^3}{P_{CH}}$$

The mole fractions of products are:

$$\begin{array}{rl}
\text{moles of B} = & X \\
\text{moles of CH} = & 1471.63 - X \\
\text{moles of H}_2 = & \underline{3X + 26.39} \\
\text{Total mole} & (1498 + 3X)
\end{array}$$

The equilibrium constant can be expressed as:

$$K = \frac{(y_B P_T)(y_H P_T)^3}{y_{CH} P_T}$$

$$6.55 \times 10^5 = \frac{\left(\dfrac{X}{1498 + 3X}\right)\left(\dfrac{3X + 26.39}{1498 + 3X}\right)^3 (20)^3}{\left(\dfrac{1471.63 - X}{1498 + 3X}\right)}$$

solving $X = 1464$ mol

$$\text{Equilibrium conversion of CH} = \frac{\text{moles of CH reacted}}{\text{moles of CH fed}} = \frac{1464}{1471.63} = 0.995$$

Barrels of benzene produced are:

$$= 1464\ \text{mol}\left(\frac{78.11\ \text{g}}{1\ \text{mol}}\right)\left(\frac{\text{cm}^3}{0.879\ \text{g}}\right)\left(\frac{264.17\ \text{gal}}{10^6\ \text{cm}^3}\right)\left(\frac{1\ \text{bbl}}{42\ \text{gal}}\right) = 0.818\ \text{bbl}$$

5.2.6. Reaction Kinetics and Catalysts

The catalyst used for reforming is a bifunctional catalyst composed of platinum metal on chlorinated alumina. Platinum acts as the centre for the dehydrogenation reaction, and chlorinated alumina acts as an acidic site to promote structure changes, such as cyclization of paraffins and isomerization of the naphthenes.

Recently additional elements have been added to platinum to promote additional properties for the catalyst. Iridium (Ir) is added to boost activity, Rhenium (Re) is added to operate at lower pressures and Tin (Sn) is added to improve yield at low pressures. The use of Pt/Re is now most common in semi-regenerative (SR) processes with Pt/Sn is used in moving bed reactors. The quantity of chlorine used is approximately 1 wt% of the catalyst and the quantity of platinum is from 0.2 to 0.6 wt%. Impurities that might cause deactivation or poisoning of the catalyst include: coke, sulphur, nitrogen, metals and water. Because of these problems, the reformer feed has to be severely hydrotreated to remove most of these impurities, and the reformer should be operated at high temperature and low pressure to minimize coke deposition.

Paraffin and naphthene dehydrogenation reactions are very rapid and usually occur in the first reactor. The isomerization of paraffin and naphthenes is fast, whereas hydrocracking is slow and takes place in the last reactor. The effect of operating conditions on reaction rate and other properties is shown in Table 5.1.

5.2.7. Process Technology

There are several commercial processes available for reforming. These include Platforming (UOP), Powerforming (Exxon), Magna forming (Engelhard), Catalytic reforming (IFP), Rheniforming (Chevron) and Ultra forming (Amoco). The old technologies are fixed bed configuration. Moving bed technology has also recently been introduced.

5.2.7.1. Semi-regenerative Fixed Bed Process

The schematic flow diagram of this process is shown in Figure 5.5. The name semi-regenerative comes from regeneration of the catalyst in the fixed bed reactors after shut down by burning off the carbon formed on the catalyst surface.

Reactions such as dehydrogenation of paraffins and naphthenes which are very rapid and highly endothermic (Table 5.1) occur in the first reactor, with high temperature drop. Reactions that are considered rapid, such as paraffin isomerization and naphthens dehydroisomerization, give moderate temperature decline in the second reactor. Furthermore, slow reactions such as dehydrocyclization and hydrocracking (Table 5.1) give low temperature decline in the third reactor.

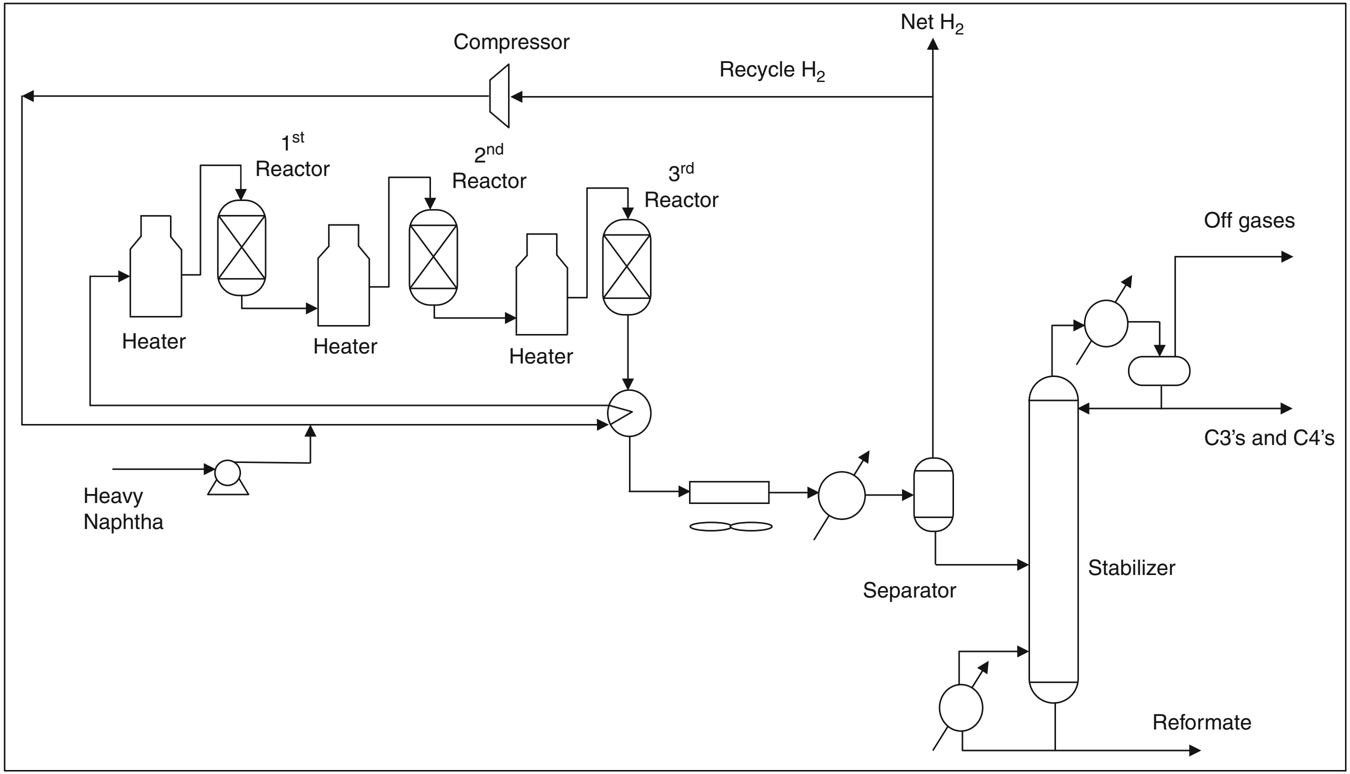


Figure 5.5 Semi-regenerative (SR) fixed bed reforming process

Table 5.1 Thermodynamic and kinetic comparison and effect of operating condition on main reactions and products (Gary and Handwerk, 1994)

Reaction type	Reactive rate	Heat effect	Reaction equilibrium	Pressure effect	Temperature effect	H_2 production	RVP[a]	Product density	Yield	Octane
Naphthene dehydrogenation	Very rapid	Very endo	Yes	−	+	Produce	−	+	−	+
Naphthene dehydroisomerization	Rapid	Very endo	Yes	−	+	Produce	−	+	−	+
Paraffin isomerization	Rapid	Slight exo	Yes	None	Slight	No	+	Slight −	Slight +	+
Paraffin dehydrocyclization	Slow	Very endo	No	−	+	Produce	−	+	−	+
Hydrocracking	Very slow	exo	No	++	++	Consume	+	−	−	+

[a] RVP is Reid vapour pressure.

The temperature and concentration profile in each reactor is shown in Figure 5.6. To prevent catalyst coking, the hydrogen partial pressure is maintained at a level such that the hydrogen-to-hydrocarbon ratio by weight (H_2/HC) is greater than 25 for monometallic catalyst. This is done by recycling some of the hydrogen produced (Figure 5.5). Some light hydrocarbons (C_1–C_4) are separated from the reformate in the stabilizer. At the top of the stabilizer residual hydrogen and C_1 to C_4 are withdrawn as condenser products, which are then sent to gas processing, and part of the liquid product (C_3 and C_4) is returned from the reflux

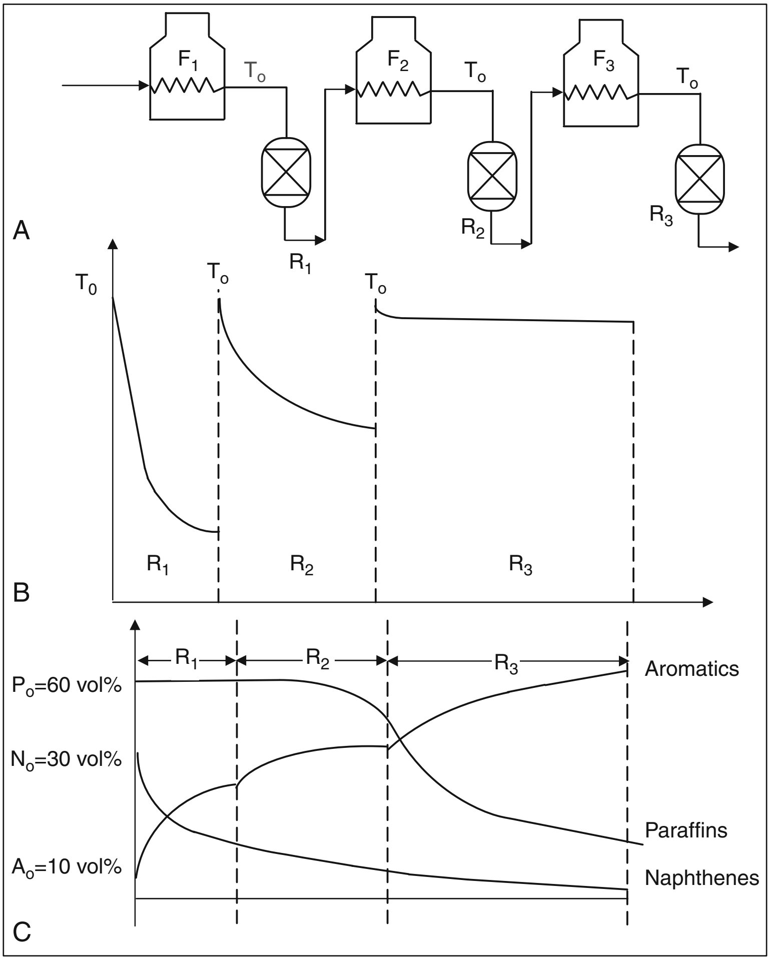


Figure 5.6 (A) Furnace and reactor layout for fixed bed reformer (B) Variation of temperature in the reactors. (C) Variation in effluent compositions; P_0, initial Paraffins; N_0, initial Napthenes and A_0, intial Aromatics (Martino, 2001)

drum back to the stabilizer (Figure 5.6). The main product of the column is stabilized reformate, which is sent to the gasoline blending plant.

A slight modification to the semi-regenerative process is to add an extra-reactor to avoid shutting down the whole unit during regeneration. Three reactors can be running while the forth is being regenerated. This modified process is called the ‘‘cyclic fixed bed’’ process.

5.2.7.2. Continuous Regenerative (moving bed) CCR Platforming UOP Process

In this process, three or four reactors are installed one on the top of the other. The schematic flow diagram of the continuous regenerative process (CCR) is shown in Figure 5.7 (Martino, 2001). UOP has licensed this process under the CCR Platforming process (Martino, 2001). The effluent from each reactor is sent to a common furnace for heating. The catalyst moves downwards by gravity from the first reactor (R1) to the forth reactor (R4). The catalyst is sent to the regenerator to burn off the coke and then sent back to the first reactor R1. The final product from R4 is sent to the stabilizer and gas recovery section.

The process can be operated at lower hydrogen partial pressure ($P_{H2} = 3$ bar) compared to the semi-generative process ($P_{H2} = 35$ bar), with a reformate yield gain of nearly 10 vol%. Table 5.2 gives a comparison of the operating conditions for the three reforming processes.

5.2.8. Material Balance in Reforming

5.2.8.1. Material Balance Using Emperical Correlations

Catalytic reforming data base compiled by Maples (1993) were correlated using multiple regression. Yield correlations for the reformer were developed as given in Table 5.3. The correlation coefficients were in the range of 0.990 – 0.999.

5.2.8.2. Material Balance Using Conversion Criteria

If detailed analysis of the reformer feed is known, the feed conversion can be calculated from the conversion data for each class of compounds as shown in Tables 5.4 and 5.5.

5.2.9. Process Simulation of Reformer by Equilibrium Reactions

The process simulator UNISIM can be used to calculate the material balance around each of the three reactors. Energy balance can also be calculated for each reactor, furnace and other units in the schematic diagram given in Figure 5.5. Simulation of equilibrium of dehydrocyclization and hydrocracking reactions using the process simulator are illustrated in examples E5.4 and E5.5.

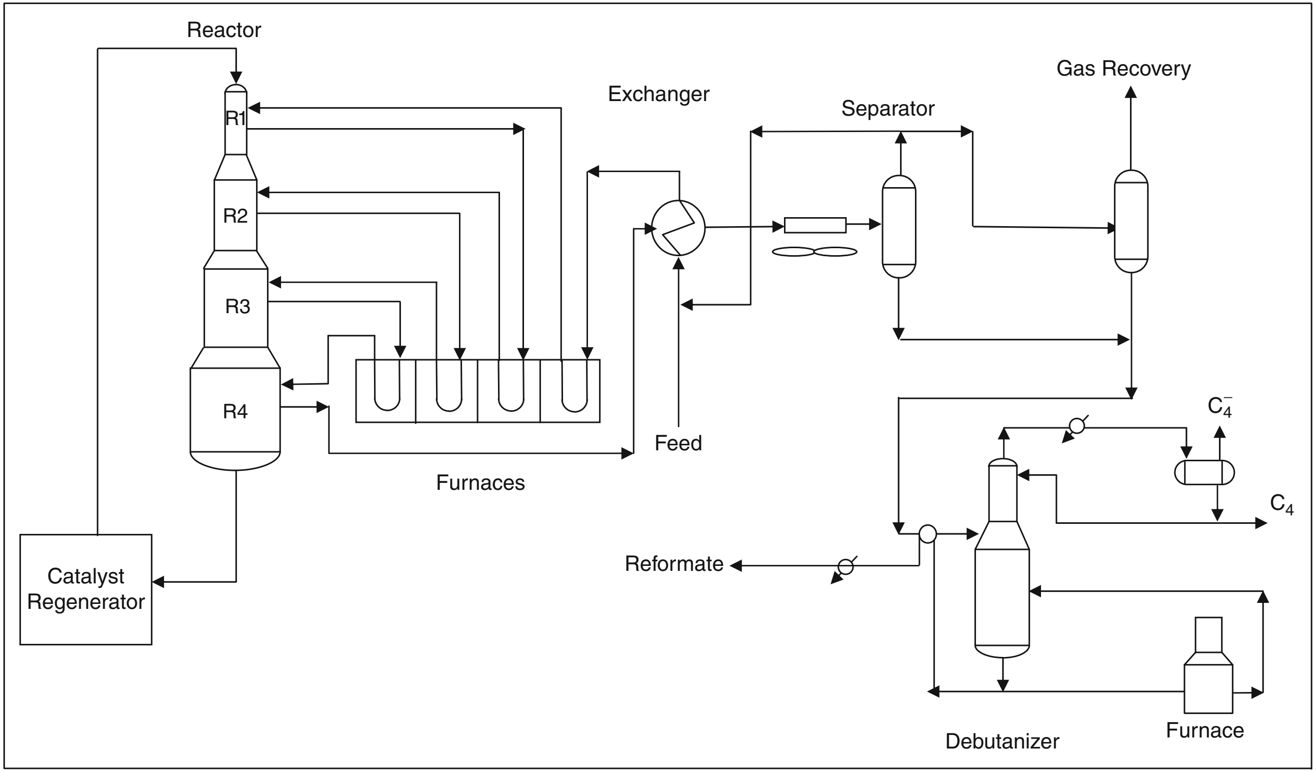


Figure 5.7 Continuous regenerative reformer (CCR), UOP Platforming process

Table 5.2 Typical operating conditions of three reforming processes (Martino, 2001)

	Catalyst	P (bar)	H_2/HC (mol/mol)	Space velocity (h^{-1})	RON
Semi-generative fixed bed	Monometallic	>25	>25	1–2	90–92
	Bimetallic	12–20	4–6	2–2.5	81–98
Cyclic bed	Bimetallic	15–20	4	2	96–98
Continuous moving bed	Bimetallic	3–10	2	2–3	100–102 >104 for aromatic production

Table 5.3 Reformer correlations

Correlation	Equations
$H_2 \text{ wt\%} = -12.1641 + 0.06134 \times C_5^+ \text{ vol \%} + 0.099482 \times \text{RON}_\text{R}$	(5.8)
$C_1 \text{ wt\%} = 11.509 - 0.125 \times C_5^+ \text{ vol \%}$	(5.9)
$C_2 \text{ wt\%} = 16.496 - 0.1758 \times C_5^+ \text{ vol \%}$	(5.10)
$C_3 \text{ wt\%} = 24.209 - 0.2565 \times C_5^+ \text{ vol \%}$	(5.11)
$\text{Total } C_4 \text{ wt\%} = 27.024 - 0.2837 \times C_5^+ \text{ vol \%}$	(5.12)
$nC_4 \text{ wt\%} = 0.585 \times \text{total } C_4 \text{ wt\%}$	(5.13)
$iC_4 \text{ wt\%} = 0.415 \times \text{total } C_4 \text{ wt\%}$	(5.14)
$C_5^+ \text{ vol\%} = -0.03806 \times \text{RON}_\text{R}^2 + 6.292793 \times \text{RON}_\text{R} - 14.4337 \times K$	(5.15)
$C_5^+ \text{ vol\%} = 132.2483 + 0.66472 \times \text{RON}_\text{R} + 0.297921 \times \text{RON}_\text{F}$	(5.16)
$C_5^+ \text{ vol\%} = 142.7914 - 0.77033 \times \text{RON}_\text{R} + 0.219122 \times (N + 2A)_\text{F}$	(5.17)
$\text{SCFB } H_2 = 0.0002 + 0.48848 \, H_2 \text{ wt\%}$	(5.18)

RON_F = research octane number of feed; RON_R = research octane number of reformate; C_5^+ vol% = volume percent of reformate yield; SCFB H_2 = standard cubic foot of H_2 produced/barrel of feed; K = characterization factor $(T_\text{B})^{1/3}/\text{SG}$; T_B = absolute mid-boiling of feed, °R; SG = specific gravity of feed; N = napthenes vol % and A = aromatics vol %.

Example E5.2

100 m^3/h of heavy naphtha (HN) with specific gravity of 0.778 has the following composition: $A = 11.5$ vol%, $N = 21.7$ vol% and $P = 66.8$ vol% is to be reformed to naphtha reformate of RON = 94. Calculate the yields of each product for that reformer.

Solution:

Given $\text{RON}_\text{R} = 94$ and $N + 2\text{A} = 44.7\%$, equation (5.18) gives the following reformer yield:

C_5^+ vol% = 142.7914 − 0.77033 × (94) + 0.219122 × (44.7) = 80.17%
The yields for the other products can then be calculated from the correlations in Table 5.3. The material balance for the reformer is presented in the following table:

	vol%	Volume (m^3/h)	Density (kg/m^3)	wt%	Yield (kg/h)
Feed HN	100	100	778	100	77,800
Products					
H_2 wt%				2.1051	1637
C_1 wt%				1.4871	1157
C_2 wt%				2.4012	1868
C_3 wt%				3.6441	2835
Total C_4 wt%				4.2784	3328
nC_4 wt%				2.5029	
iC_4 wt%				1.7755	
C_5^+ vol%	80.17	80.17	835	(86.086)	(66,975)

Values in brackets are calculated by material balance between feed and products.

Table 5.4 Naphthenes conversion to aromatics by dehydrogenation (Gary and Handwerk, 2001)

Feed (naphthenes)	Conversion	Products (aromatics)
Methylcylohexane (MCC_6)	0.98	Toluene
Cyclohexane (CC_6)	0.98	Benzene
Dimethylcyclopentane ($DMCC_5$)	0.98	Toluene
Dimethylcyclohexane ($DMCC_6$)	0.98	Xylene
Cycloheptane (CC_7)	0.98	Toluene
Methylcycloheptane (MCC_7)	0.98	Xylene

Table 5.5 Paraffin conversion to aromatics by dehydrocyclization (Gary and Handwerk, 2001)

Feed (paraffins)	Conversion	Products (aromatics)
Hexane	0.05	Benzene
Heptane	0.10	Toluene
Octane	0.25	Xylene
Nonane	0.45	1,3,4-Trimethylbenzene (TMB)
Decane	0.45	1,2,3,4Teramethyl benzene

Example E5.3

Heavy naphtha, which has the following detailed analysis in mol%, is fed to a reformer unit.

Cycloheptane (C_7H_{14}):	20%
Heptane (C_7H_{16}):	40%
Dimethylcyclohexane (C_8H_{16}):	30%
1,3,5-Trimethylbenzene (C_9H_{12}):	10%

Find the composition of the products.

Solution:

The data, given in Tables 5.4 and 5.5, are used to estimate the composition of the products as follows:

For 100 mol of feed:

- Naphthenes

20 mol of cycloheptane (C_7H_{14}) will give 0.98 (20) = 19.6 mol Toluene
30 mol of dimethylcyclohexane (C_8H_{16}) will give 0.98 × (30) = 29.4 Xylene

- Paraffins

40 mol of heptane (C_7H_{16}) will give 0.10 (40) = 4.0 mol Toluene

- Aromatics

1,3,5-trimethylbenzene stays as it is.
Final composition (mol%)

Cycloheptane	Heptane	Toluene	DMCC$_6$	Xylene	1,3,5-TMB
C_7H_{14} 0.4%	C_7H_{16} 36%	C_7H_8 23.6%	C_8H_{16} 0.6%	C_8H_{10} 29.4%	C_9H_{12} 10%

Example E5.4

The following feed of 100 lb mol/h of naphtha was introduced to a reformer

Compound	C_6H_{14}	C_7H_{16}	C_8H_{18}	C_9H_{20}
mol% feed	25	25	25	25
a	-32.6×10^3	-31.24×10^3	-29.7×10^3	-28.94×10^3
b	51.17	53.36	53.36	53.78

Knowing that:

$$\ln K_{eq} = a/T + b$$

K_{eq} is the equilibrium constant and T in K.

The constants *a* and *b* are given in the table above.
Assuming that the main reaction in reforming is the conversion of paraffin to the corresponding aromatics:

(a) Calculate the composition of reformate produced at 500 °C and 10 bar pressure.
(b) Repeat the calculations using the process simulator UNISIM with three equilibrium reactors.
(c) Compare the results and comment.

Solution:

(a) *Reaction 1*

$$\underset{1-x}{C_6H_{14}} \rightleftarrows \underset{x}{C_6H_6} + \underset{4x}{4H_2}$$

where x is reaction conversion

$$\begin{aligned} K_{eq} &= \exp(a/T + b) \\ &= \exp(-32.6 \times 10^3/(500 + 273.15) + 57.77) \\ &= 8142.33 \end{aligned}$$

$$\begin{aligned} K_{eq} &= P_{C_6H_6} P_{H_2}^4 / P_{C_6H_{14}} \\ &= y_{C_6H_6} y_{H_2}^4 P^4 / y_{C_6H_{14}} \end{aligned}$$

$$K_{eq} = \frac{\left(\dfrac{x}{1+4x}\right)\left(\dfrac{4x}{1+4x}\right)^4 P^4}{\left(\dfrac{1-x}{1+4x}\right)}$$

$x = 0.7266.$

Reaction 2

$$\underset{1-x}{C_7H_{16}} \rightleftarrows \underset{x}{C_7H_8} + \underset{4x}{4H_2}$$

where x is reaction conversion

$$\begin{aligned} K_{eq} &= \exp(a/T + b) \\ &= \exp(-31.24 \times 10^3/(500 + 273.15) + 53.36) \\ &= 4.22 \times 10^5 \end{aligned}$$

$$\begin{aligned} K_{eq} &= P_{C_7H_8} P_{H_2}^4 / P_{C_7H_{16}} \\ &= y_{C_7H_8} y_{H_2}^4 P^4 / y_{C_7H_{16}} \end{aligned}$$

$$K_{eq} = \frac{\left(\dfrac{x}{1+4x}\right)\left(\dfrac{4x}{1+4x}\right)^4 P^4}{\left(\dfrac{1-x}{1+4x}\right)}$$

$x = 0.9905$.

Reaction 3

$$\underset{1-x}{C_8H_{18}} \rightleftharpoons \underset{x}{C_8H_{10}} + \underset{4x}{4H_2}$$

where x is reaction conversion

$$\begin{aligned} K_{eq} &= \exp(a/T + b) \\ &= \exp(-29.7 \times 10^3/(500 + 273.15) + 53.36) \\ &= 3.1 \times 10^6 \end{aligned}$$

$$\begin{aligned} K_{eq} &= P_{C_8H_{10}} P_{H_2}^4 / P_{C_8H_{18}} \\ &= y_{C_8H_{10}} y_{H_2}^4 P^4 / y_{C_8H_{18}} \end{aligned}$$

$$K_{eq} = \frac{\left(\dfrac{x}{1+4x}\right)\left(\dfrac{4x}{1+4x}\right)^4 P^4}{\left(\dfrac{1-x}{1+4x}\right)}$$

$x = 0.9987$.

Reaction 4

$$\underset{1-x}{C_9H_{20}} \rightleftharpoons \underset{x}{C_9H_{12}} + \underset{4x}{4H_2}$$

where x is reaction conversion

$$\begin{aligned} K_{eq} &= \exp(a/T + b) \\ &= \exp(-28.94 \times 10^3/(500 + 273.15) + 53.78) \\ &= 1.26 \times 10^7 \end{aligned}$$

$$\begin{aligned} K_{eq} &= P_{C_9H_{12}} P_{H_2}^4 / P_{C_9H_{20}} \\ &= y_{C_9H_{12}} y_{H_2}^4 P^4 / y_{C_9H_{20}} \end{aligned}$$

$$K_{eq} = \frac{\left(\dfrac{x}{1+4x}\right)\left(\dfrac{4x}{1+4x}\right)^4 P^4}{\left(\dfrac{1-x}{1+4x}\right)}$$

$x = 0.9997$.

The composition of the reformate can be calculated from the equilibrium conversions as shown in Table E5.4.1.

(b) The simulation of these reactions is carried out using equilibrium reactors in the process simulator UNISIM. The feed is defined as the four components with the given compositions, temperature and pressure. The reactions are entered in the simulator with stoichiometry only and no conversion is required since equilibrium reactors are used. In the calculations, adiabatic equilibrium reactors are used. Since the reactions are endothermic the temperature in the reactor decreases. The outlet from each reactor is heated back to the same inlet temperature using a heater. The simulator performs the necessary energy balances on the reactors and the heaters. Figure E5.4.1 shows the UNISIM reactor flowsheet. In addition, UNISIM results are shown in Table E5.4.2.

Table E5.4.1 Composition of reformate produced

Component	Moles	Composition
C_6H_6	$25 \times 0.7266 = 18.165$	0.03852
C_7H_8	$25 \times 0.9905 = 24.763$	0.05251
C_8H_{10}	$25 \times 0.9987 = 24.9675$	0.05295
C_9H_{12}	$25 \times 0.9997 = 24.9925$	0.05300
C_6H_{14}	$25 \times (1 - 0.7266) = 6.835$	0.01449
C_7H_{16}	$25 \times (1 - 0.9905) = 0.2375$	0.000504
C_8H_{18}	$25 \times (1 - 0.9987) = 0.0325$	0.0000689
C_9H_{20}	$25 \times (1 - 0.9997) = 0.0075$	0.0000159
H_2	371.55	0.7879
Total	471.55	1

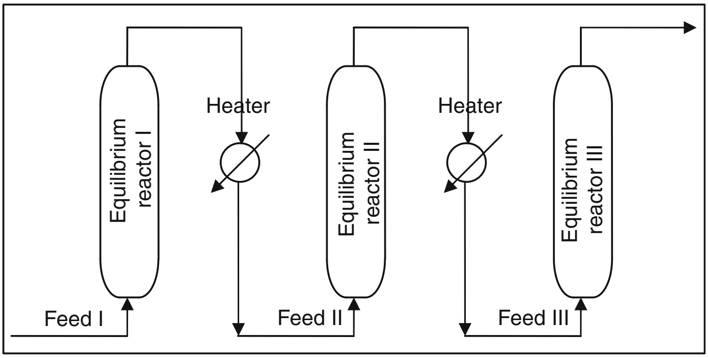


Figure E5.4.1 UNISIM flowsheet

Table E5.4.2 Comparison of hand calculation and UNISIM simulator

	Composition	
	Calculations	UNISIM
C_6H_6	0.03852	0.048281
C_7H_8	0.05251	0.05038
C_8H_{10}	0.05295	0.05043
C_9H_{12}	0.05300	0.05045
C_6H_{14}	0.01449	0.00218
C_7H_{16}	0.000504	0.000081
C_8H_{18}	0.0000689	0.000036
C_9H_{20}	0.0000159	0.00001
H_2	0.7879	0.79815

(c) From Table E5.4.2, it can be observed that the UNISIM results and calculation in part (a) are in good agreement.

Example E5.5

Use UNISIM simulator to calculate the exit compositions and temperatures for a series of three equilibrium reactors. The composition of the feed is shown in the following table with the flow rate for each component in m^3/h. The total feed volumetric flow rate is 1325 m^3/h at 93.3 °C and 689.5 kPa.

H_2	**C_1**	**C_2**	**C_3**	**iC_4**	**C_4**	**iC_5**	**C_5**	**C_6**	**C_7**	**C_8**	**C_9**
0	0	0	0	0	0	0	0	81.3	239.5	297	233.8
C_{10}	**CC_6**	**CC_7**	**MCC_6**	**1,1-MCC_6**	**B**	**T**	**X**	**1,3,5-MB**	**PCUM**	**1,3,5-MCC_6**	**1,2,3,4-$TMCC_6$**
33.4	28.8	0	73.5	103.7	4.6	36	77	34.7	0	74	7.1

Assume that the following equilibrium reactions take place in the three reactors (Kaes, 2000):

$$C_6 \leftrightarrows B + 4H_2$$

$$C_7 \leftrightarrows T + 4H_2$$

$$C_8 \leftrightarrows X + 4H_2$$

$$C_9 \leftrightarrows 1,3,5\text{-MB} + 4H_2$$

$$C_{10} \leftrightarrows \text{Para-cummene} + 4H_2$$

$$CC_6 \leftrightarrows B + 3H_2$$

$$MCC_6 \leftrightarrows T + 3H_2$$

$$1,1\text{-}MCC_6 \leftrightarrows X + 3H_2$$

$$1,3,5\text{-}MCC_6 \leftrightarrows 1,3,5\text{-MB} + 3H_2$$

$$1,2,3,4\text{-}TMCC_6 \leftrightarrows \text{Para-cummene} + 3H_2$$

$$C_6 + H_2 \leftrightarrows iC_5 + C_1$$

$$C_7 + H_2 \leftrightarrows iC_5 + C_2$$

$$C_8 + H_2 \leftrightarrows iC_5 + C_3$$

$$C_9 + H_2 \leftrightarrows iC_5 + C_4$$

$$C_{10} + H_2 \leftrightarrows 2iC_5$$

Figure E5.5.1 shows the reformer flowsheet used in the UNISIM simulation. Compare the UNISIM simulation results with the correlations from Table 5.3.

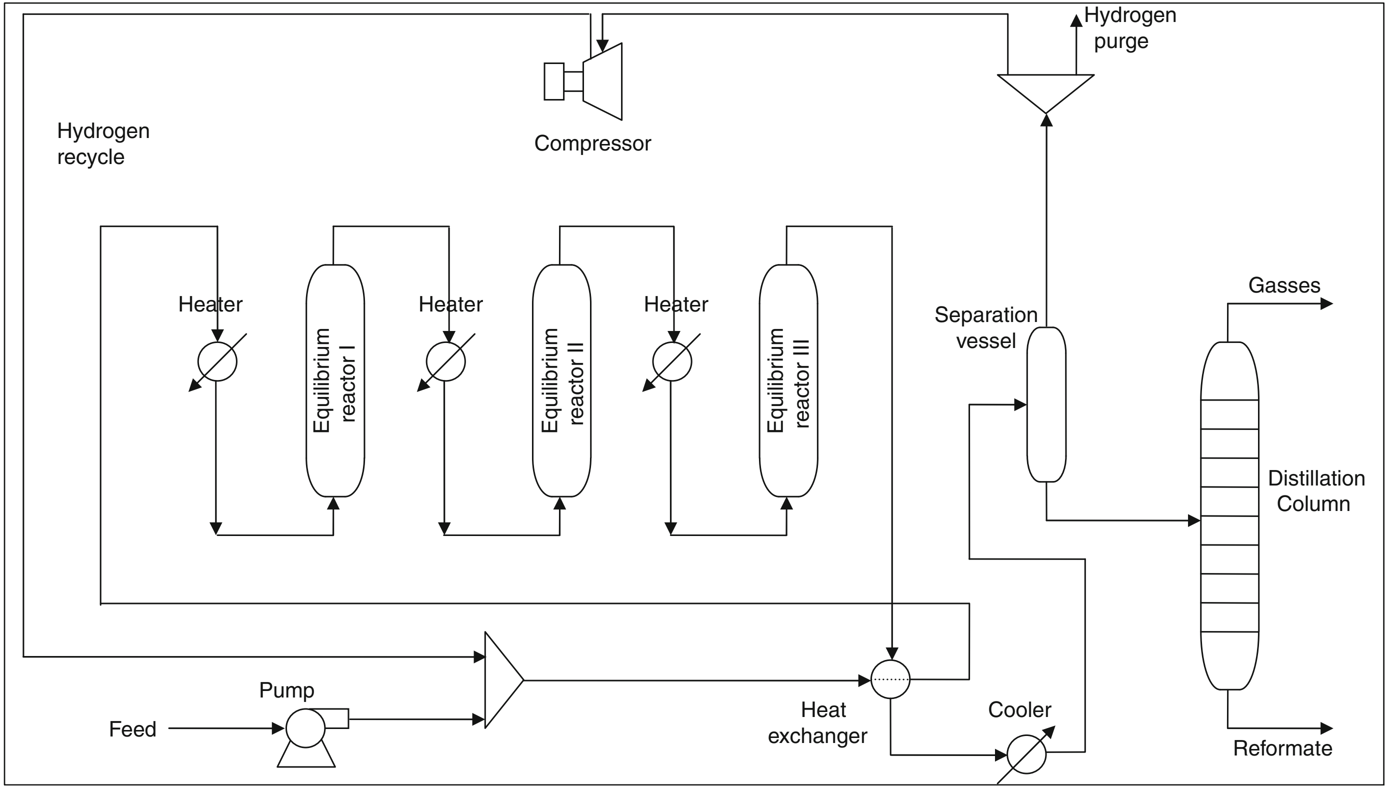


Figure E5.5.1 UNISIM simulation of reformer process

Solution:

The results of the UNISIM simulator are given in Table E5.5.1.

Table E5.5.1 Feed and product composition from each reactor

	Main feed (m^3/h)	Feed			Out		
		R1 (m^3/h)	R2 (m^3/h)	R3 (m^3/h)	R3 (m^3/h)	R3 (kg/h)	Reformate (m^3/h)
H_2	0.0000	15.1417	84.0284	128.4116	154.1731	11,207.0368	0.0000
C_1	0.0000	5.0571	55.5408	55.5034	55.4811	16,615.5011	0.0000
C_2	0.0000	12.3100	94.9343	87.5736	83.4081	24,923.6757	0.0000
C_3	0.0000	6.9888	94.2487	85.4533	60.1856	30,795.9545	0.0000
iC_4	0.0000	0.0563	0.0563	0.0563	0.0563	0.6784	0.0000
C_4	0.0000	1.3736	92.3584	89.3048	86.8241	40,382.7662	0.2572
iC_5	0.0000	3.2338	501.0640	455.3109	501.0640	264,459.0124	173.6960
C_5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
C_6	81.2637	81.2637	0.0049	0.0044	0.0041	2.6826	0.0035
C_7	239.4952	239.4952	0.0421	0.0354	0.0316	21.3128	0.0302
C_9	233.8160	233.8160	0.0139	0.0118	0.0105	7.4043	0.0105
C_{10}	33.4063	33.4063	0.0393	0.0327	0.0288	20.6296	0.0288
C_8	297.0433	297.0433	0.0491	0.0405	0.0359	24.7825	0.0354
CC_6	28.8036	28.8036	0.0001	0.0001	0.0001	0.0618	0.0001
CC_7	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MCC_6	73.5187	73.5187	0.0130	0.0102	0.0090	6.7627	0.0086
1,1-MCC_6	103.7000	103.7000	0.0046	0.0034	0.0029	2.2108	0.0028
B	4.5504	4.5508	0.1489	0.2110	0.2481	227.1990	0.2213

		Feed			Out		
	Main feed (m^3/h)	R1 (m^3/h)	R2 (m^3/h)	R3 (m^3/h)	R3 (m^3/h)	R3 (kg/h)	Reformate (m^3/h)
T	36.0111	36.0437	42.3245	51.5524	56.7741	50,470.6546	55.0311
X	77.0384	77.0654	127.0019	139.4240	146.8633	128,367.6313	146.1156
135-MB	34.7444	34.7542	154.0493	158.2945	161.7427	140,948.5347	161.6444
pCum	0.0000	0.0086	178.8872	192.6322	199.4044	172,667.3075	199.3185
1,3,5-MCC_6	74.3908	74.3908	0.0019	0.0014	0.0012	0.8981	0.0012
1,2,3,4-$TMCC_6$	7.1145	7.1145	0.0436	0.0283	0.0229	18.0522	0.0229
Total	1324.8964	1369.1361	1424.8551	1443.8961	1506.3719	881,170.7496	736.4281
Temperature (°C)	93.3	523.9	523.9	523.9			
Pressure (atm)	6.8	22.46	21.77	21.1			

Now let us compare these results with those given by the reformer correlations of equations (5.9)–(5.19). The feed has ($N + 2A$) equal to 44.7. The reformate yield is calculated to be 80.17 at RON = 94. The comparison between UNISIM and correlations is presented in Table E5.5.2.

Table E5.5.2 Comparison between UNISIM and correlations

	Correlation	
A vol%	11.499	
N vol%	21.702	
P vol%	66.800	
($N + 2A$) vol%	44.69905	
	Correlation	**UNISIM**
C_5^+ vol%	80.17	80.4775
H_2 wt%	2.1051	1.1465
C_1 wt%	1.4871	1.6997
C_2 wt%	2.4012	2.5496
C_3 wt%	3.6441	3.1504
C_4 wt%	4.2784	4.1312

5.3. Isomerization of Light Naphtha

Isomerization is the process in which light straight chain paraffins of low RON (C_6, C_5 and C_4) are transformed with proper catalyst into branched chains with the same carbon number and high octane numbers. The hydrotreated naphtha (HTN) is fractionated into heavy naphtha between 90–190 °C (190–380 °F) which is used as a feed to the reforming unit. Light naphtha $C_5 - 80\,^\circ C$ ($C_5 - 180\,^\circ F$) is used as a feed to the isomerization unit. There are two reasons for this fractionation: the first is that light hydrocarbons tend to hydrocrack in the reformer. The second is that C_6 hydrocarbons tend to form benzene in the reformer. Gasoline specifications require a very low value of benzene due to its carcinogenic effect (Travers, 2001).

5.3.1. Thermodynamics of Isomerization

The isomerization reactions are slightly exothermic and the reactor works in the equilibrium mode. There is no change in the number of moles and thus the reaction is not affected by pressure change. Better conversions are achieved at lower temperature as shown in Figure 5.8. Operating the

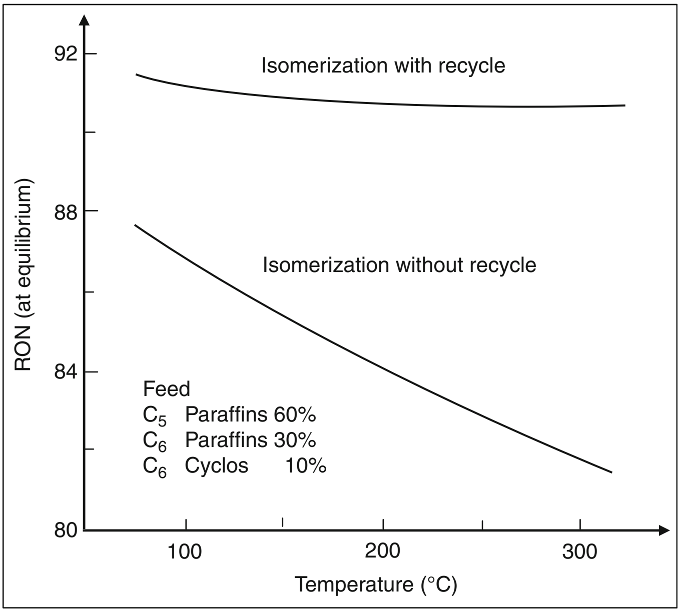


Figure 5.8 Thermodynamic equilibrium with and without recycling normal paraffin (Travers, 2001)

reactor at 130 °C (260 °F) will give good results. In this figure, the degree of conversion to iso-paraffins is measured by the increase of the RON. Paraffin recycle substantially increases the conversion (Travers, 2001).

5.3.2. Isomerization Reactions

Isomerization is a reversible and slightly exothermic reaction:

$$n\text{-paraffin} \rightleftarrows i\text{-paraffin}$$

The conversion to iso-paraffin is not complete since the reaction is equilibrium conversion limited. It does not depend on pressure, but it can be increased by lowering the temperature. However operating at low temperatures will decrease the reaction rate. For this reason a very active catalyst must be used.

5.3.3. Isomerization Catalysts

There are two types of isomerization catalysts: the standard Pt/chlorinated alumina with high chlorine content, which is considered quite active, and the Pt/zeolite catalyst.

5.3.3.1. Standard Isomerization Catalyst

This bi-functional nature catalyst consists of highly chlorinated alumina (8–15 w% Cl_2) responsible for the acidic function of the catalyst. Platinum is deposited (0.3–0.5 wt%) on the alumina matrix. Platinum in the presence of hydrogen will prevent coke deposition, thus ensuring high catalyst activity. The reaction is performed at low temperature at about 130 °C (266 °F) to improve the equilibrium yield and to lower chlorine elution.

The standard isomerization catalyst is sensitive to impurities such as water and sulphur traces which will poison the catalyst and lower its activity. For this reason, the feed must be hydrotreated before isomerization. Furthermore, carbon tetrachloride must be injected into the feed to activate the catalyst. The pressure of the hydrogen in the reactor will result in the elution of chlorine from the catalyst as hydrogen chloride. For all these reasons, the zeolite catalyst, which is resistant to impurities, was developed.

5.3.3.2. Zeolite Catalyst

Zeolites are crystallized silico-aluminates that are used to give an acidic function to the catalyst. Metallic particles of platinum are impregnated on the surface of zeolites and act as hydrogen transfer centres. The zeolite catalyst can resist impurities and does not require feed pretreatment, but it does have lower activity and thus the reaction must be performed at a higher temperature of 250 °C (482 °F). A comparison of the operating conditions for the alumina and zeolite processes is shown in Table 5.6.

5.3.4. Isomerization Yields

The reformate yield from light naphtha isomerization is usually very high (>97 wt%). Typical yields are given in Table 5.7.

Table 5.6 Comparison of operating conditions of isomerization

Operating condition	Pt/Chlorine Alumina catalyst	Pt/Zeolite catalyst
Temperature (°C)	120–180	250–270
Pressure (bar)	20–30	15–30
Space velocity (h^{-1})	1–2	1–2
H_2/HC (mol/mol)	0.1–2	2–4
Product RON	83–84	78–80

Table 5.7 Isomerization yield

Component	Yield (wt%)
C_3	0.348
iC_4	0.619
nC_4	1.770
C_5^+	97.261

Example E5.6

Light naphtha with a specific gravity of 0.724 is used as a feed to the isomerization unit at a rate of 100 m^3/h. Find the product composition.

Solution:

Appling the yield guidelines of Table 5.7, the product composition is presented in Table E5.6.1.

Table E5.6.1 Isomerization yields

	wt%	kg/h
Feed	100	72,400
Product		
C_3	0.348	251.9
iC_4	0.619	448.2
nC_4	1.770	1281.5
C_5^+	97.261	70,417
Total		72,399

QUESTIONS AND PROBLEMS

5.1. Why must C_6 hydrocarbons be removed from the reformer feed? How are they removed?

5.2. Show the role of the reformer in the refinery.

5.3. List the types of reforming reactions and show their relative importance.

5.4. Why was the CCR process developed as an alternative to the SR fixed bed process?

5.5. The following feed of 5000 BPD of naphtha of 50 API was introduced in a reformer:

Compound	C_6H_{12}	C_6H_{14}	C_7H_{14}	C_7H_{16}	C_8H_{16}	C_8H_{18}
wt%	20	10	20	20	10	20

(a) How much hydrogen is produced?
(b) Calculate the composition of naphtha reformate.

5.6. Heavy naphtha of 1000 kg/h having a specific gravity of 0.75 is used as a feed to a reformer. This feed has a boiling range of (190–380 °F). Make a material balance around the reformer knowing that the reformate RON is 96.

5.7. Calculate the barrel of toluene formed from one barrel of methylcyclohexane (MCH) at 1100 °F and 500 psi. 80,000 SCF/bbl of hydrogen is recycled and enters with the feed. Assume the free energy of the reaction at this condition is −20,000 cal/gmol.

5.8. One thousand m^3/h of light naphtha of API equaling 70 is fed into an isomerization unit. Make a material balance around this unit.

5.9. Develop a UNISIM flowsheet simulation for three equilibrium bed reactors at 550 °C and 10 bar pressure.

The following feed is fed to the reformer:

Cycloheptane (C_7H_{14}):	25 mol%
Heptane (C_7H_{16}):	25 mol%
Dimethylcyclohexane (C_8H_{16}):	50 mol%

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CHAPTER SIX

THERMAL CRACKING AND COKING

6.1. INTRODUCTION

Thermal cracking is the cracking of heavy residues under severe thermal conditions. The liquid products of this process are highly olefinic, aromatic and have high sulphur content. They require hydrogen treatment to improve their properties. Coking is the process of carbon rejection from the heavy residues producing lighter components lower in sulphur, since most of the sulphur is retained in the coke.

The thermal treatment of hydrocarbons follows a free radical mechanism where cracking reactions take place in the initiation step. The reactions in the final step result in the formation of heavy fractions and products like coke.

Reaction pathways of different fractions are expressed in Figure 6.1. There are three classes of industrial thermal cracking processes. The first is mild cracking (as in visbreaking) in which mild heating is applied to crack the residue just enough to lower its viscosity and also to produce some light products. The second process is delayed coking in which moderate thermal cracking converts the residue into lighter products, leaving coke behind. The third process involves severe thermal cracking: part of the coke is burned and used to heat the feed in the cracking reactor, as in fluid coking. In other version of the process, steam is used to gasify most of the coke (flexicoking). More detailed operating conditions about the three processes are given in Table 6.1 (Speight, 1991).

The complexity of the mixtures that represent petroleum fractions and their vacuum residues makes the identification of the reaction pathways of individual hydrocarbon compound a very difficult task.

6.2. COKE FORMATION

Coke can be formed from the condensation of polynuclear aromatics (such as *n*-butylnapthalene) as shown in equation (6.1)

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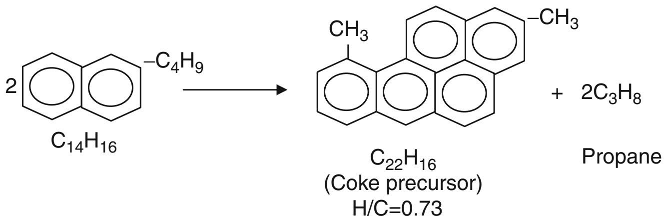

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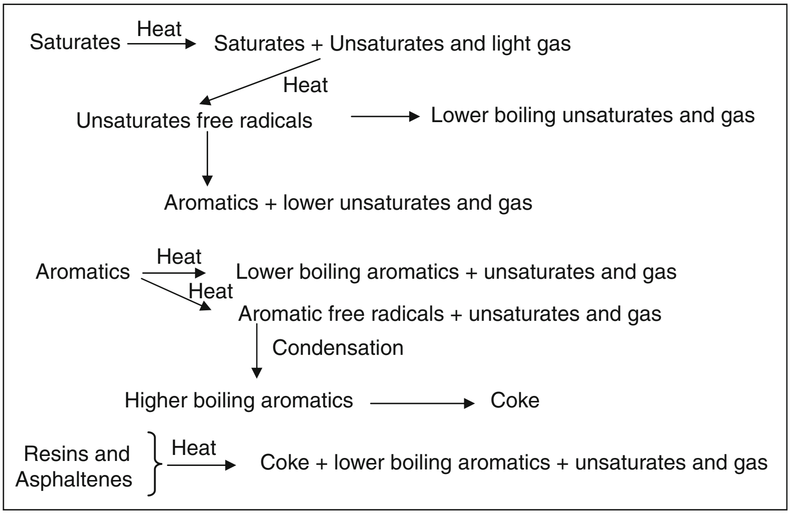


Figure 6.1 Thermal cracking mechanism

Table 6.1 Thermal cracking process

Visbreaking
Mild heating 471–493 °C (880–920 °F) at 50–200 psig
Reduce viscosity of fuel oil
Low conversion (10%) at 221 °C (430 °F)
Heated coil or soaking drum
Delayed coking
Moderate heating 482–516 °C (900–960 °F) at 90 psig
Soak drums 452–482 °C (845–900 °F)
Residence time: until they are full of coke
Coke is removed hydraulically
Coke yield ~ 30 wt%
Fluid coking and flexicoking
Severe heating 482–566 °C (900–1050 °F) at 10 psig
Fluidized bed with steam
Higher yields of light ends
Less coke yield (20% for fluid coking and 2% for flexicoking)

The coke formed from the condensation of polynuclear aromatics has a H/C ratio of 0.73 (Chang and Robinson, 2006). The coke formed through other reactions might have the formula CH_α where $\alpha = 0.2–0.8$. Coke formation can occur through the condensation of olefins and butadiene with aromatics to yield low hydrogen content coke. Thermal cracking of C_6 hydrocarbons may yield certain amount of coke ($CH_{0.8}$) as shown in Table 6.2. These reactions also yield unsaturated hydrocarbons which might react with aromatics to yield coke precursors (Zhorov, 1987).

Table 6.2 Model reactions of coke formation

Reaction No.	Reaction	Coke yield mass fraction	Type of light-end product
1	$C_6H_{14} \leftrightarrows 1.15\ C_5H_{12} + 0.34\ CH_{0.8}$	0.05	Alkane
2	$C_6H_{14} \leftrightarrows 1.33\ C_4H_{10} + 0.68\ CH_{0.8} + 0.8\ H_2$	0.10	Alkane
3	$C_6H_{14} \leftrightarrows 1.32\ C_2H_4 + 3.36\ CH_{0.8} + 3.01\ H_2$	0.50	Alkene
4	$C_6H_{14} \leftrightarrows 0.66\ C_4H_6 + 3.36\ CH_{0.8} + 3.68\ H_2$	0.50	Diene
5	$C_6H_{12} \leftrightarrows 1.36\ C_2H_4 + 3.28\ CH_{0.8} + 2.97\ H_2$	0.50	Alkene
6	$C_6H_6 \leftrightarrows 1.48\ C_2H_4 + 3.04\ CH_{0.8} + 2.82\ H_2$	0.50	Alkene

6.3. THERMODYNAMICS OF COKING OF LIGHT HYDROCARBONS

Thermal cracking reactions are highly endothermic and require heat which is either provided by heating furnaces or generated by burning some of the produced coke. The enthalpies and Gibbs free energies of the six reactions listed in Table 6.2 are given in Table 6.3 (Zhorov, 1987).

Table 6.3 Enthalpies and Gibbs energies of reaction

	ΔH (kJ) at T (K)			ΔG (kJ) at T (K)		
Reaction	300	500	1000	300	500	1000
1	1.8	1.4	2.0	−2.1	−4.7	−9.9
2	3.3	4.9	2.7	−8.1	−16.8	−37.7
3	266	274	276	161	90	−96
4	267	280	288	54	−29	−261
5	141.4	146	146.1	74.9	29.5	−88.5
6	21.1	20.3	12.0	36.3	47.3	78.3

Data shown in Table 6.3 indicates that coking is enhanced by high temperatures. For example, reactions 3 and 5 become thermodynamically possible only close to 1000 K, while at 300–500 K, they cannot proceed. An aromatic coke forms due to poly-condensation with the evolution of hydrogen. The reaction for producing coke from benzene (reaction 6) with the simultaneous separation of a light-end aliphatic hydrocarbon (C_2H_4) is thermodynamically improbable.

The evolution of substantial amounts of methane and hydrogen in coking can be explained by thermodynamic considerations. The formation of light-end product from diene cracking (reaction 4) becomes thermodynamically probable at high temperatures, which is consistent with experimental data. The formation of coke from alkanes, alkenes and cycloalkanes is generally endothermic, while it is exothermic for aromatics.

When determining the composition of the equilibrium mixture for a coke formation reaction. It is important that the equilibrium constant K_P is expressed in terms of the partial pressures of only the gaseous products.

For example, for reaction 3, in Table 6.2:

$$K_P = \frac{P_{C_2H_4}^{1.32} P_{H_2}^{3.01}}{P_{C_6H_{14}}} = \exp\left(\frac{-\Delta G}{RT}\right) \tag{6.2}$$

At $T = 500$ K

$$K_P = \exp\left(-\frac{90,000}{8.31 \times 500}\right) = 3.92 \times 10^{-10}$$

At $T = 1000$ K

$$K_P = \exp\left(-\frac{-96,000}{8.31 \times 1000}\right) = 1.04 \times 10^{5}$$

Thus, while the reaction does not proceed at 500 K, it proceeds favourably at 1000 K.

6.4. VISBREAKING

Visbreaking is a mild thermal cracking of vacuum or atmospheric residues to produce light products and 75–85% cracked material of lower viscosity that can be used as fuel oil.

6.4.1. Feed Sources

The feed to visbreaker can be either

- Atmospheric residue (AR)
- Vacuum residue (VR)

Vacuum residue is the heaviest distillation product and it contains two fractions: heavy hydrocarbons and very heavy molecular weight molecules, such as asphaltene and resins.

6.4.2. Visbreaking Reactions

The main reaction in visbreaking is thermal cracking of heavy hydrocarbons, since resins are holding asphaltene and keep them attached to the oil. The cracking of resin will result in precipitation of asphaltene forming deposits in the furnace and will aslo produce unstable fuel oil. The cracking severity or conversion is limited by the storage stability of the final residual fuel. The possible reactions in visbreaking are:

- Paraffinic side chain breaking which will also lower the pour point;
- Cracking of naphthens rings at temperature above 482 °C (900 °F);
- Coke formation by polymerization, condensation, dehydrogenation and dealkylation; and
- Further cracking will be the result of asphaltene and coke leaving the liquid phase (delayed coking).

6.4.3. Visbreaking Severity

The severity of visbreaking can be defined according to the following considerations:

- Stability of residual fuel on storage
- Material produced that boils below 160 °C (330 °F) (conversion)
- Percent reduction in product viscosity (25–75%)

6.4.4. Kinetics of Visbreaking

The thermal decomposition of hydrocarbons having lower molecular weight than resins is rather fast and highly endothermic. The mechanism of the thermal cracking reactions is the result of chain reactions by radicals. The kinetics can be described as first order:

$$kt = -\ln(1 - x) \tag{6.3}$$

and

$$k = k_o \exp\left(\frac{-E}{RT}\right) \tag{6.4}$$

where x is the weight fraction converted, t is the time, k is the reaction rate constant, T is the reaction temperature, and the activation energy (E) varies according to feed from 150 to 315 kJ/mol. The corresponding activation energies for asphaltene and coke are 250 and 380 kJ/mol, respectively.

6.4.5. Product Yield and Properties

Four products are produced in the visbreaking process: gases (C_4^-), Naphtha $C_5 - 166\ °C$ ($C_5 - 330\ °F$), gas oil 166–350 °C (330–660 °F) and residue or tar 350+ °C (660+ °F). Typical yields are given in Table 6.4.

Visbreaking results in an increase of API of 2–5 for the vacuum residue feed and a reduction of viscosity of 25–75%. A specific example for Kuwait residue visbreaking with product yields and properties is given in Table 6.5.

Table 6.4 Typical yields of visbreaking process

Product	wt% of charge
Gases (C_4^-)	2–4
Naphtha (C_5–330 °F)	5–7
Gas oil (330–660 °F)	10–15
Tar (660+ °F)	75–85

Table 6.5 Visbreaking of Kuwait residue

	Feed	Gases	Gasoline (naphtha)	Gas oil (GO)	Tar (residue)
API	14.4		65.0	32.0	11.0
Sulphur (wt%)	4.1		1.0	2.5	4.3
Viscosity cSt at 50 °C	720	–	–	–	250
Yield (wt%)	–	2.5	5.9	13.5	78.1

6.4.6. Prediction of Visbreaking Yields

The following correlations are generated from plant operation data compiled by Maple (1993). The correlation coefficients range from 0.981 to 0.999.

Products yields:

$$\text{Conversion} = \%\,\text{Conv} = \left(\frac{\text{Gas wt\%} + \text{Naphtha wt\%}}{\text{Feed(VR) wt\%}}\right) \times 100 \qquad (6.5)$$

$$\text{Gas wt\%} = 0.189825 \times \%\,\text{Conv} + 0.677163 \tag{6.6}$$

$$\text{Gasoline wt\%} = 0.738321 \times \%\,\text{Conv} + 0.260174 \tag{6.7}$$

$$\text{Residue wt\%} = -0.146668 \times (\%\,\text{Conv})^2 - 2.203644 \times \%\,\text{Conv} + 98.677947 \tag{6.8}$$

$$H_2S \text{ in Gas wt\%} = 0.02023 \times \%\,\text{Conv} + 0.06043 \times \text{wt\%}S_f - 0.156 \tag{6.9}$$

where S_f refers to sulphur in feed

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Gasoline wt\%} - \text{Residue wt\%} - H_2S \text{ wt\%} \tag{6.10}$$

Sulphur(S) in visbreaker products:

$$\text{S in } H_2S \text{ in Gas} = (H_2S \times 32/34) \tag{6.11}$$

$$\text{wt\% S in Gasoline} = 0.260112 \times \text{wt\%}S_f \tag{6.12}$$

$$\text{wt\% S in Gas oil} = 0.539924 \times \text{wt\%}S_f \tag{6.13}$$

$$\text{S in Residue} = \text{S in Feed} - \text{S in gasoline} - \text{S in GO} - \text{S in } H_2S \tag{6.14}$$

Gravity of visbreaking products:

$$\text{Gasoline API} = -0.26215 \times \%\,\text{Conv} + 0.315121 \times \text{API}_f + 56.83723 \tag{6.15}$$

$$\text{Gas oil API} = -0.052919 \times \%\,\text{Conv} + 0.52228042 \times \text{API}_f + 12.9318914 \tag{6.16}$$

$$\text{Residue API} = -0.7462183 \times \%\,\text{Conv} + 1.29131825 \times \text{API}_f - 2.6831388 \tag{6.17}$$

where API_f is feed API gravity and S_f is the sulphur content in feed.

Example E6.1

A vacuum residue is fed into a coil visbreaker at a rate of 200,000 lb/h. It has an API = 8.5 and sulphur content of 3%. Assume 6 wt% conversion.

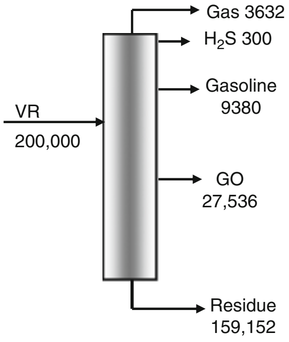
Make a material balance for the visbreaker.

Solution:

The solution of this example is summarized in Table E6.1.

Table E6.1 Results of example E6.1

	Feed rate =	200,000	lb/h
	S_f =	3	wt%
	Conversion =	6	wt%
Visbreaking	API_f =	8.5	
Products yield		**wt%**	**lb/h**
Gas = 0.189825 × %Conv + 0.677163		1.82	3632
Gasoline = 0.738321 × %Conv + 0.260174		4.69	9380
Residue = $-0.146668 \times \%Conv^2 - 2.203644 \times \%Conv + 98.677947$		79.58	159,152
$H_2S = 0.02023 \times \%Conv + 0.06043 \times wt\%\ S - 0.156$		0.15	300
Gas oil = 100 − Gas − Gasoline − Residue − H_2S		13.76	27,536
		100.00	200,000
Sulphur in visbreaker products			
S in H_2S = H_2S in gas × (32/34))		94.12	282
S in Gasoline = 0.260112 S_f		0.78	73
S in GO = 0.539924 S_f		1.62	444
S in Residue = S in Feed − S in gasoline − S in GO − S in H_2S		3.48	5200
			6000
Gravity of visbreaking products		**API**	**SG**
Gasoline = $-0.26215 \times \%Conv + 0.315121 \times API_f + 56.83723)$		57.9	0.75
Gas oil = $-0.052919 \times \%Conv + 0.52228042 \times API_f + 12.9318914$		17.1	0.95
Resid = $-0.7462183 \times \%Conv + 1.29131825 \times API_f - 2.6831388$		3.8	1.05



6.4.7. Process Description

There are two types of visbreakers: coil visbreaking, in which thermal cracking occurs in the coil of the furnace, and the soak visbreaker, in which cracking occurs in a soak drum.

6.4.7.1. Coil Visbreaker

Vacuum or atmospheric residue feedstock is heated and then mildly cracked in the visbreaker furnace. Reaction temperatures range from 850 to 900 °F (450 to 480 °C), and operating pressures vary from as low as 3 bar to as high as 10 bar. As shown in Figure 6.2A, coil furnace visbreaking is used and the visbroken products are immediately quenched to stop the cracking reaction. The quenching step is essential to prevent coking in the fractionation tower. The gas oil and the visbreaker residue are most commonly used as quenching streams (Parakash, 2003).

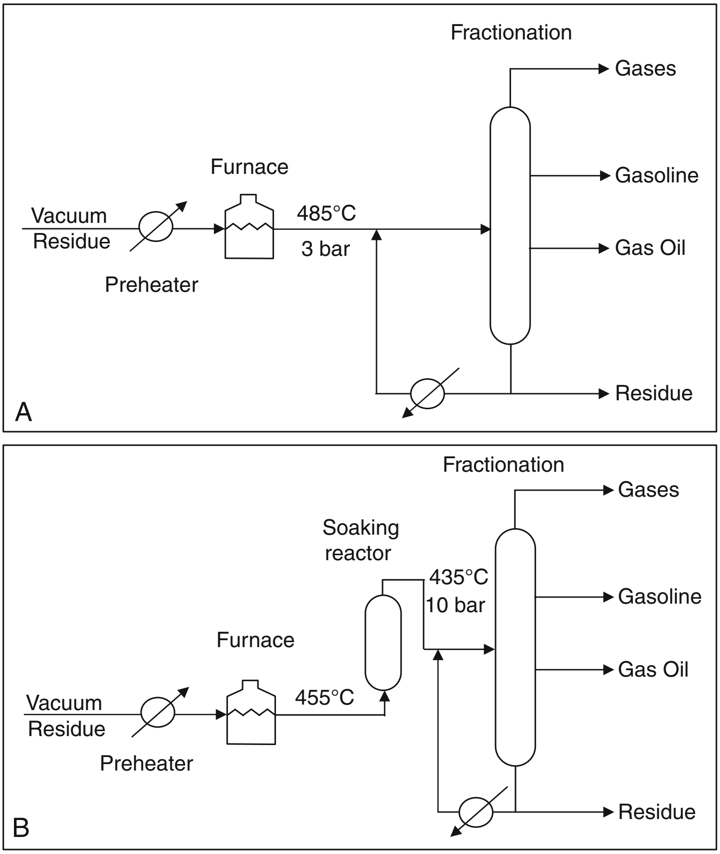


Figure 6.2 (A) Coil type visbreaker. (B) Soaker type visbreaker (Leprince, 2001)

Table 6.6 Soaking time–temperature relationship for equal conversion

Time (min)	°C	°F
1	485	905
2	470	878
4	455	850
8	440	825

After quenching, the effluent is directed to the lower section of the fractionator where it is flashed. The fractionator separates the products into gas, gasoline, gas oil and visbreaker tar (residue). The gas oil withdrawn from the fractionator is steam-stripped to remove volatile components and then blended with the visbreaker bottoms or routed for further processing, such as hydrotreating, catalytic cracking or hydrocracking. The un-stabilized naphtha and fuel gas, recovered as overhead products, are treated and then used as feedstock for catalytic reforming, blended into finished products or sent to the fuel system. The visbreaker bottoms are withdrawn from the fractionator, heat exchanged with the visbreaker feedstock, mixed with stripped gas oil (optional) and routed to storage.

6.4.7.2. Soaker Visbreaker

The process scheme described above is usually referred to as furnace or coil cracking. Some visbreakers employ a soaker between the visbreaker furnace and the quenching step, similar to the conventional thermal cracking processes. This type of operation is termed soaker cracking as shown in Figure 6.2B (Leprince, 2001).

According to the fundamentals of thermal cracking technology, the conversion is mainly a function of two operating parameters, temperature and residence time. Coil cracking is described as a high temperature, short residence time route whereas soaker cracking is a low temperature, long residence time route. The yields achieved by both options are in principle the same, as are also the properties of the products.

Both process configurations have their advantages and applications. Coil cracking yields a slightly more stable visbreaker products, which are important for some feedstocks and applications. It is generally more flexible and allows the production of heavy cuts, boiling in the vacuum gas oil range. Soaker cracking usually requires less capital investment, consumes less fuel and has longer on-stream times. Table 6.6 shows the relation between temperature and soaking time for equal conversion.

Example E6.2

It is required to decoke a visbreaker coil with an inside diameter = 9 cm and 700 m long with a coke layer of 0.35 cm thickness. This is done in two steps:

(a) Air is introduced to combust the coke layer whose density is 1202 Kg/m^3.

(b) Steam at 450 °C and flow rate of 1000 Kg/hr is introduced to the coil to remove debris and cleaning-up. The exit temperature is 700 °C. Coke contains 92 wt% carbon and 8 wt% sulphur.

For how long should steam be switched on, in hours?
Data: specific heat of steam = 2.13 kJ/(Kg °C) heat of carbon combustion = 32,770 kJ/Kg, heat of sulphur combustion = 9300 kJ/Kg

Solution:
Volume of coke layer = 3.14(0.09) (700) (0.0035) = 0.6924 m^3
Weight of coke = 0.6924(1202) = 832.3 Kg
Heat of carbon combustion in coke = 832.2(0.92) (32,770) = 25×10^6 kJ
Heat of sulphur combustion in coke = 832.2(0.08)(9300) = 0.69×10^6 kJ
Total heat = 25.69×10^6 kJ
Rate of heat gained by steam = $m_s\ C_s(T_{out} - T_{in})$
1000(2.13) (700–450) = 0.53×10^6 kJ/h
Time for switching steam = $25.69 \times 10^6/0.53 \times 10^6 = 48.5$ h

6.5. DELAYED COKING

Delayed coking is a type of thermal cracking in which the heat required to complete the coking reactions is supplied by a furnace, while coking itself takes place in drums operating continuously on a 24 h filling and 24 h emptying cycles. The process minimizes residence time in the furnace, while sufficient time is allowed in the drums where coking takes place (hence the term "delayed coking.") Coke is rejected in the drums, thus increasing the H/C ratio in the rest of the products. However, these products are still unstable and unsaturated, and require further hydrogenation.

The feed to coker is usually vacuum residue which is high on asphaltenes, resins, aromatics, sulphur and metals. The deposited coke contains most of the asphaltenes, sulphur, and metals present in the feed, and the products are unsaturated gases (olefins) and highly aromatic liquids.

6.5.1. Role of Delayed Coker

The feed to the delayed coker can be any undesirable heavy stream containing high metal content. A common feed is vacuum residue but it can also accept fluid catalytic cracking (Chapter 8) slurry and visbreaking tar (residues).

The products from the coker are unsaturated gases (C_1–C_4), olefins ($C_2^= - C_4^=$) and iC_4. The olefins are very desirable feedstocks to the petrochemical industry. Isobutane and olefins can be sent to alkaylation units (Chapter 10), and the C_3/C_4 gases are sent to the LPG plant. The coker is

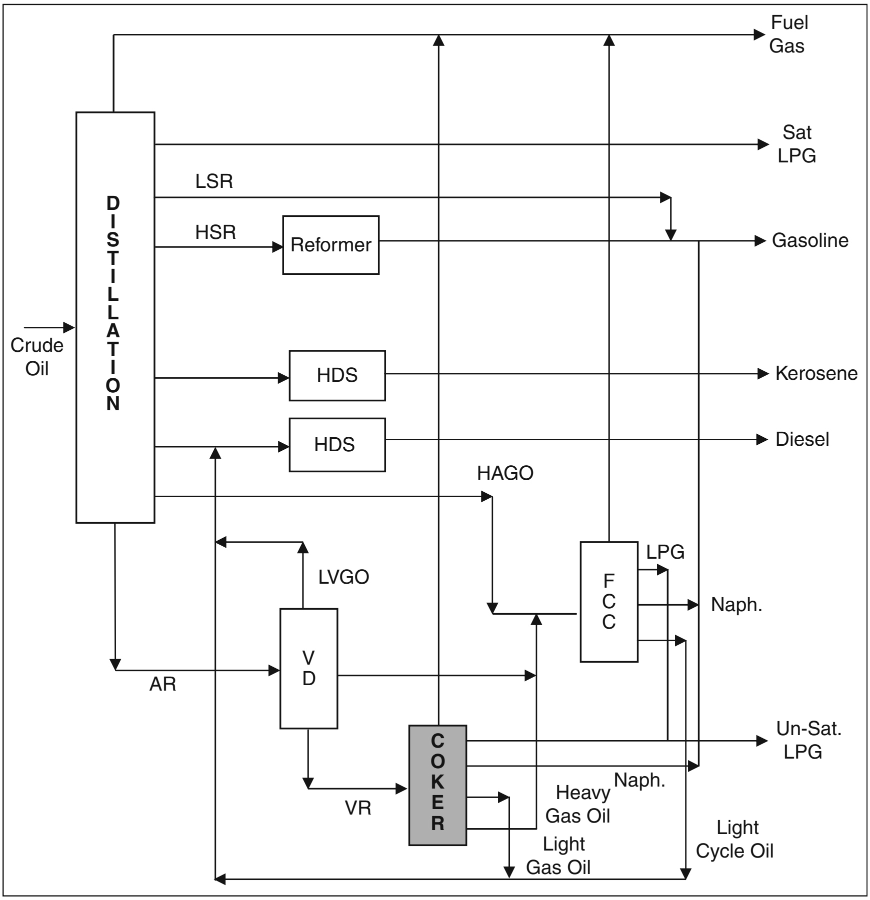


Figure 6.3 Role of delayed coker in the refinery

the only unit in the refinery which produces coke. The highly aromatic naphtha does not need reforming and is sent to the gasoline pool. Light gas oil (LCO) is hydrotreated and sent to the kerosene pool. Heavy coker gas oil is sent to the FCC for further cracking. The role of the delayed coker is to handle very heavy undesirable streams and to produce desirable refinery products as shown in Figure 6.3.

The overall refining yield of light products increases as a result of coke removal.

6.5.2. Process Description

A schematic flow diagram of the delayed coking is shown in Figure 6.4. The process includes a furnace, two coke drums, fractionator and stripping section. Vacuum residue enters the bottom of the flash zone in the

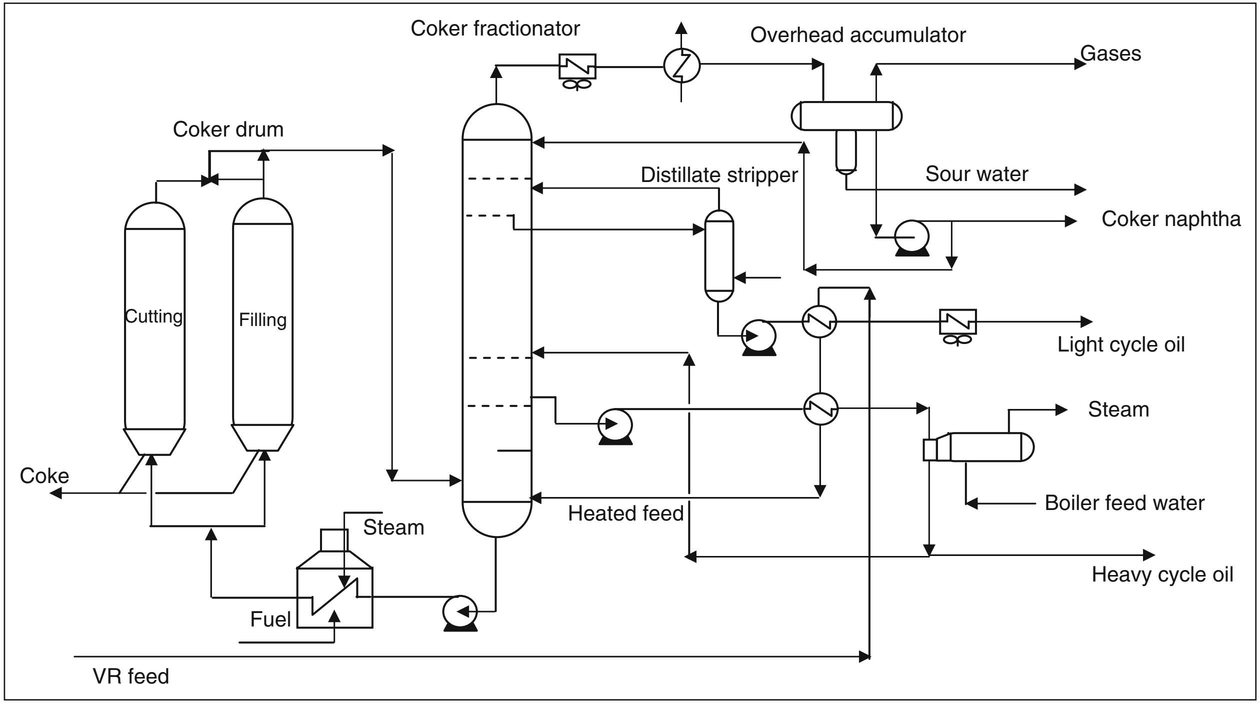


Figure 6.4 Delayed coker unit

distillation column or just below the gas oil tray. Fractions lighter than heavy gas oil are flashed off and the remaining oil are fed to the coking furnace.

Steam is injected in the furnace to prevent premature coking. The feed to the coker drums is heated to just above 482 °C (900 °F). The liquid–vapour mixture leaving the furnace passes to one of the coking drum. Coke is deposited in this drum for 24 h period while the other drum is being decoked and cleaned.

Hot vapours from the coke drum are quenched by the liquid feed, thus preventing any significant amount of coke formation in the fractionator and simultaneously condensing a portion of the heavy ends which are then recycled.

Vapours from the top of the coke drum are returned to the bottom of the fractionator. These vapours consist of steam and the products of the thermal cracking reaction (gas, naphtha and gas oils). The vapours flow up through the quench trays of the fractionator. Above the fresh feed entry in the fractionator, there are usually two or three additional trays below the gas oil drawoff tray. These trays are refluxed with partially cooled gas oil to provide fine trim control of the gas oil end point and to minimize entrainment of any fresh feed liquid or recycle liquid into the gas oil product. The gas oil side draw is a conventional configuration employing a six-to-eight-tray stripper with steam introduced under the bottom tray for vaporization of light ends to control the initial boiling point (IBP) of the gas oil.

Steam and vaporized light ends are returned from the top of the gas oil stripper to the fractionator, one or two trays above the draw tray. A pump-around reflux system is provided at the draw tray to recover heat at a high-temperature level and minimize the low-temperature level heat removed by the overhead condenser. This low-temperature level heat cannot normally be recovered by heat exchange and is rejected to the atmosphere through a water cooling tower or aerial coolers. Eight to ten trays are generally used between the gas oil draw and the naphtha draw or column top. If a naphtha side draw is employed, additional trays are required above the naphtha draw tray.

A control valve system directs the feed to enter one of the drums, where the reactions take place and coke is deposited on the drum walls, and the products flow back to the distillation column. In this case, the drum is in the "filling" mode. At the same time, the other drum is cut off from the rest of the system while the coke is being removed. The drum in this case is in the "cutting" mode.

6.5.3. Delayed Coking Variables

There are three classes of variables affecting coking. They are related to process operating variables, feedstock characterization and engineering variables as shown in Table 6.7. Temperature is used to control the severity of coking. In delayed coking, the temperature controls the quality of the coke produced. High temperature will remove more volatile materials. Coke yield decreases as temperature increases. If the furnace temperature is high this might lead to coke formation in the furnace. A low inlet furnace temperature

Table 6.7 Delayed coking variables

Process variables	Feedstock variables	Engineering variables
Cycle time	Characterization factor	Mode of operation
Temperature	Conradson carbon	
Pressure	Sulphur content	Capacity
Recycle ratio	Metal content, characterization	Equipment used for coke removal and handling

will lead to incomplete coking. Short cycle time will increase capacity but will give lower amounts of liquid products and will shorten drum lifetime.

Increasing pressure will increase coke formation and slightly increase gas yield. However, refinery economics require operating at minimum coke formation. New units are built to work at 1 bar gauge (15 psig), while existing units work at 2.4 bar gauge (35 psig). In a case of production of needle coke, a pressure of 150 psig is required. Recycle ratio is used to control the endpoint of the coker gas oil. It has the same effect as pressure. Units are operating at a recycle ratio as low as 3%.

Feedstock variables are the characterization factor and the Conradson carbon which affect yield production. Sulphur and metal content are usually retained in the coke produced. Engineering variables also affect the process performance. These include mode of operation, capacity, coke removal and handling equipment.

6.5.4. Types of Coke and their Properties

Coke amount can be upto 30 wt% in delayed coking. It is produced as green coke which requires calcination to remove the volatiles as fuel product. Green coke can also be used as fuel. The most common types of coke are:

Sponge coke

Sponge coke is named for its sponge-like appearance. It is produced from feeds having low to moderate asphaltene content.

Needle coke

This coke has a needle-like structure and is made from feed having no asphaltene contents such as decant oils from FCC. It is used to make expensive graphite electrodes for the steel industry.

Shot coke

This coke is an undesirable product and is produced when feedstock asphaltene content is high and/or when the drum temperature is too high. Discrete mini-balls of 0.1–0.2 in. (2–5 cm) in diameter are produced. There are some methods of eliminating shot coke formation including adding aromatic feed, such as FCC decant oil, decreasing temperature, increasing pressure and the recycle ratio. Summary of coke types, properties and end uses is shown in Table 6.8.

Table 6.8 Coke characterization and uses from delayed coker

Type of coke	Operating condition	Feed characterization	Coke property	End use as calcinated coke
Sponge	Reflux ratio >35% Operating pressure 2–4 bar	Low metal Low *S* Tar residue FCC heavy dist Low to moderate asphaltene	$M < 200$ $S < 2.5\%$ High density >780 HGI[a] ~ 100	Anodes for aluminium industry
Shot	Low pressure Low reflux ratio Large drums	High *S* High metal Low asphaltene	High *S* and metal Low HGI<50 Low surface area	Fuel (green)
Needle	Pressure > 4 bar Reflux ratio = 60–100% to maximize coke yield High temperature to reduce volatile material	High aromatic content Tars, FCC decant Low *S* <0.5 wt% Low ash <0.1 wt% No asphaltene	Crystalline structure Small needles of high conductivity	Graphite electrodes

[a] HGI = Hard grove grindability index

6.5.5. Coking and Decoking Operation

Pilot plant data have shown that coke formation in the drums takes the "channel branching theory" in which channel formation allows further gas flow while coke is formed progressively. In commercial operations this can take up to 24 h. The decoking operation involves drilling a vertical hole in coke after cooling using a mechanical boring tool (shown in Figure 6.5A). Further coke removal is carried out by using a hydraulic cutting tool (Figure 6.5B), where a jet of water is capable of the removal of the remaining coke from the drum. However, this requires using a great amount of water which has to be treated later on (Feintuch and Negin, 2003).

The progression of the decoking operation is shown in Figure 6.6 (Feintuch and Negin, 2003). The decoking cycle involves switching

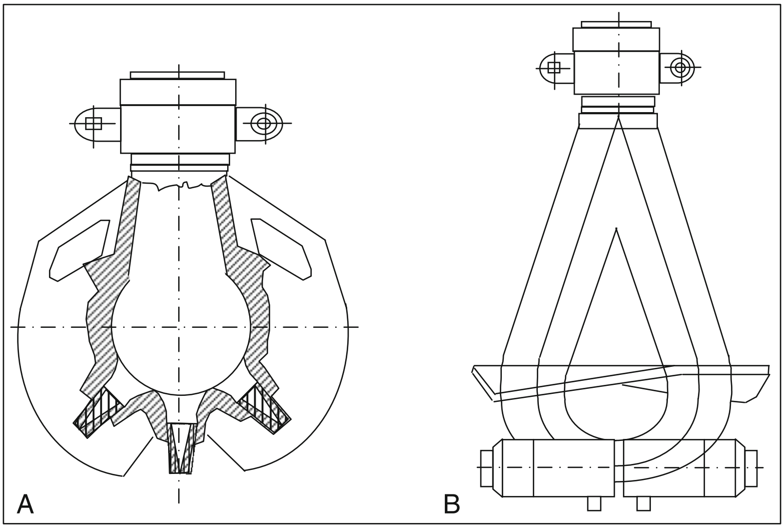


Figure 6.5 (A) Mechanical first boring tool. (B) Final hydraulic tool

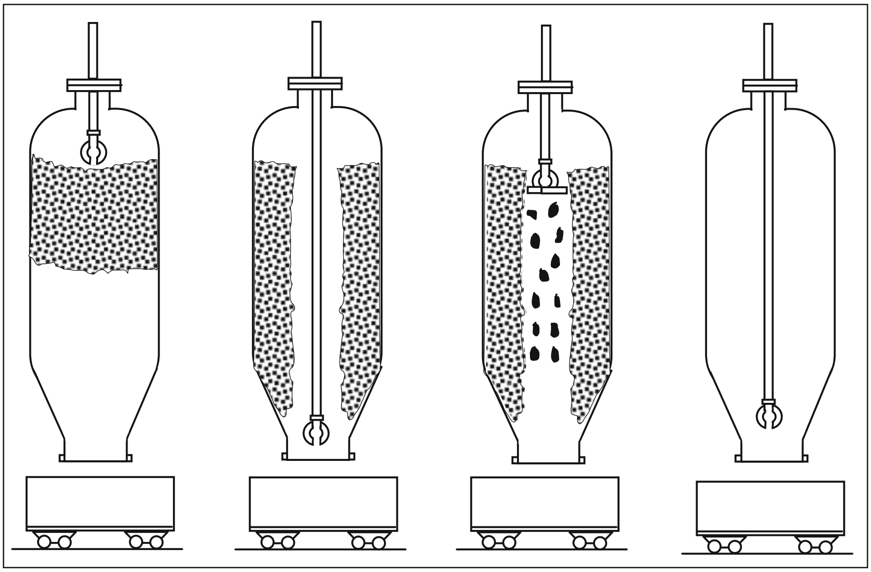


Figure 6.6 Steps of decoking operation

Table 6.9 Time cycle for delayed coking

Operation	Time (h)
Coking	24
Decoking	24
Switching	0.5
Steam cooling	6.0
Decoking, drain	7.0
Warm-up	9.0
Contingency time	1.5

the drums, cooling by steam, draining in the coke, warming up the drum and leaving spare time for contingency. Meanwhile, the other drum is under coking reactions. A typical time cycle in delayed cooking is shown in Table 6.9.

6.5.6. Delayed Coker Yield Prediction

Estimation of product yields can be carried out using correlations based on the weight percent of Conradson carbon residue (wt% CCR) in the vacuum residue (Gary and Handwerk, 2001).

$$\text{Gas}(\text{C}_4^-)\text{wt\%} = 7.8 + 0.144 \times (\text{wt\% CCR}) \tag{6.18}$$

$$\text{Naphtha wt\%} = 11.29 + 0.343 \times (\text{wt\% CCR}) \tag{6.19}$$

$$\text{Coke wt\%} = 1.6 \times (\text{wt\% CCR}) \tag{6.20}$$

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Naphtha wt\%} - \text{Coke wt\%} \tag{6.21}$$

The naphtha can be split in light naphtha (LN) and heavy naphtha (HN). The split in wt% is 33.22 and 66.78, respectively, assuming corresponding gravities of 65 API and 50 API, also respectively.

The gas oil (GO) can be split also into light cycle gas oil (LCO) and heavy cycle gas oil (HCO). The spilt in wt% is 64.5 and 35.5, respectively, and the corresponding gravities are 30 API and 13 API.

Typical sulphur distribution in the products for delayed coking is presented in Table 6.10 (Gary and Handwerk, 2001).

Table 6.10 Delayed coker sulphur distribution based on the amount of sulphur in feed

Products	Gas	LN	HN	LCO	HCO	Coke
S (wt%)	30	1.7	3.3	15.4	19.6	30

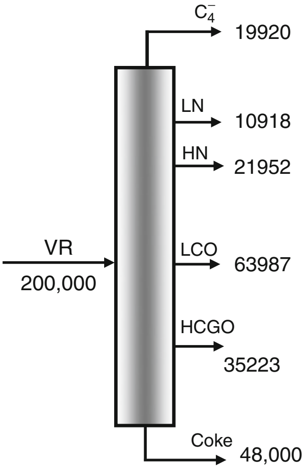
Example E6.3

A vacuum residue of Conradson carbon (wt% CCR = 15) is fed into a delayed coker at a rate of 200,000 lb/h, of API= 8.5 and with a sulphur content of 3.0 wt%. Find the amount of yield (lb/h) and their sulphur content. Calculate yield of liquid products in BPD.

Solution:

The solution of the example is summarized in Table E6.3.

Table E6.3 Results of delayed coking example

Delayed coker			
Feed rate =	200,000	lb/h	
CCR =	15	wt%	
S_f =	3	wt%	
Feed API =	8.5		
Products yield	**wt%**	**lb/h**	
Gas = (7.8+0.144 × CCR%)	9.96	19,920	
Naphtha = (11.29 + 0.343 × CCR%)	16.44	32,870	
Coke = (1.6 × CCR%)	24.00	48,000	
Gas oil (100 − Gas% − Napthta% − Coke%)	49.61	99,210	
	100.00	200,000	
Naphtha (assumed split wt%)			
Light naphtha LN = 33.2%	33.22	10,918	
Heavy naphtha HN = 66.78%	66.78	21,952	
	100.00	32,870	
Gas oil (assumed split wt%)			
Light gas oil LGO	64.50	63,987	
Heavy gas oil HGO	35.50	35,223	
	100.00	99,210	
Sulphur distribution in delayed coker products (assumed wt%)			
S in gas	30.00	1800	
S in light naphtha	1.70	102	
S in heavy naphtha	3.30	198	
S in light gas oil	15.40	924	
S in heavy gas oil	19.60	1176	
S in coke	30.00	1800	
	100.00	6000	

(continued)

Table E6.3 (*continued*)

Delayed coker	Feed rate =	200,000	lb/h
	CCR =	15	wt%
	S_f =	3	wt%
	Feed API =	8.5	
Gravity of products (assumed gravities)	**API**	**SG**	**BPD**
Light naphtha	65	0.72	1041.5
Heavy naphtha	50	0.78	2894.3
Light gas oil	30	0.88	4994.0
Heavy gas oil	13	0.98	2468.5

Gas composition

The gas produced is fuel gas, which can be sent to a fuel gas network after amine washing. The gas can also be used in the alkylation unit because of its high olefin content. A typical coker gas composition is given in Table 6.11 (Gary and Handwerk, 2001).

Table 6.11 Typical gas composition from delayed coker (sulphur-free basis)

Gas	C_1	$C_2^=$	C_2	$C_3^=$	C_3	$C_4^=$	iC_4	C_4	H_2	CO_2
Mole %	51.4	1.5	15.9	3.1	8.2	2.4	1.0	2.6	13.7	0.2

6.5.7. Process Simulation of Delayed Coking

The composition of vacuum residue is quite complex and the thermal decomposition reactions are difficult to simulate in a single model. For this reason, the following model reaction is used to describe the thermal cracking of vacuum residue.

$$2.3\,C_{14}H_{16} \rightarrow C_2H_4 + 4.4\,H_2 + C_6H_6 + C_{10}H_8 + C_{12}H_{10} + 2.2\,C \qquad (6.22)$$

Example E6.4

Vacuum residue at a rate of 8359 kg/h is fed into a delayed coker. The composition of the feed used in this example is described in Table E6.4.1. Applying a UNISIM process simulator was used to simulate the delayed coker process using reaction (6.22) in the reactor block. The simulator flow diagram is shown in Figure E6.4.

Table E6.4.1 Component presentation of each stream

Component	Formula	Petroleum cut representing	Composition (mole fraction) in feed
n-Butyl-naphthalene	$C_{14}H_{16}$	Vacuum residue	1.0
Ethylene	C_2H_4	Gas	0
Hydrogen	H_2	Gas	0
Benzene	C_6H_6	Naphtha	0
Naphthalene	$C_{10}H_8$	LGO	0
Di-phenyl	$C_{12}H_{10}$	HGO	0
Carbon	C	Coke	0

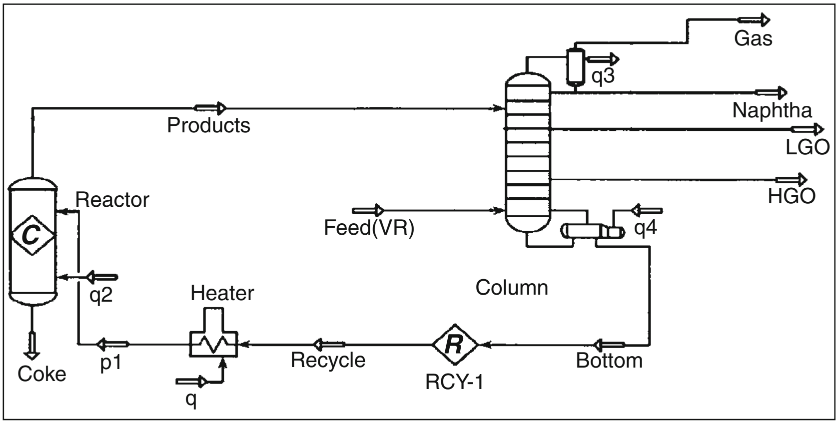


Figure E6.4 Simulation flow diagram in UNISIM

Solution:

Summary of the results is given in Tables E6.4.2 and E6.4.3

Table E6.4.2 Material balance sheet of simulation results

	Feed (VR)	Gas	Naphtha	LGO	HGO	Coke
Vapour fraction	0	1	0	0	0	0
Temp. (°C)	176	37.8	37.8	214	252	343
Press (kPa)	294	172	172	181	196	206
Mass flow (kg/h)	8359	1917	175	4722	1052	493

Table E6.4.3 Stream compositions (mole fraction)

	Feed (VR)	Gas	Naphtha	LGO	HGO	Coke
$C_{14}H_{16}$	1.000	0	0	0.007	0.341	0
C_2H_4	0	0.160	0.004	0	0	0
H_2	0	0.705	0	0	0	0
C_6H_6	0	0.135	0.996	0	0.007	0
$C_{10}H_8$	0	0	0	0.528	0.111	0
$C_{12}H_{10}$	0	0	0	0.445	0.541	0
C	0	0	0	0	0	1.000

6.6. FLUID COKING

Fluid coking is a thermal cracking process consisting of a fluidized bed reactor and a fluidized bed burner as shown in Figure 6.7. Vacuum residue is heated to 260 °C (500 °F) and is fed into the scrubber which is located above the reactor for coke fine particle recovery, and it operates at 370 °C (700 °F). The heavy hydrocarbons in the feed are recycled with the fine particles to the reactor as slurry recycle. The reactor operating temperature is 510–566 °C (950–1050 °F). The heavy vacuum residue feed is injected through nozzles to a fluidized bed of coke particles. The feed is cracked to vapour and lighter gases which pass through the scrubber to the distillation column.

Coke produced in the reactor is laid down on the coke bed particles, typically in a layering manner. Steam is introduced at the bottom of the reactor, where a scrubber is also added to scrub any heavy hydrocarbons from the surface of the coke particles. This steam is also used to fluidize the bed. Part of the coke flows into the burner where 15–30% is combusted by the injection of air into the burner. The rest of the hot coke is recycled back to the reactor to provide the required heat. The operating temperature of the burner is in the range of 593–677 °C (1100–1250 °F) (Hammond *et al.*, 2003).

The combustion of the coke produces flue gases with low heating value (20 Btu/SCF). A block diagram showing the flow of heat and mass in the process is shown in Figure 6.8 (Hammond *et al.*, 2003). An example of material balance for fluid coking of Arab light vacuum residue containing 22 wt% CCR and the end use of products are shown in Figure 6.9.

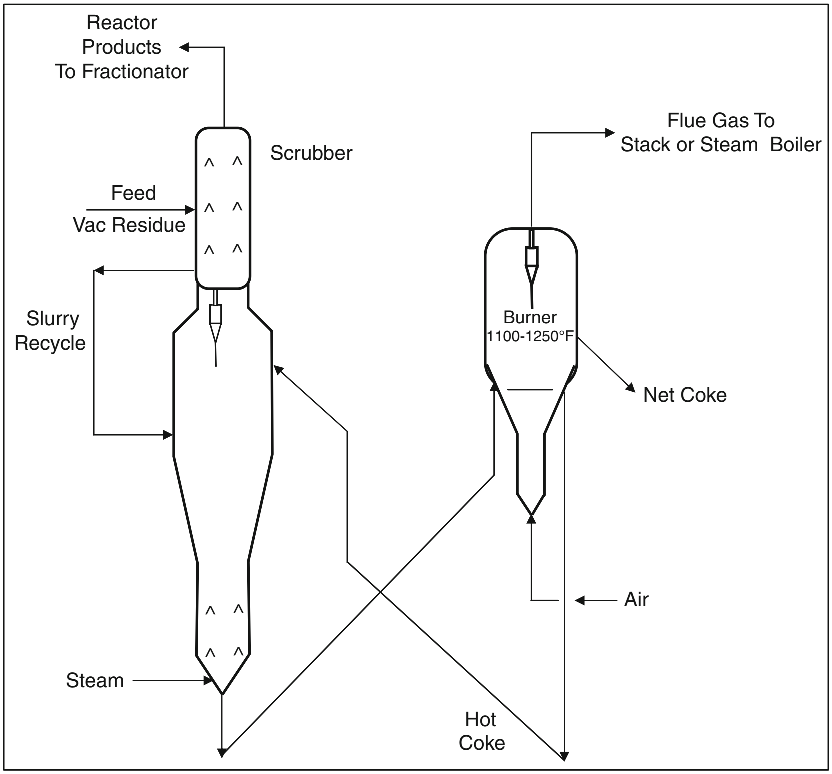


Figure 6.7 Fluid coking process

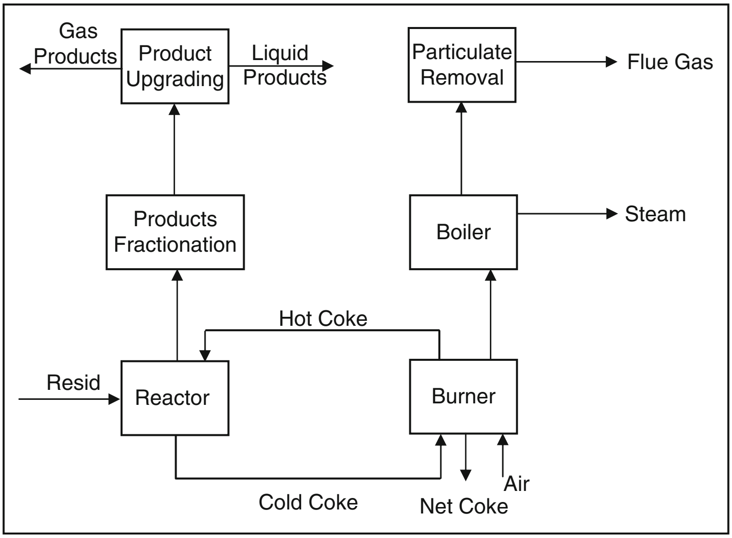


Figure 6.8 Block diagram of fluid coking

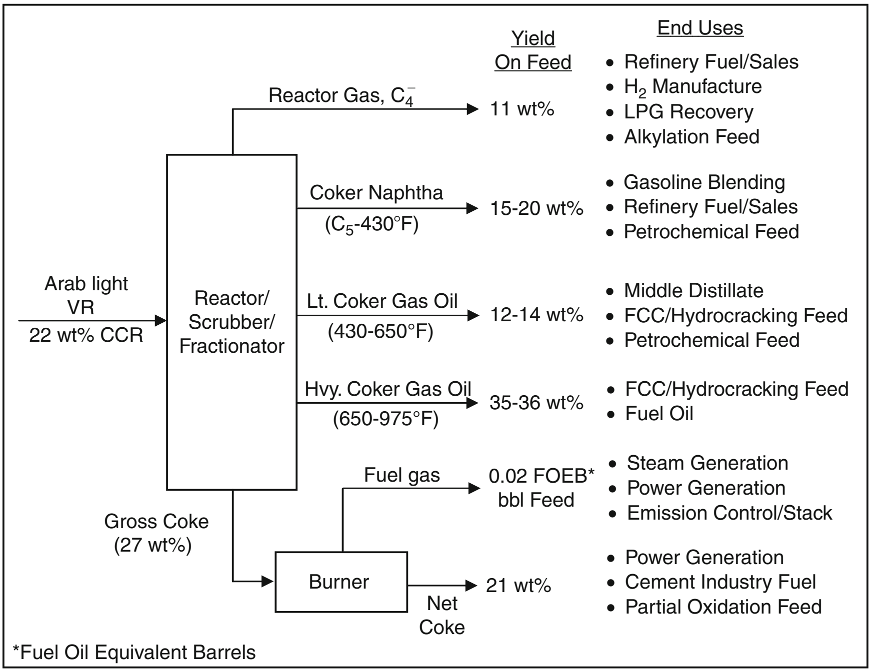


Figure 6.9 Yield and end uses of fluid coker process (Hammond *et al.*, 2003)

Example E6.5

A vacuum residue with Conradson carbon of (wt% CCR = 15) is fed into a fluid coker at a rate of 200,000 lb/h, API = 8.5 and with a sulphur content of 3.0 wt%. Find the amounts of products and their sulphur content using the yield guidelines given in Figure 6.9.

Solution:

The solution of the example is summarized in Table E6.5.

Table E6.5 Summary of fluid coking summary results

Feed rate		200,000 lb/h
CCR	15 wt%	
S_f	3 wt%	
Products	**wt%**	**lb/h**
Gases	11	22,000
Naphtha	18	36,000
Light gas oil	14	28,000
Heavy gas oil	36	72,000
Coke	21	42,000
Total	100	200,000

6.7. FLEXICOKING

The flexicoking process is a development of the fluid coking process where only 2 wt% of coke is produced, thus most of the coke is used to heat the feed. A fluidized bed is added to the process which acts as a gasifier in which steam and air are injected to produce synthesis gas called Low Btu Gas (LBG) as shown in Figure 6.10. The gasifier which operates at 816–982 °C (1500–1800 °F) produces hot coke which remains after combustion. This coke flows into the middle vessel, which acts as a heat exchanger to heat cold coke coming from the reactor. It operates at 593 °C (1100 °F). The operation of the reactor is the same as fluid coker. The net coke is purged in the heater. A block diagram of the process is shown in Figure 6.11 (Hammond *et al.*, 2003).

In the oxidation zone of the gasifier, the following reactions take place very rapidly:

$$C + 0.5\ O_2 \rightarrow CO \tag{6.23}$$

$$CO + 0.5\ O_2 \rightarrow CO_2 \tag{6.24}$$

In the reduction zone, the following reactions take place slowly:

$$C + H_2O \rightarrow CO + H_2 \tag{6.25}$$

$$H_2O + CO \rightarrow CO_2 + H_2 \tag{6.26}$$

6.7.1. Yield Correlations for Flexicoking

The yield correlations for flexicoking are based on the Conradson carbon content of the vacuum residue (CCR, wt%), its API gravity and sulphur content (S_f). Data compiled by Maples (1993) are correlated to express weight percent yields.

$$\text{Gas wt\%} = 0.171943 \times \text{CCR wt\%} + 5.206667 \tag{6.27}$$

$$\text{Gasoline wt\%} = -0.115234 \times \text{CCR wt\%} + 18.594587 \tag{6.28}$$

$$\text{Coke wt\%} = 1.037233 \times \text{CCR wt\%} + 1.875742 \tag{6.29}$$

$$\text{Gas oil wt\%} = 100 - \text{Gas wt\%} - \text{Gasoline wt\%} - \text{Coke wt\%} \tag{6.30}$$

Gas composition:

$$C_4\ \text{wt\%} = -0.028627 \times \text{CCR wt\%} + 3.200754 \tag{6.31}$$

$$C_2^-\ \text{wt\%} = 0.647791 \times [\text{Gas wt\%} - C_4\ \text{wt\%}] + 0.456001 \tag{6.32}$$

$$C_3\ \text{wt\%} = \text{Gas wt\%} - C_4\ \text{wt\%} - C_2^-\ \text{wt\%} \tag{6.33}$$

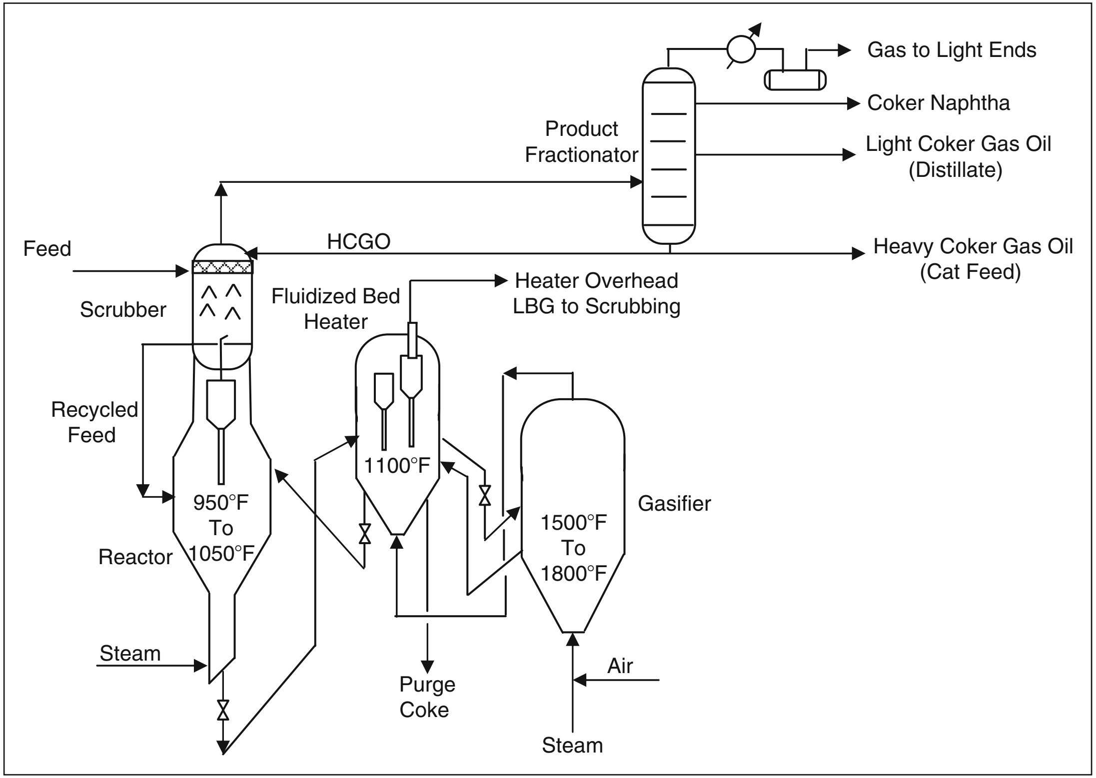


Figure 6.10 Flexicoking process

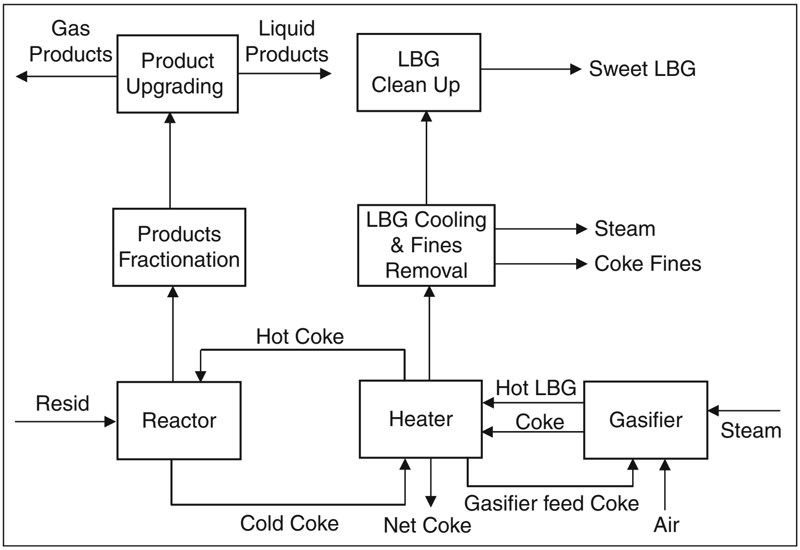


Figure 6.11 Block diagram for flexicoking

Sulphur distribution in products:

$$S\text{ wt\% in Gasoline} = 0.193461 S_f \tag{6.34}$$

$$S\text{ wt\% in Gas oil} = 0.91482 S_f + 0.16921 \tag{6.35}$$

$$S\text{ wt\% in Coke} = 1.399667 S_f + 0.18691 \tag{6.36}$$

$$S\text{ in Gas} = S\text{ in Feed} - S\text{ in Gasoline} - S\text{ in Gas oil} - S\text{ in Coke} \tag{6.37}$$

Gravity of flexicoker feed and gas oil

$$\text{Feed API}_f = 0.5 \times \text{CCR wt\%} + 0.932644 \tag{6.38}$$

$$\text{Gas oil API} = 1.264942 \times \text{API}_f + 0.506675 \times \text{CCR wt\%} - 0.79976 \tag{6.39}$$

Example E6.6

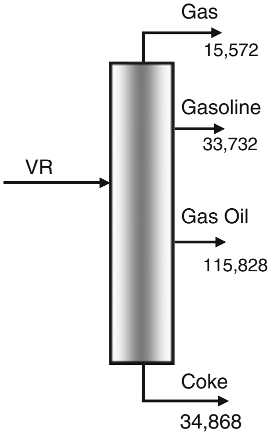
Resolve example E6.1 for the case of flexicoking.

Solution:

The result of this example for flexicoking is given in Table E6.6.

Table E6.6 Flexicoking example

Flexicoking		
Feed rate =	200,000	lb/h
CCR =	15	wt%
S_f =	3	wt%
Feed API =	8.5	
Products yield	**wt%**	**lb/h**
Gas wt% = (0.171943 × CCR% + 5.206667)	7.79	15,572
Gasoline wt% = (−0.115234 × CCR% + 18.594587)	16.87	33,732
Coke wt% = (1.037233 × CCR% + 1.875742)	17.43	34,868
Gas oil wt% = (100 − Gas% − Gasoline% − Coke%)	57.91	115,828
	100.00	200,000
Gases		
C_4 wt% = (−0.028627 × CCR% + 3.200754)	2.77	5543
$C_2{}^-$ wt% = (0.647791 × (Gas% − C_4%) + 0.456001)	3.70	7409
C_3 wt% = (Gas% − C_4% − C_2^- %)	1.31	2620
	7.79	15,572
Sulphur in flexicoker products		
S in Gasoline = (0.193461 S_f)	0.58	196
S in Gas oil = (0.91482 S_f + 0.16921)	2.91	3375
S in Coke = (1.399667 S_f + 0.18691)	4.39	1529
S Gas = (*S* Feed − *S* in Gasoline − *S* in Gas oil − *S* in Coke)	0.06	900
		6000
Gravity of flexicoker products	**API**	**SG**
Gas oil API = (1.264942 × API_f + 0.506675 × CCR% − 0.79976)	17.6	0.95
Feed API = (0.5 × CCR% + 0.932644)	8.43	1.00



QUESTIONS AND PROBLEMS

6.1. 5000 BPD of vacuum residue (API = 11.5) is fed into a delayed coker. Estimate the material balance around the delayed coker and sulphur content if the feed contains 0.38 wt% of sulphur and CCR is 12%.

6.2. Make the mass balance for the coker gas (M = 22.12 lb/lb mol), produced from the vacuum residue in problem 6.1, based on the chemical gas composition of the delayed coker (sulphur-free gas basis).

6.3. In the operation of coil visbreaker, if a layer of carbon of 0.5 cm thickness is deposited on the inside of a 10 cm diameter coil with an 800 m length. The coke is combusted by air in the coil and the heat is removed by introducing steam at 400 °C and exiting at 700 °C. Calculate the flow rate of steam for 60 h of cleaning time. Take C_s = 1 kcal/kg °C; Density of Coke = 1200 kg/m^3; heat of combustion of carbon = 8000 kca1/kg and heat of combustion of sulphur = 2218 kcal/kg. Assume the coke contains 90% carbon and 10% sulphur.

6.4. Make a sketch for

(a) The Coil visbreaker
(b) The Delayed coker
(c) The Flexicoker.

6.5. A thousand pounds per hour of vacuum residue is fed into a flexicoker which has a CCR of 15%. Find the circulation rate of coke between the reactor and the burner in order to keep the temperature of the reactor, heater and burner (gasifier) at 1000, 1300 and 1500 °F, respectively. The low Btu gas (LBG) flow rate is 2000 lb/h. The specific heat of carbon = 0.17 Btu/lb °F and the specific heat (Cp) for the gases = 0.24 Btu/lb °F. The net coke production in this case is 2.0 wt%. Assume 70% of the coke is consumed in the burner.

6.6. 100,000 BPD of crude is introduced to the crude distillation unit (CDU). The vacuum residue (VR 1050+ °F) from the vacuum tower goes to the coker unit. The coker produces heavy naphtha (HN) (190–380 °F) to be combined with the (HN) from the CDU and is fed to the reformer unit. Calculate the amount (lb/h) of the reformate produced.

Crude assay equation:

$$\mathrm{TBP(K)} = \left\{\left(2.2263\ln\left(\frac{100}{100-\mathrm{LV\%}}\right)\right)^{0.368}+1\right\}260$$

Crude API polynomial for atmospheric cuts as:

$$\text{API} = -0.0004\,(\text{LV\%})^3 + 0.0506(\text{LV\%})^2 - 2.4284\,\text{LV\%} + 76.149$$

Crude API polynomial for vacuum cuts:

$$\text{API} = -0.0004(\text{LV\%})^3 + 0.0506(\text{LV\%})^2 - 2.4284\,\text{LV\%} + 143.2$$

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CHAPTER SEVEN

HYDROCONVERSION

7.1. INTRODUCTION

Hydroconversion is a term used to describe all different processes in which hydrocarbon reacts with hydrogen. It includes hydrotreating, hydrocracking and hydrogenation. The term hydrotreating is used to describe the process of the removal of sulphur, nitrogen and metal impurities in the feedstock by hydrogen in the presence of a catalyst. Hydrocracking is the process of catalytic cracking of feedstock to products with lower boiling points by reacting them with hydrogen. Hydrogenation is used when aromatics are saturated by hydrogen to the corresponding naphthenes. The use of the hydroconversion technique depends on the type of feedstock and the desired products as shown in the Table 7.1.

7.2. HYDROTREATING

7.2.1. Objectives of Hydrotreating

Hydrotreating achieves the following objectives:

1. Removing impurities, such as sulphur, nitrogen and oxygen for the control of a final product specification or for the preparation of feed for further processing (naphtha reformer feed and FCC feed);
2. Removal of metals, usually in a separate guard catalytic reactor when the organo-metallic compounds are hydrogenated and decomposed, resulting in metal deposition on the catalyst pores (e.g. atmospheric residue desulphurization (ARDS) guard reactor); and,
3. Saturation of olefins and their unstable compounds.

7.2.2. Role of Hydrotreating

Hydrotreating units are needed in the refinery to clean streams from material such as sulphur, nitrogen or metals harmful to the catalysts. That is why they are located before the reformer, hydrocracker and FCC as shown in Figure 7.1. They are also needed to adjust the final product

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Table 7.1 Hydroconversion techniques

Feedstock	Products	Type of process	Impurities removal
Naphtha	Reformer feed	Hydrotreating	S
	LPG	Hydrocracking	
Atmospheric gas oil	Diesel	Hydrotreating	S, aromatics
	Jet fuel	Mild hydrocracking	S, aromatics
	Naphtha	Hydrocracking	
Vacuum gas oil	Low sulphur fuel oil (LSFO)	Hydrotreating	S
	FCC feed	Hydrotreating	S, N, metals
	Diesel	Hydrotreating, Hydrocracking	S, aromatics
	Kerosene/Jet	Hydrotreating	S, aromatics
	Naphtha	Hydrotreating	S, aromatics
	Lube oil	Hydrotreating	S, N, aromatics
Residuum	LSFO	Hydrotreating	S
	FCC feedstock	Hydrotreating	S, N, CCR and metals
	Coker feedstock	Hydrotreating	S, CCR, metals
	Diesel	Hydrocracking	

specification for various streams, such as light naphtha, kerosene and low sulphur fuel oils (LSFOs).

Hence, the main role of hydrotreating can be summarized as follows:

1. Meeting finished product specification.
   - Kerosene, gas oil and lube oil desulphurization.
   - Olefin saturation for stability improvement.
   - Nitrogen removal.
   - De-aromatization for kerosene to improve cetane number, which is the percentage of pure cetane in a blend of cetane and alpha-methyl-naphthalene. The latter matches the ignition quality of kerosene sample.
2. Feed preparation for downstream units:
   - Naphtha is hydrotreated for removal of metal and sulphur.
   - Sulphur, metal, polyaromatics and Conradson carbon removal from vacuum gas oil (VGO) to be used as FCC feed.
   - Pretreatment of hydrocracking feed to reduce sulphur, nitrogen and aromatics.

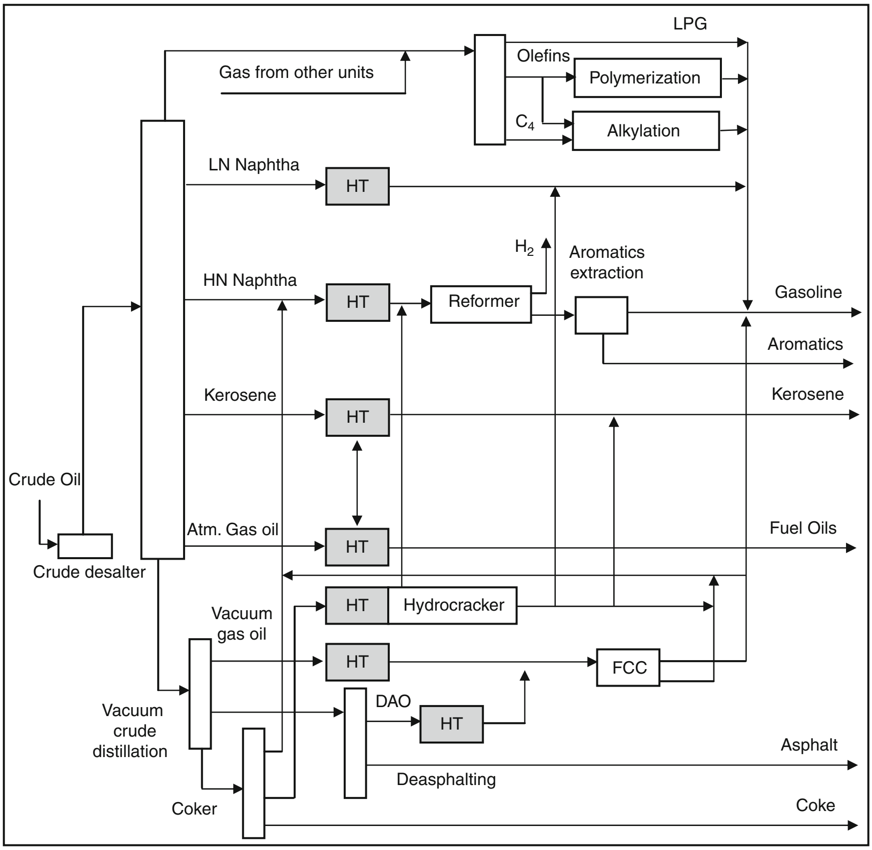


Figure 7.1 Role of hydrotreating (HT) in the refinery

7.2.3. Chemistry of Hydrotreating

Petroleum fraction contains foreign elements, such as S, N, O, and Cl, which can be removed by hydrotreating. Hydrotreating is also used to transform unsaturated compounds to the corresponding saturated hydrocarbons. Sometimes it is used to safeguard the catalyst from metals and organo-metallic compounds by providing a cheap guard catalyst where metals are deposited. Hydrotreating reactions can be classified as follows:

1. Desulphurization
   a. Mercaptanes:

$$RSH + H_2 \rightarrow RH + H_2S \tag{7.1}$$

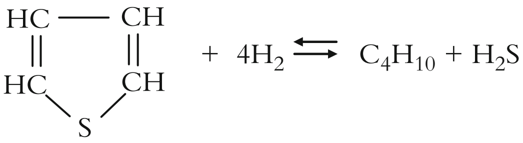
b. Sulphides:

$$R_2S + 2H_2 \rightarrow 2RH + H_2S \tag{7.2}$$

c. Disulphides:

$$(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S \tag{7.3}$$

d. Thiophenes:



(7.4)

2. Denitrogenation
   a. Pyrrole:

$$C_4H_4NH + 4H_2 \rightarrow C_4H_{10} + NH_3 \tag{7.5}$$

b. Pyridine:

$$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3 \tag{7.6}$$

3. Deoxidation
   a. Phenol:

$$C_6H_5OH + H_2 \rightarrow C_6H_6 + H_2O \tag{7.7}$$

b. Peroxides:

$$C_7H_{13}OOH + 3H_2 \rightarrow C_7H_{16} + 2H_2O \tag{7.8}$$

4. Hydrogenation of chlorides

$$RCl + H_2 \rightarrow RH + HCl \tag{7.9}$$

5. Hydrogenation of olefins

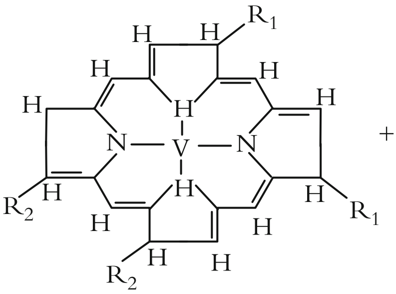
$$C_5H_{10} + H_2 \rightarrow C_5H_{12} \tag{7.10}$$

6. Hydrogenation of aromatics

$$C_6H_6 + 3H_2 \rightarrow \text{Cyclohexane} \tag{7.11}$$

$$\text{Naphthalene} + H_2 \rightarrow \text{Tetraline} \tag{7.12}$$

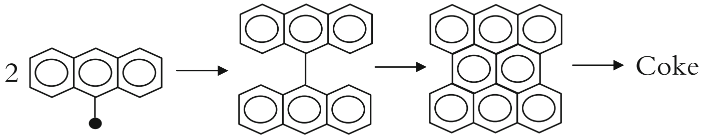
7. Hydrogenation of organo-metallic compounds and deposition of metals



$$+ \quad H_2 \longrightarrow 2NH_3 + 2R_1H_4 + 2R_2H + V \tag{7.13}$$

Vanadium deposited as vanadium sulphide (V_2S_3)

8. Coke formation by the chemical condensation of polynuclear radicals



(7.14)

7.2.4. Hydrotreating Catalysts

The hydrotreating catalyst is a porous alumina matrix impregnated with combinations of cobalt (Co), nickel (Ni), molybdenum (Mo) and tungsten (W). The catalysts mainly have pores with a surface area of (200–300 m^2/g). Co–Mo catalysts are the most popular for desulphurization of straight run petroleum fractions. Ni–Mo catalysts are chosen when higher activity is required for the saturation of polynuclear aromatic compounds or for the removal of nitrogen and refractory sulphur compounds, while Ni–W catalysts are chosen only when very high activity aromatic saturation is required (Speight, 2000). The reactivities of each catalyst are given in Table 7.2. The pore size of a catalyst should be chosen carefully because a smaller size will favour hydrodesulphurization (HDS) on the expense of hydrodemetallization (HDM).

Table 7.2 Reactivities of hydrotreating catalysts

Catalyst	Hydro-desulphurization	Hydro-denitrogenation	Aromatics hydrogenation
Co–Mo/Alumina	Excellent	Good	Fair
Ni–Mo/Alumina	Very good	Very good	Good
Ni–W/Alumina	Good	Good	Excellent

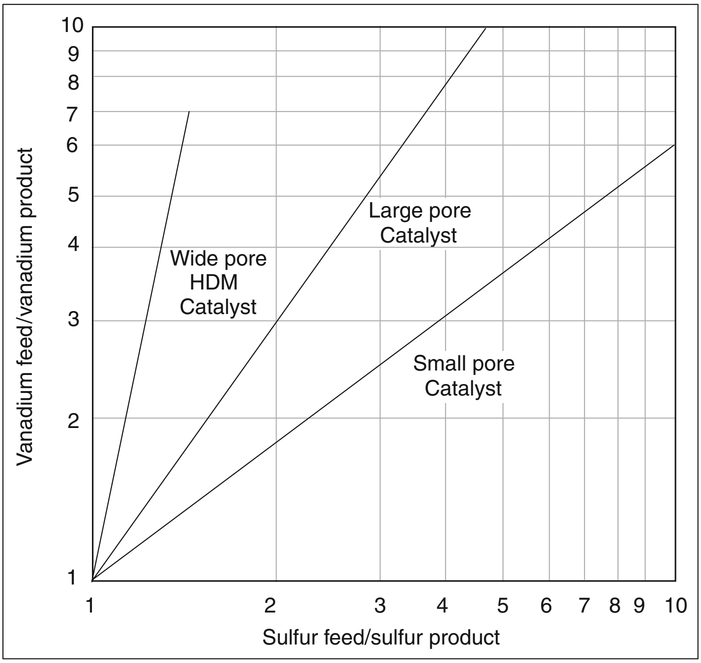


Figure 7.2 General relationship between vanadium and sulphur removal for different Co–Mo catalyst

In the case of a guard reactor, which is used to protect the main catalyst from metal deposition, catalysts with wide pores are chosen and are generally plugged by metal deposition. Figure 7.2, shows that catalysts with different pore diameters can influence the balance between hydrodesulphurization and hydrodemetallization (Raseev, 2003).

Catalysts are available in several different compositions and reactivity. Cobalt–molybdenum (Co–Mo) and nickel–molybdenum (Ni–Mo) catalysts resist poisoning and are the most universally applied catalysts for hydrodesulphurization of feedstocks ranging from naphtha to residue. In addition, they promote both demetallization and desulphurization. The vanadium deposition rate at a given desulphurization level is a function of the pore structure of the alumina support and the types of metals on the support.

7.2.5. Thermodynamics of Hydrotreating

Hydrotreating reactions are highly exothermic and reversible. Table 7.3 lists typical heat of reaction values for some hydrotreating reactions. The logarithm equilibrium constants (K_{eq}) for several hydrodesulphurization reactions are positive (Figure 7.3), indicating that the reactions can virtually proceed to completion if hydrogen is present in the stoichiometric quantity. The reactions given below as reaction A, B and C are examples of such behaviour. Although the equilibrium conversions decrease with temperature rise,

Table 7.3 Heat of reaction for some hydrotreating reactions

Reaction	ΔH (kJ/mol)
Desulphurization of sulphides	−117.0
Desulphurization of disulphides	−209.0
Desulphurization of thiophenes	−284.2
Deoxidation of phenol	−66.9
Hydrogenation of benzene	−209.0
Hydrogenation of naphthene	−125.4

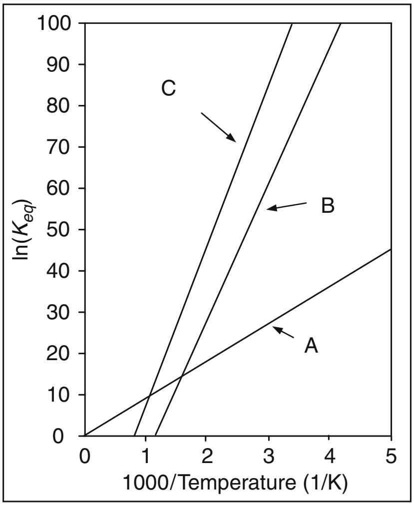
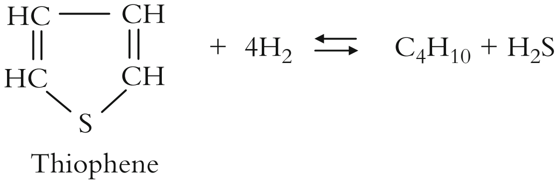


Figure 7.3 Thermodynamic limitations of HDS

commercial hydrotreating is run at rather high temperatures to promote the kinetics of these reactions.

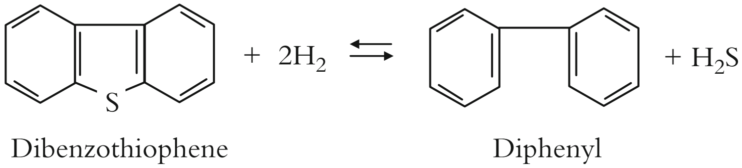
A: $$\mathrm{CH_3SH + H_2 \rightleftharpoons CH_4 + H_2S} \tag{7.15}$$

B:



(7.16)

C:



(7.17)

The equilibrium constant of reaction A can be expressed as:

$$(K_{eq})_A = \frac{P_{H_2S}P_{CH_4}}{P_{CH_3SH}P_{H_2}} \tag{7.18}$$

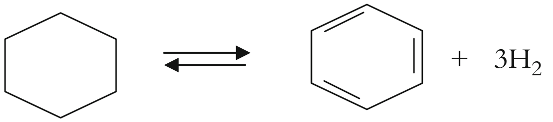
Olefin hydrogenation is usually complete; however an aromatic hydrogenation reaction can reach equilibrium under certain condition, as in kerosene and gas oil hydrogenation. Hydrodesulphurization can be carried out easier than denitrogenation, while aromatic saturation is the most difficult reaction.

A conversion of 0.99 for thiophene hydrogenated to butane can be achieved at 15 bar (220 psia) and 395 °C (743 °F), while pyridine conversion to pentane at the same condition is 0.97. A conversion of 0.4 is achieved for hydrogenation of naphthalene (aromatics) to tetra-hydronaphthalene at the same operating conditions.

The thermodynamics of hydrogenation of benzene to cyclohexane can be studied by finding the equilibrium conversion (x_e). Saturation of aromatic compounds is important in hydrotreating. This reaction is reversible and the equilibrium between the forward and reverse reaction can hinder the extent of saturation at normal operating conditions. The hydrogenation reaction is favoured by high hydrogen partial pressures and low operating temperatures. This can be illustrated by considering the simplest aromatic hydrogenation/dehydrogenation reaction, the one between benzene and cyclohexane.

Example E7.1

Consider the following dehydrogenation reaction:



Determine and plot the equilibrium conversion as a function of temperature and pressure, given the following data:

The free energy $\Delta G = 200,100 - 396T$

where ΔG is in J/mol and T is in Kelvin

The equilibrium constant, K_{eq}, is related to the free energy as follows:

$$\Delta G = -RT\ln K_{eq}$$

where R is the gas law constant.

Solution:

The equilibrium constant (K_{eq}) can be written in terms of reactants and products partial pressure as follows:

$$K_{\mathrm{eq}} = \frac{P_{\mathrm{H_2}}^3 P_{\mathrm{Bz}}}{P_{\mathrm{CH}}}$$

Starting with one mole cyclohexane and letting x equal the fraction of cyclohexane converted, the following table can be obtained:

	Initial feed	Final product
Cyclohexane	1	$1 - x$
Benzene	0	x
Hydrogen	0	$3x$
Total	1	$1 + 3x$

Thus,

$$K_{\mathrm{eq}} = \frac{\left(\frac{x}{1+3x}\right) P_{\mathrm{T}} \left(\frac{3x}{1+3x}\right)^3 P_{\mathrm{T}}^3}{\left(\frac{1-x}{1+3x}\right) P_{\mathrm{T}}}$$

The equilibrium constant, K_{eq}, and amount of benzene converted can be calculated at several temperatures and pressures as shown graphically in Figure E7.1. The plots indicate that hydrogenation of benzene to produce cyclohexane will occur at high pressures and low temperatures, whereas the reverse reaction in which cyclohexane is dehydrogenated to produce benzene will be maximized at high temperatures and low pressures.

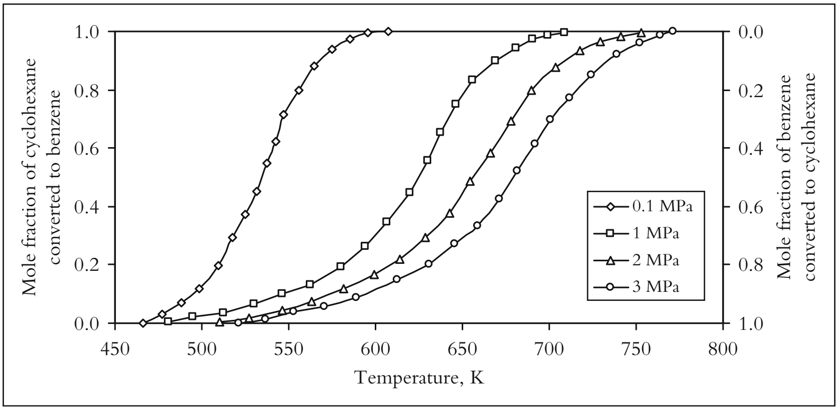


Figure E7.1 Effect of temperature and pressure on the equilibrium conversion of benzene to cyclohexane

7.2.6. Reaction Kinetics

If we assume that the rate of a hydrotreating reaction follows n order:

$$-\frac{dC}{dt} = kC^n \tag{7.19}$$

this equation can be integrated to:

$$kt = \frac{1}{n-1}\left(\frac{1}{C^{n-1}} - \frac{1}{C_0^{n-1}}\right) \tag{7.20}$$

where t is the reaction time (h), k is the reaction rate constant (h^{-1}), C_0 is the initial sulphur content in feedstock (wt%), C is the final sulphur content in the product (wt%), and n is the reaction order $\neq 1$. Equation (7.19) can be integrated for first order to $kt = ln(C/Co)$.

The first order is found for the narrow cuts (naphtha and kerosene). Reaction order n >1.0 (1.5–1.7) is found for gas oil and 2.0 for VGO or residue.

Example E7.2

Find the catalyst volume needed for the desulphurization of VGO. The initial sulphur content is 2.3 wt% and the final sulphur content of the product is 0.1 wt%. The reaction rate constant (h^{-1}) can be expressed as:

$$k = 2.47 \times 10^{10} \exp\left(\frac{-14,995}{T}\right)$$

The reaction conditions are $T = 415$ °C and $P = 5.1$ MPa. The order of the reaction was found to be $n = 1.7$. The feed flow rate is 167,500 kg/h and has a density of 910 kg/m^3.

Solution:

At $T = 415$ °C, $k = 8.455\ h^{-1}$ using equation (7.20)

$$8.455t = \frac{1}{1.7-1}\left(\frac{1}{0.1^{0.7}} - \frac{1}{2.3^{0.7}}\right)$$

$t = 0.75$ h.

The liquid hourly space velocity (LHSV) is calculated as:

$$\text{LHSV} = \frac{1}{0.75} = 1.33\ h^{-1}$$

$$\text{Feed volumetric flow rate} = \frac{167,500\ \text{kg/h}}{910\ \text{kg/m}^3} = 184\ \text{m}^3/\text{h}$$

$$\text{Catalyst volume} = \frac{\text{volume of hourly feed rate}}{\text{LHSV}} = \frac{184}{1.33} = 138\text{m}^3.$$

As a parctial example, hydrogenation of aromatics for arabian gas oil is shown in Figure 7.4. The results were compared with a kinetic model for aromatics hydrogenation based on a simple first order reversible reaction (Yui and Sanford, 1985). Agreement with the model was excellent. This particular reaction is limited by equilibrium at temperatures above 360 °C

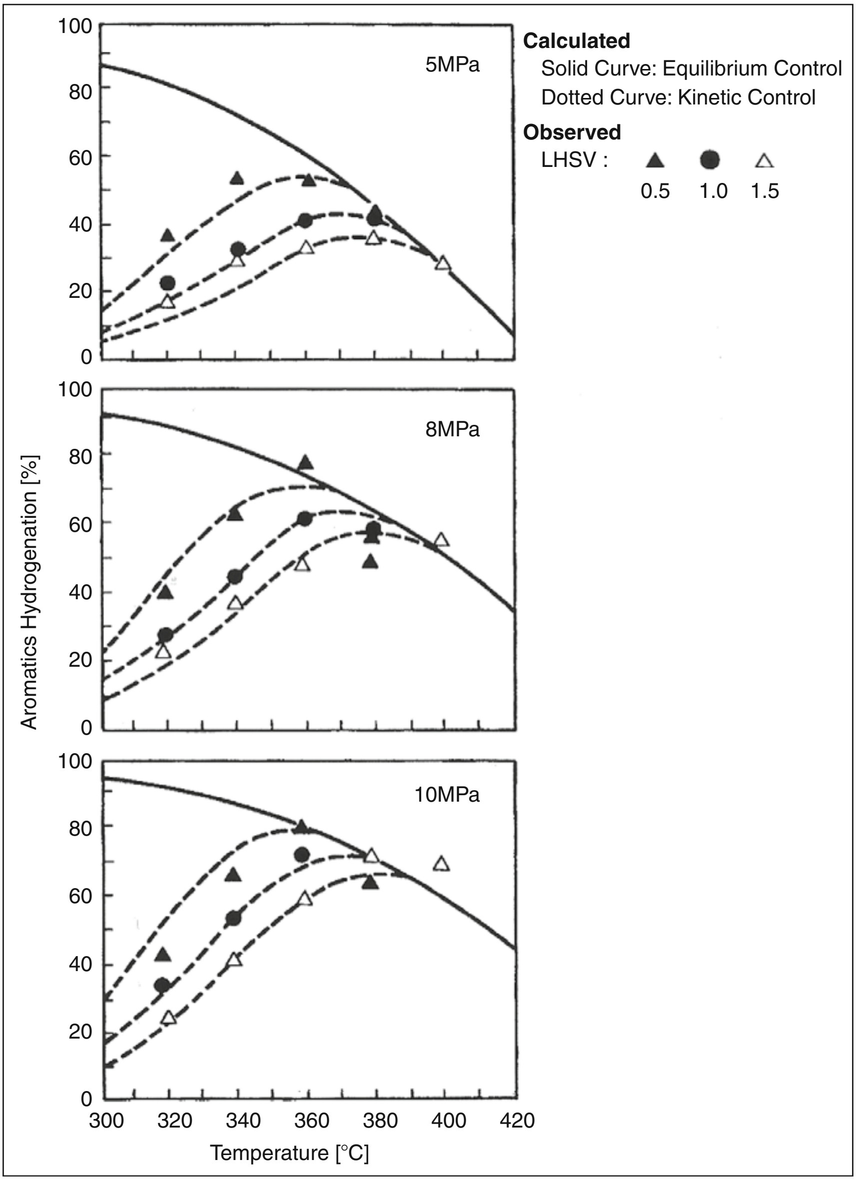


Figure 7.4 Observed and calculated % aromatic hydrogenation at various operating conditions Arabian light gas oil (Yui and Sanford, 1985)

(680 °F) when operating at pressures of 5–10 MPa (725–1450 psia). Higher space velocities result in lower conversion.

7.2.7. Hydrotreating Processes

Hydrotreating processes are similar in common elements and in general can be represented as shown in Figure 7.5. The liquid feed is mixed with hydrogen and fed into a heater and the mixture is brought to the reaction temperature in a furnace and then fed into a fixed bed catalytic reactor. The effluent is cooled and hydrogen-rich gas is separated using a high pressure separator. Before the hydrogen is recycled, hydrogen sulphide can be removed using an amine scrubber. Some of the recycle gas is also purged to prevent the accumulation of light hydrocarbons (C_1–C_4) and to control hydrogen partial pressure. The liquid effluent for the reactor is introduced to a fractionator for product separation.

7.2.7.1. Naphtha Hydrotreating

Heavy naphtha hydrotreating is usually used to remove the impurities so that the hydrotreated naphtha can be introduced to the catalytic reformer. The expensive platinum based catalyst used in the reformer is sensitive to poisoning by such impurities. A schematic flow diagram for the naphtha hydrotreating process is shown in Figure 7.6. The naphtha reformer consists of a feed heater, reactor, high and low pressure separators, recycle compressor and treated naphtha fractionator. A hydrogen sulphide scrubber might be placed between the high and low pressure separators. Some of the recycled gas is purged to lower the concentration of light hydrocarbon (C_1–C_4). A catalyst of Co–Mo on alumina is used.

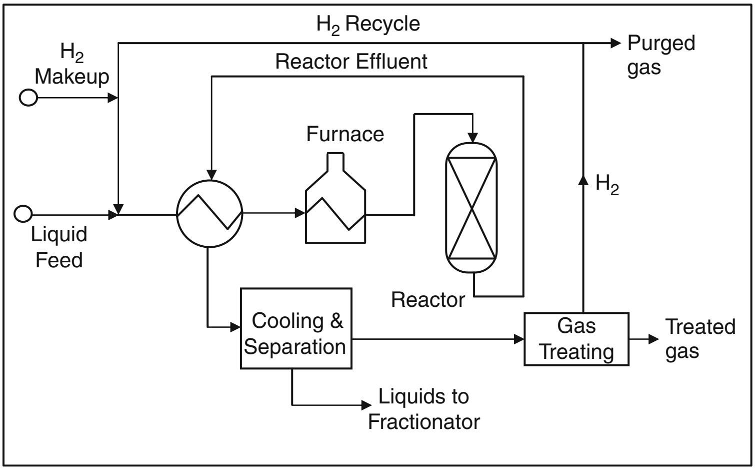


Figure 7.5 The main elements of a hydrotreating process

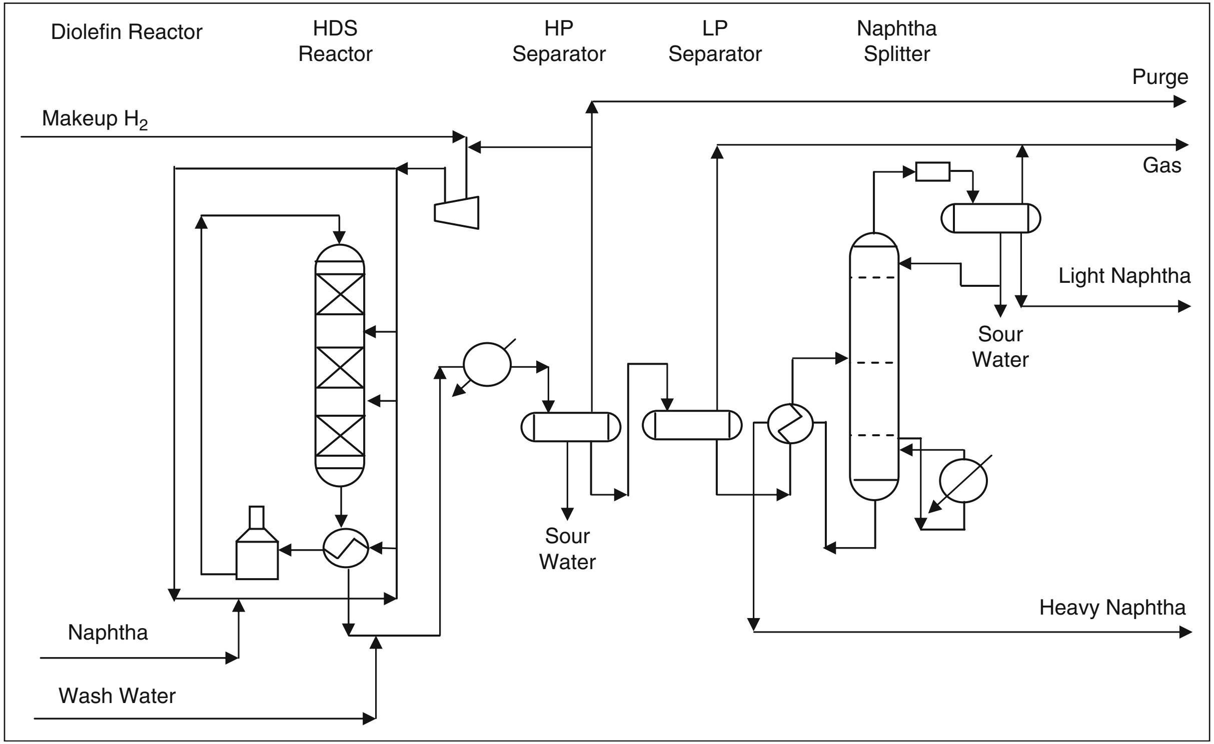


Figure 7.6 Naphtha hydrotreating process

7.2.7.2. Middle Distillates Hydrotreating

Middle distillate is mainly composed of saturated paraffins and also some aromatics which include simple compounds with up to three aromatic rings.

Kerosene, jet fuel oil and diesel fuel are all derived from middle distillate fractions. Typical kerosene feed and product properties are given in Table 7.4. The typical overall yield balance for a kerosene hydrodesulphurization (HDS) unit is given in Table 7.5 (Parakash, 2003). Diesel hydrotreating is shown here as an example of this class in Figure 7.7. The feed stream is combined with recycled hydrogen and make-up hydrogen and heated in a fired heater. The reactor effluent is separated in a high pressure separator into a liquid and recycled hydrogen. The liquid is then flashed into the low pressure separator, producing a gas which is sent to the C_3 and C_4 recovery unit and a liquid which is sent to a fractionator which produce gases, naphtha and hydrotreated diesel. A hydrogen sulphide scrubber and a gas purging are usually used to improve the quality of recycled hydrogen.

Table 7.4 Kerosene HDS unit feed and product properties (Parakash, 2003)

Property	Feed	Naphtha	ATK[a]	Heavy kerosene
Aniline point (°F)	143			156.5
API	46.44	58.89	44.82	41.17
Density	0.7952	0.7432	0.8025	0.8195
Aromatics (vol%)	22	10.3	19.1	19.9
Cloud point (°F)				2
ASTM distillation (°F)				
(IBP)	192	124	384	452
5 vol%	306	178	396	464
10 vol%	324	202	400	472
20 vol%	346	232	404	478
30 vol%	362	256	406	484
50 vol%	396	292	412	500
70 vol%	440	316	422	518
90 vol%	504	348	440	544
95 vol%	526	360	448	556
(EBP)	556	394	470	576
Flash point (°F)			184	226
Freeze point (°F)			−65.2	
Pour point (°F)				Zero
Smoke point (mm)	24		26	25
Sulphur (ppm)	4500	1900	3.6	41.1
Kinematic viscosity at 122 °F (cSt)	1.1		1.32	2.2

[a] Aviation turbine kerosene.

Table 7.5 Kerosene HDS unit overall yields (Parakash, 2003)

Stream	Weight fraction
Feed	
Kerosene feed	1
H_2 gas	0.0137
Total feed	1.0137
Products	
Gas	0.0109
HP[a] gas	0.0060
Acid gas	0.0018
Naphtha	0.1568
ATK	0.7582
Heavy kerosene	0.0800
Total product	1.0137

[a] HP, high pressure

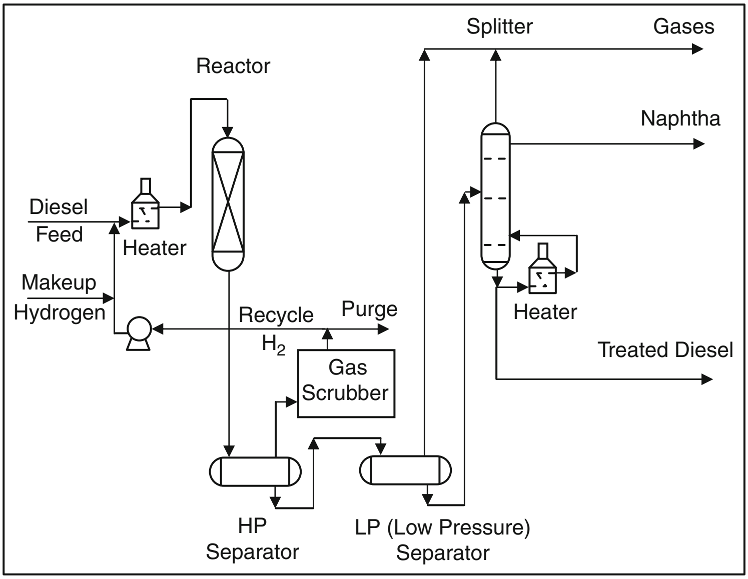


Figure 7.7 Diesel fuel hydrotreating unit

7.2.7.3. Atmospheric Residue Desulphurization

Atmospheric residue can be desulphurized using the process shown in Figure 7.8. Middle East atmospheric residue has a sulphur content of 4–5 wt% and metals (Ni + V) of 75–90 wppm. The purpose of this process is to remove most of the metals and reduce sulphur content in the product to less than 0.5 wt%.

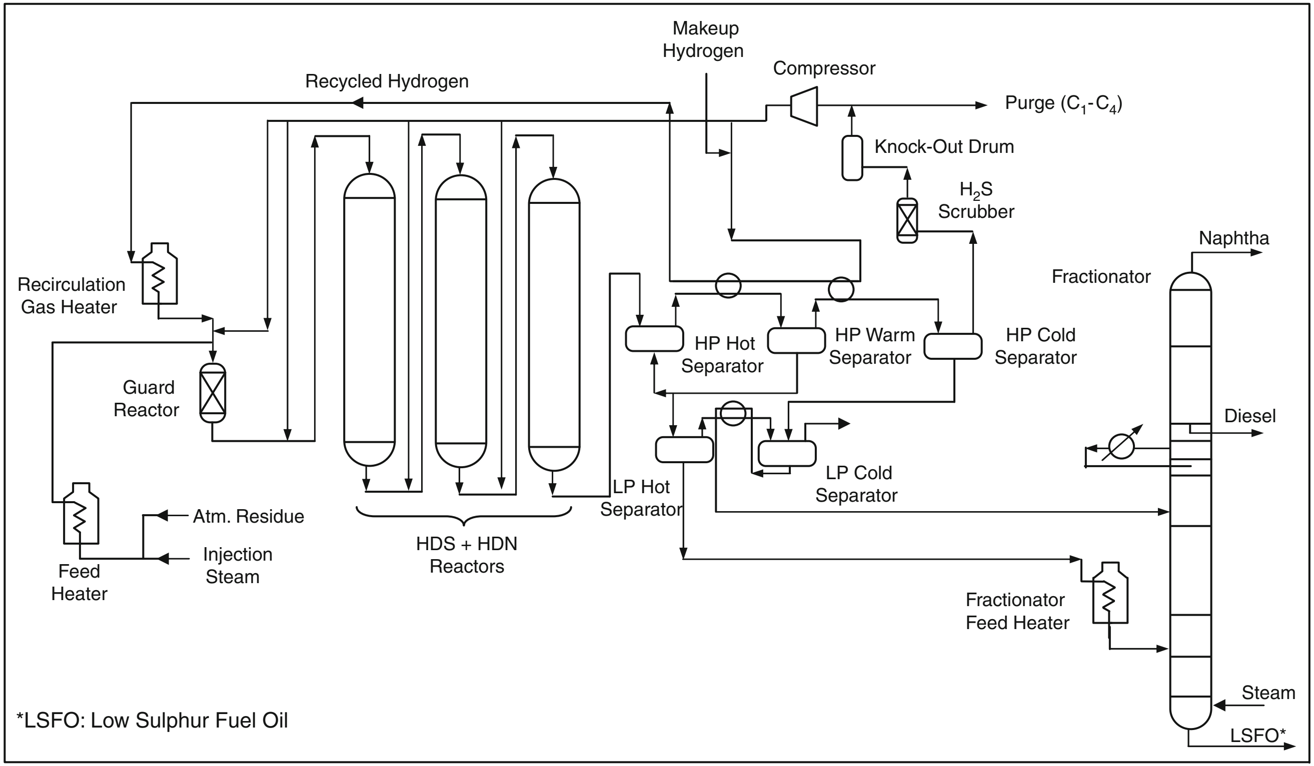


Figure 7.8 Atmosphere residue desulphurization process

The feed is introduced into the heater where steam is injected (to prevent coking) to a temperature below 371 °C (700 °F). The heated recycled hydrogen is mixed with feed and together, they are introduced into a guard reactor which contains a hydrogenation catalyst similar to that in the main reactor but usually cheaper. The catalyst should have wide pores to avoid plugging due to metal deposition. In the reactor, organo-metalic compounds are hydrogenated and metal is deposited. Salts from crude desalters are also removed here. Due to the fast deactivation of this catalyst, usually two reactors are used and the catalyst is changed in one of them while the other reactor is still online. The catalyst in the guard reactor contains 8% of the total catalyst used in the process. Desulphurization, denitrification and hydrodemetallization reactions require severe conditions. Three to four reactors are usually used with different combinations of catalysts to achieve desired objectives. In some units there is a provision for online catalyst replacement in the guard reactor (Parakash, 2003).

The stream leaving the guard reactor is quenched with cold recycle hydrogen and introduced to the first of the three fixed bed reactors. The main reactions of hydrodemetallization, hydrodesulphurization, denitrogenation and aromatic hydrogenation take place in the reactors. The flow diagram also contains high and low pressure separators, recycled hydrogen stream with online amine treatment and purge. The liquid stream from the separators are send to a fractionator to produce naphtha, diesel and low sulphur fuel oil (LSFO).

The ARDS unit reactor temperature is increased at the end of the run (EOR) to burn off any deposited carbon; where thermal cracking occurs at these temperatures. It is possible to use the same unit as a hydrocracker by switching the catalyst to a bifunctional type in which hydrotreating and hydrocracking take place as explained under hydrocracking. Typical ARDS feed and products properties are given in Table 7.6, and typical ARDS yields are given in Table 7.7 (Parakash, 2003).

Table 7.6 Typical ARDS feed and product properties

	Feed	Naphtha	Diesel	LSFO
TBP cut point (°F)	680	C_5–320	320–680	680
API gravity	13.2	52.5	33.5	22.7
Sulphur (wt%)	4.2	0.1	0.05	0.5
Nitrogen (wt%)	0.26	–	0.02	0.13
Metal (Ni + V) (wppm)	75–90	–	–	28

Table 7.7 Typical ARDS yields

	Weight fraction
Feed	
Atmospheric Residue	1
Hydrogen	0.016
Total input	1.016
Products	
Acid gases	0.038
C_1–C_4	0.02
Naphtha	0.027
Diesel	0.186
LSFO	0.745
Total output	1.016

7.2.8. Make-up Hydrogen

A certain hydrogen partial pressure should be maintained in the reactors by recycling un-reacted hydrogen and adding a make-up hydrogen to compensate for the amount consumed. The make-up hydrogen can be calculated by the following expression (Kaes, 2000):

$$\begin{aligned}\text{Make-up hydrogen} = {} & \text{hydrogen in feed} - \text{hydrogen consumed for chemical requirement} \\ & - \text{hydrogen purged} - \text{amount of hydrogen dissolved in product}\end{aligned}$$

Hydrogen requirements for hydrotreating are classified into:

(1) Chemical requirement: This is the amount of hydrogen required to remove impurities such as sulphur, oxygen, nitrogen, olefins and organometalic compounds, according to the stoichiometry of these reactions. Sometimes, it might be required to convert aromatics and naphthenes to corresponding paraffins.
(2) Hydrogen lost due to the dissolution of hydrogen in the hydrocarbons treated. This hydrogen can be predicted by an equation of state under hydrotreating condition.
(3) Amount of hydrogen lost with the purging of light hydrocarbons (C_1–C_4) and hydrogen sulphide (if not removed by amine treatment). This hydrogen can be predicted using flash calculation, or using the purge gas ratio.

The purge ratio is defined as:

$$\text{Purge ratio} = \frac{\text{volume of hydrogen in the purged gas}}{\text{volume of hydrogen in the make-up gas}}$$

Table 7.8 Purge requirement of HDS processes

Feed	Purge H_2/H_2 make-up
Naphtha HDS	0.10
Kerosene HDS	0.15
Diesel HDS	0.20
VGO HDS	0.30

This ratio influences the purity of hydrogen in the recycle gas. Typical purge ratios are summarized in Table 7.8. In addition, some mechanical loss of hydrogen in the compressor can take place.

7.2.9. Operating Conditions

The operating conditions of the hydrotreating processes include pressure, temperature, catalyst loading, feed flow rate and hydrogen partial pressure. The hydrogen partial pressure must be greater than the hydrocarbon partial pressure. High pressure and high hydrogen flow rate (make-up and recycle) would insure that. Increasing hydrogen partial pressure improves the removal of sulphur and nitrogen compounds and reduces coke formation (Heinrich and Kasztelan, 2001).

Higher temperatures will increase the reaction rate constant and improve the kinetics. However, excessive temperatures will lead to thermal cracking and coke formation. The space velocity is the reverse of reactor residence time (θ). High space velocity results in low conversion, low hydrogen consumption and low coke formation. The range of operating conditions for hydrotreating of different feed fractions is given in Table 7.9.

7.2.10. Hydrotreating Correlations

Empirical equations can be used to predict the amount of hydrogen required for certain feeds. Regression of plant data resulted in the correlations listed below (Maples, 1993).

7.2.10.1. Naphtha and Gas Oil Hydrotreating Correlations

The standard cubic foot of hydrogen per barrel of feed (SCFB) required for complete sulphur removal is calculated as:

$$\text{SCFB H}_2 = 191S_f - 30.7 \qquad (7.21)$$

where S_f is the sulphur wt% in feed.

Table 7.9 Process parameters for hydrotreating different feedstocks (Heinrich and Kasztelan, 2001)

Feedstock	Naphtha	Kerosene	Gas oil	Vacuum gas oil	Residue
Boiling range, °C	70–180	160–240	230–350	350–550	>550
Operating temperature, °C	260–300	300–340	320–350	360–380	360–380
Hydrogen pressure, bar	5–10	15–30	15–40	40–70	120–160
Hydrogen consumption, wt%	0.05–0.1	0.1–0.2	0.3–0.5	0.4–0.7	1.5–2.0
[a]LHSV, hr^{-1}	4–10	2–4	1–3	1–2	0.15–0.3
H_2/HC ratio, std m^3/m^3	36–48	36–48	36–48	36–48	12–24

[a] LHSV = Liquid volumetric flow rate at 15°C (ft^3/h)/Volume of catalyst (ft^3)

The increase in the API gravity of a product is calculated as:

$$\Delta(\text{API})_p = 0.01 \times (\text{SCFB H}_2) + 0.036 \times (\text{API})_f - 2.69 \tag{7.22}$$

where p and f refer to product and feed, respectively.

In some cases, if it is required to saturate aromatics and naphthenes to the corresponding paraffin, a set of correlations for PNA analysis is required to predict the naphtha composition. These are:

$$\text{Vol\% Paraffins} = 12.8K_f^2 - 259.5K_f + 1330.0 \tag{7.23}$$

$$\text{Vol\% Naphthene} = -78.5K_f^2 + 1776.6K_f - 9993.7 \tag{7.24}$$

$$\text{Vol\% Aromatics} = 38.4K_f^2 - 894.3K_f + 5219.4 \tag{7.25}$$

where K_f is the feed Watson characterization factor.

Example E7.3

It is required to hydrotreat naphtha which has 1 wt% S and API = 50. Find:

a. How much hydrogen is required to remove all the sulphur in the feed by empirical correlations.
b. How much of this H_2 is used for chemical requirements.
c. If the mean average boiling point of this naphtha is 135 °F. Assuming that the naphthene and aromatic present in the naphtha are cyclohexane and benzene, respectively. Find the volume of hydrogen (SCFB) to convert all cyclohexane and benzene into hexane.

Solution:

Assume a basis of one bbl naphtha feed

a. Hydrogen required for desulphurization:

$$\text{SCFB H}_2 = 191(1) - 30.7 = 160.3$$

Hydrogenated naphtha API:

$$\Delta(\text{API})_P = 0.01(160.3) + 0.036(50) - 2.69 = 0.7$$
$$(\text{API})_P = 50 + 0.7 = 50.7$$

b. To find the chemical hydrogen required:

For the given feed of API = 50, $\rho_f = 273$ lb/bbl

$$\text{Amount of S} = 273 \times 0.01 = 2.73 \text{ lb/bbl}$$
$$\text{Mole } S = 2.73/32 = 0.0853 \text{ mol/bbl}$$
$$\text{For reaction S} + \text{H}_2 \rightarrow \text{H}_2\text{S}$$
$$\text{H}_2 \text{ required} = 0.0853 \text{ mol} \times 379 \text{ ft}^3/\text{mol} = 32.3 \text{ ft}^3/\text{bbl}$$

(Note: At standard gas condition, 1 lb mol occupies 379 ft^3.)

Difference in H_2 requirement = 160.3 – 32.3 = 128 ft^3
This difference includes purge and dissolution hydrogen.

c. From API = 50 then SG = 0.78

$$K_f = \frac{(135 + 460)^{1/3}}{0.78} = 10.9$$

Using equations (7.23), (7.24) and (7.25), the normalized vol% of naphtha composition is:

$$\text{Vol\% Praffins(hexane)} = 22.07 \text{ vol\%}$$
$$\text{Vol\% Naphthenes(cyclohexane)} = 44.33 \text{ vol\%}$$
$$\text{Vol\% Aromatics(benzene)} = 33.60 \text{ vol\%}$$

Hexane does not need H_2.
One mole of cyclohexane needs one mole H_2:

$$C_6H_{12} + H_2 \rightarrow C_6H_{14}$$

One mole of benzene needs 4 moles H_2:

$$C_6H_6 + 4H_2 \rightarrow C_6H_{14}$$

Thus the following table can be constructed for the calculation of the volume of H_2 required to convert cyclohexane and benzene to hexane (assuming 1 bbl feed).

	Volume fraction	MW (lb/lb mol)	SG	Density (lb/bbl)	Weight (lb)	Moles	Mole H_2 required
Hexane	0.221	86	0.66	232.6	51.33	0.59	0
Cyclohexane	0.443	84	0.80	280.7	124.4	1.48	1.48
Benzene	0.336	78	0.88	308.7	103.7	1.33	5.32
	1.0				279.43		6.80

The final amount of H_2 required can be summed up as:

$$H_2 \text{ required} = 6.80 \text{ mol} \times 379 \text{ ft}^3/\text{mol} = 2577 \text{ ft}^3/\text{bbl}$$

It can be seen that the amount of hydrogen for naphthenes and aromatics saturation is much higher than that needed for other requirements such as sulphur removal.

Example E7.4

It is required to remove all S in a feed of atmospheric gas oil (AGO) by hydrotreating. The feed contains 2 wt% S and sulphur compounds distributed is as follows:

Compound	RSH	R_2S	$(RS)_2$	Thiophene (C_4H_4S)
wt %	45	25	20	10

The AGO has an API = 30. Calculate the chemical hydrogen requirement in SCFB.

Solution:

The corresponding hydrogenation reactions are:

$$RSH + H_2 \rightarrow RH + H_2S$$

$$R_2S + 2H_2 \rightarrow 2RH + H_2S$$

$$(RS)_2 + 3H_2 \rightarrow 2RH + 2H_2S$$

$$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$$

AGO of 30 API has a density of 306 lb/bbl. For one barrel of AGO, the corresponding sulphur content ($S_f = 0.02$) is:

$$306\ \text{lb/bbl} \times 0.02 = 6.12\ \text{lb S/bbl}$$

The amount of hydrogen required can be calculated as shown in the following table:

S distribution in feed (lb S/bbl feed)	Moles (H_2/mol S)	Hydrogen required (ft^3/bbl feed)
6.12 × 0.45 = 2.75	1	(2.75/32) × (379) × (1) = 32.6
6.12 × 0.25 = 1.53	2	(1.53/32) × (379) × (2) = 36.3
6.12 × 0.20 = 1.22	1.5	(1.22/32) × (379) × (1.5) = 21.8
6.12 × 0.10 = 0.61	4	(0.61/32) × (379) × (4) = *29.0*
		Total 119.7

The total chemical hydrogen required is about 120 SCF H_2/bbl AGO.

7.2.10.2. Middle Distillate Hydrotreating Correlations

The amount of hydrogen required can be calculated as:

$$\text{SCF H}_2/\text{bbl} = 110.8 \times (S_f) + 10.2 \times (\text{HDS\%}) - 659.0 \qquad (7.26)$$

where S_f is the wt% sulphur in the feed and HDS% is the percent of hydrodesulphurization required (degree of severity). The increase in product API is calculated as:

$$\Delta(\text{API})_p = 0.00297 \times (\text{SCF H}_2/\text{bbl}) - 0.11205 \times (\text{API})_f + 5.54190 \qquad (7.27)$$

This equation is used for feed sulphur content of 0.5–6.0 wt%.

Example E7.5

Gas oil has an API of 30, and a sulphur content of 1.5 wt% is fed into a hydrotreater. It is required to carry out HDS at a severity of 90%. Calculate the hydrogen required and the product API.

Solution:

Assume 1 bbl of GO, API = 30 (306 lb/bbl)
Amount of S in feed = 306 × 0.015 = 4.6 lb/bbl feed
Total hydrogen required (SCFB H_2)

$$= 110.8(1.5) + 10.2(90) - 659 = 425\ \text{ft}^3/\text{bbl}$$

$$\Delta(\text{API})_P = 0.00297(425) - 0.11205(30) + 5.5419 = 3.4$$

Product API = 30 + 3.4 = 33.4

7.2.10.3. Atmospheric Residue Desulphurization (ARDS)

In atmospheric residue desulphurization (ARDS), thermal cracking occurs and no reliable correlations were found in literature. The hydrogen requirement, however, can be calculated for equation (7.26). The main products in this process are low sulphur fuel oil (LSFO) with a yield from 70 to 75 weight percent. Naphtha and diesel are also produced. A typical ARDS yields are presented in Table 7.10.

Table 7.10 Typical ARDS yields (Parakash, 2003)

	Mass fraction
Feed	
Atmospheric residue	1.0
Hydrogen	0.016
Total input	1.016
Products	
Acid gas	0.038
Off gas	0.020
Naphtha	0.017
Diesel	0.186
Fuel oil	0.755
Total output	1.016

7.2.11. Simulation of ARDS Unit

The unit is basically designed to remove sulphur and other impurities from atmospheric residue. It is important to consider two main reactions: desulphurization and hydrocracking. The details of the simulation are given in example E7.6.

Example E7.6

A heavy residue stream that contains mostly n-C_{30} (990 lb mol/h) and some amount of thiophene (10 lb mol/h) is prepared to enter an ARDS process to crack the heavy component n-C_{30} to more lighter components such as n-C_{20}, *n*-C_{10} and *n*-C_4. In addition, thiophenes should be completely removed. The feed stream is initially at 100 °F and 120 psia. This feed needs to be mixed with hydrogen stream (1250 lb mol/h) available at 150 °F and 200 psia. The mixed feed should be heated and compressed to 700 °F and 1500 psia before entering the reactor. The reactions are shown in Table E.7.6.1.

Table E.7.6.1 Typical reactions in ARDS

Rxn #	Reaction	Reactor type	Conversion
1	$C_4H_4S + 4H_2 \rightarrow C_4H_{10} + H_2S$	Conversion	100%
2	$C_{30}H_{62} + H_2 \rightarrow C_{20}H_{42} + C_{10}H_{22}$	Conversion	70%

The reactor products are cooled to 200 °F before entering a gas–liquid separator. 300 lb mol/h of the hydrogen coming from this separator is recycled back with the feed. The rest is vented to the atmosphere. The liquid stream coming out from the separator is then expanded by a valve to reduce the pressure to 250 psia. This makes it ready to enter a distillation column in order to separate the extra hydrogen left with the hydrocarbons. A typical flowsheet of the ARDS process is shown in Figure E7.6.1. Perform a material and energy balance for the ARDS process using UNISIM simulator.

Solution:

1. Enter the simulation basis environment in UNISIM.
2. Add the components as follows:
   Thiophene, *n*-C_{30}, *n*-C_{20}, *n*-C_{10}, *n*-C_4, H_2 and H_2S.
3. Select Peng–Robinson as the fluid package.
4. Insert Reaction-1 stoichiometry and conversion and do the same for Reaction-2.
5. Enter simulation environment.
6. Insert the first unit for the oil feed as shown in the flow chart with compositions, temperature and pressure as given in Table E7.6.2.
7. Continue inserting units as shown in the flowsheet.
8. The reactor is a conversion reactor.
9. The distillation column is 15 trays with reflux ratio equal to 1.0 and full reflux. The active specification to run the distillation column is a hydrogen recovery of 100% and an *n*-decane recovery of 90%.
10. Finally, add the recycle control unit to optimize the connections.

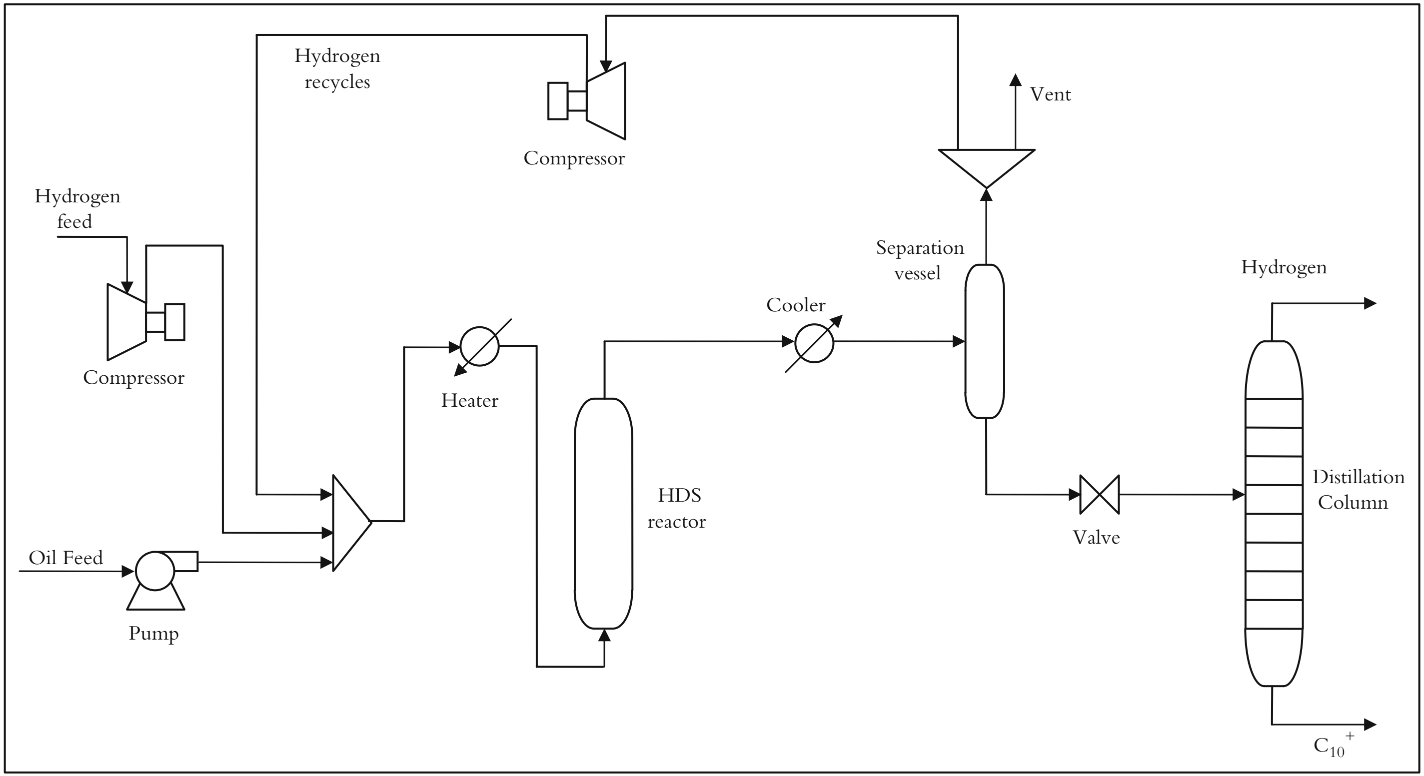


Figure E7.6.1 ARDS process flow chart

Table E7.6.2 UNISIM results

Stream name	Hydrogen feed	Comp out 1	Oil feed	Pump out	Comp out 2	Mixed feed	Reactor feed	Reactor vapour	Reactor liquid	Product	Cooler out	Separator vapour	Separator liquid	Vent	Recycle hydrogen	Dist feed	Hydrogen	C_{10}^{+}
Temperature (°F)	150	790.2	100	101.5	205.2	126.4	700	756.6	756.5	756.5	200	200	200	200	200	209	444	930
Pressure (psia)	200	1500	120	1500	1500	1500	1495	1475	1475	1475	1470	1470	1470	1470	1470	250	225	240
Total molar flow (lb mole/h)	1250	1250	1000	1000	300	2550	2550	217.5	2303	2520	2520	638.8	1881.2	338.8	300	1881	268	1613
Thiophene (lb mol/h)	0	0	10	10	0	10	10	0	0	0	0	0	0	0	0	0	0	0
H_2S (lb mol/h)	0	0	0	0	1	1	1	1.5	9.5	11	11	2	9	1	1	9	9	0
H_2 (lb mol/h)	1250	1250	0	0	299	1549	1549	176.5	639	815.5	815.5	635.8	179.7	337.2	298.6	180	180	0
n-C_{30} (lb mol/h)	0	0	990	990	0	990	990	1	296	297	297	0	297	0	0	297	0	297
n-C_{20} (lb mol/h)	0	0	0	0	0	0	0	7.5	685.5	693	693	0	693	0	0	693	0	693
n-C_{10} (lb mol/h)	0	0	0	0	0	0	0	30	664	693.5	693.5	0.4	692.8	0.2	0.2	693	69	623
n-C_4 (lb mol/h)	0	0	0	0	0	0	0	1	9	10	10	0.6	9.7	0.4	0.2	10	10	0

7.3. HYDROCRACKING

Hydrocracking is a catalytic hydrogenation process in which high molecular weight feedstocks are converted and hydrogenated to lower molecular weight products. The catalyst used in hydrocracking is a bifunctional one. It is composed of a metallic part, which promotes hydrogenation, and an acid part, which promotes cracking. Hydrogenation removes impurities in the feed such as sulphur, nitrogen and metals. Cracking will break bonds, and the resulting unsaturated products are consequently hydrogenated into stable compounds.

7.3.1. Role of Hydrocracking in the Refinery

Hydrocracking plays an important role as one of the main conversion processes in the refinery as shown in Figure 7.9. It is mainly used to produce middle distillates of low sulphur content such as kerosene and diesel. If mild hydrocracking is used, a LSFO can be produced. More recently, it has been used to remove wax by catalytic dewaxing and for aromatic removal by hydrogen saturation. This has been applied to the lube oil plants and is gradually replacing the old solvent dewaxing and aromatic solvent extraction.

7.3.2. Feeds and Products

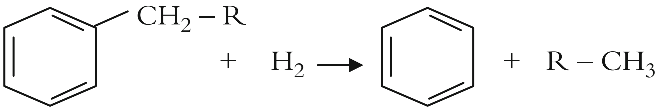
VGO is the main feed for hydrocrakers, however a variety of feeds can be used as shown in Table 7.11. The feedstock type has an important influence on the final products.

7.3.3. Hydrocracking Chemistry

1. Alkane hydrocracking

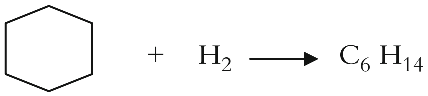
$$R-CH_2 \vdots CH_2-R' + H_2 \longrightarrow R-CH_3 + R'-CH_3 \qquad (7.28)$$

2. Hydrodealkylation



(7.29)

3. Ring opening



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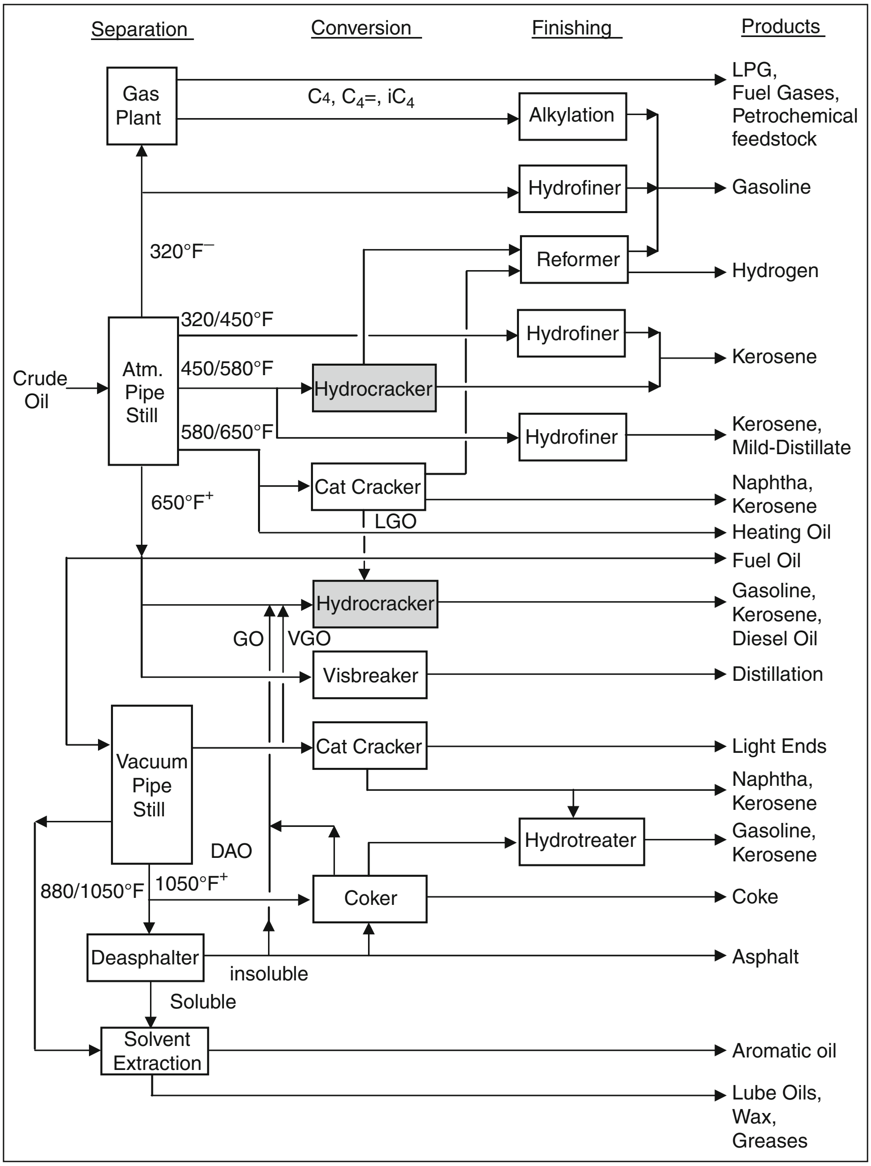
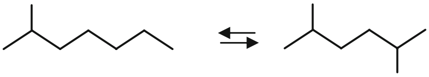


Figure 7.9 Role of the hydrocracker in the refinery

Table 7.11 Typical feedstocks and products

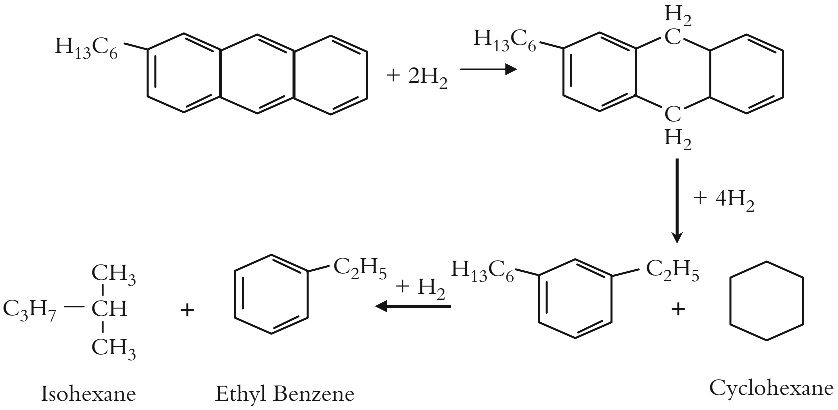
Feedstocks	Products
Kerosene	Naphtha
Straight-run diesel	Naphtha and/or jet fuel
Atmospheric gas oil	Naphtha, jet fuel, and/or diesel
Vacuum gas oil	Naphtha, jet fuel, diesel, lube oil
FCC LCO	Naphtha
FCC HCO	Naphtha and/or distillates
Coker LCO	Naphtha and/or distillates
Coker HCO	Naphtha and/or distillates
Deasphalted oil	Olefin plant feedstocks

4. Hydroisomerization



(7.31)

5. Polynuclear aromatics hydrocracking



(7.32)

7.3.4. Hydrocracking Catalysts

Hydrocracking catalysts have a cracking function and a hydrogenation–dehydrogenation function (Figure 7.10). The cracking function is provided by an acidic support, whereas the hydrogenation–dehydrogenation

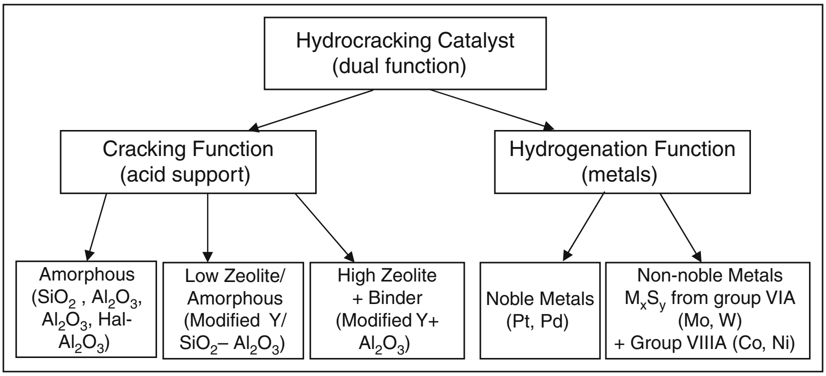


Figure 7.10 Classification of hydrocracking catalyst (Secherzer and Gruia, 1996)

function is provided by active metals. The acidic support can be (a) amorphous oxides (e.g. silica–alumina), (b) a crystalline zeolite (mostly modified Y zeolite) plus binder (e.g. alumina) or (c) a mixture of crystalline zeolite and amorphous oxides. Cracking and isomerization reactions take place on the acidic support (Secherzer and Gruia, 1996).

The metals providing the hydrogenation–dehydrogenation function can be noble metals (palladium, platinum) or non-noble metal sulphides from Group VI.A (molybdenum, tungsten) and group VIII.A (cobalt, nickel). These metals catalyze the hydrogenation of the feedstock, making it more reactive for cracking and heteroatom removal and 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 to optimize activity and selectivity. The relative strength of different hydrogenation components and cracking (acid) components in hydrocracking catalysts are shown in Table 7.12.

Table 7.12 Bifunctional catalyst strength for hydrogenation and cracking

Hydrogenation function	Co/Mo	Ni/Mo	Ni/W	Pt(Pd)
	x	xx	xxx	xxxx
Cracking function	Al_2O_3	Al_2O_3–Hal	SiO_3–Al_2O_3	Zeolite
	x	xx	xxx	xxxx

x represents order of strength

Catalysts with amorphous supports are still in commercial use, primarily where maximizing the production of middle distillates or conversion to lube oil blending stock are the objective. Amorphous hydrocracking catalysts contain primarily amorphous silica–alumina. The hydrocracking catalysts described so far are used primarily for hydrocracking gas oils and FCC cycle oils. For hydroprocessing residues, amorphous hydrocracking catalysts as well as specially designed hydrotreating catalysts and iron-containing catalysts are used.

Catalysts used for mild hydrocracking have a composition similar to that of hydrotreating catalysts. They consist of Group VI and VIII non-noble metals supported on γ-alumina. The metals used are cobalt, nickel, molybdenum, and tungsten in sulphided form. Under mild process conditions, gas oil hydrocracking catalysts may also be used for mild hydrocracking. Dewaxing catalysts usually consist of a hydrogenation metal (Pt, Pd, Ni) supported on a medium-pore zeolite (e.g. ZSM-5) combined with a binder, commonly alumina. A zeolite catalyst Y type is shown in Figure 7.11. The reacting molecules pass inside the cages and are brought in close contact for reaction. The zeolite channels (or pores) are microscopically small and in fact have molecular size dimension such that they are often termed "molecular sieves."

The composition of a hydrocracking catalyst depends on the final product requirements and mode of the operation (one or two-stage). A guideline of catalysts composition is shown in Table 7.13. In the first stage of a two-stage operation, a hydrocracking hydrogenation catalyst is usually used for hydrodesulphurization, hydrodenitrogenation and aromatics removal. In the second stage a hydrocracking catalyst is used for a hydrocracking and hydroisomerization. In Table 7.14, the types of catalysts used for mild and high conversion hydrocracking are shown along with FCC and hydrotreating catalysts. Residue conversion processes (fixed, moving and ebulated beds) use

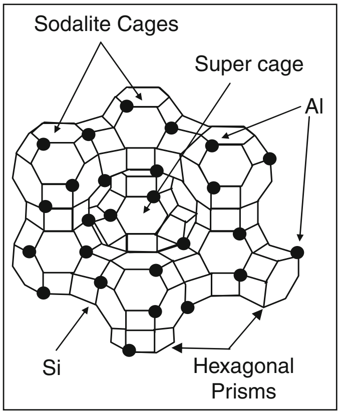


Figure 7.11 Structure of Y-type zeolite catalyst

Table 7.13 Types of catalyst used in different hydrocracking processes (Billon and Bigeard, 2001)

		Hydrogenerating function			Acid function	
Application type	Process type (# stages)	Pd	Ni–Mo	Ni–W	Y-type zeolite	SiO_2/Al_2O_3 amorphous
Max. Naphtha	One	xxx	x	x	xxx	
Max. Naphtha	Two	xxx			xxx	
Max. Kerosene	One		xxx	x	xxx	
Max. Kerosene	Two	x	x	x	x	x
Max. Diesel oil	One		x	x	x	x
Max. Diesel oil	Two		x	x		x
Max. Lube oils	One		x	x	x	x

x represents frequency of use

Table 7.14 Catalysts used for VGO treatment

High conversion hydrocracking	Bifunctional	A	Amorphous Silica–Alumina
			Zeolite
		H	Pd, Pt
			Ni (Co), Mo (W)
Mild hydrocracking	Mono-functional or bifunctional	A	Amorphous Silica–Alumina
			Alumina
		H	Ni (Co), Mo (W)
FCC	Mono-functional	A	Zeolite+ Amorphous Silica–Alumina
Hydrotreating	Mono-functional	H	Ni (Co), Mo (W)

A is acidic function; H is hydrogenation function.

supported palletized catalysts of bifunctional composition. Slurry reactors employ dispersed catalysts.

7.3.5. Thermodynamics and Kinetics of Hydrocracking

7.3.5.1. Thermodynamics

Aromatic hydrogenation, paraffin hydrocracking, naphthenes hydrocracking and aromatic hydrodealkylation reactions are all exothermic and careful control of the fixed bed temperature is required. This is usually done by gaseous quenches in the reactor. Catalyst partitioning of the bed must be

Table 7.15 Heat of reaction (Billon and Bigeard, 2001)

Reaction type	Average heat of reaction at 400 °C (kJ/mol)
Aromatics hydrogenation	−210
Paraffin hydrocracking	−46 to −58
Naphthenes hydrocracking	−42 to −50
Aromatics hydroalkylation	−42 to −46

applied. Table 7.15 gives average heat of a reaction at 400 °C (kJ/mol) of different classes of reactions.

7.3.5.2. Kinetics

Hydrocracking conversion is usually defined in terms of a change of the end point:

$$\%\text{Conversion} = \left(\frac{(\text{EP}^{+})_{\text{feed}} - (\text{EP}^{+})_{\text{products}}}{(\text{EP}^{+})_{\text{feed}}}\right) \times 100 \qquad (7.33)$$

where EP^{+} is the fraction of material in the feed or product boiling above the desired end point usually as wt% or vol%.

The detailed analysis of reaction kinetics is rather complicated because it involves several successive reactions, as in the hydrocracking of polyaromatics and naphthenes shown in Figure 7.12. Different reaction rate constants indicate the relative reaction rate of each reaction. Comprehensive mathematical models have recently been proposed in literature to consider all possible reactions, and adsorption constants are usually important factors in these models. As an example, the hydrocracking of vacuum residue is presented as a network of nested reactions Figure 7.13.

7.3.6. Hydrocracking Processes

The following factors can affect operation (product quality), yield (quantity), and the total economics of the process:

- Process configuration: one stage (once-through or recycle) or two stages
- Catalyst type
- Operating condition (depends on process objective)
    - Conversion level
    - Maximization of certain product
    - Product quality
    - Catalyst cycle
    - Partial hydrogen pressure
    - Liquid hourly space velocity
    - Feed/hydrogen recycle ratio

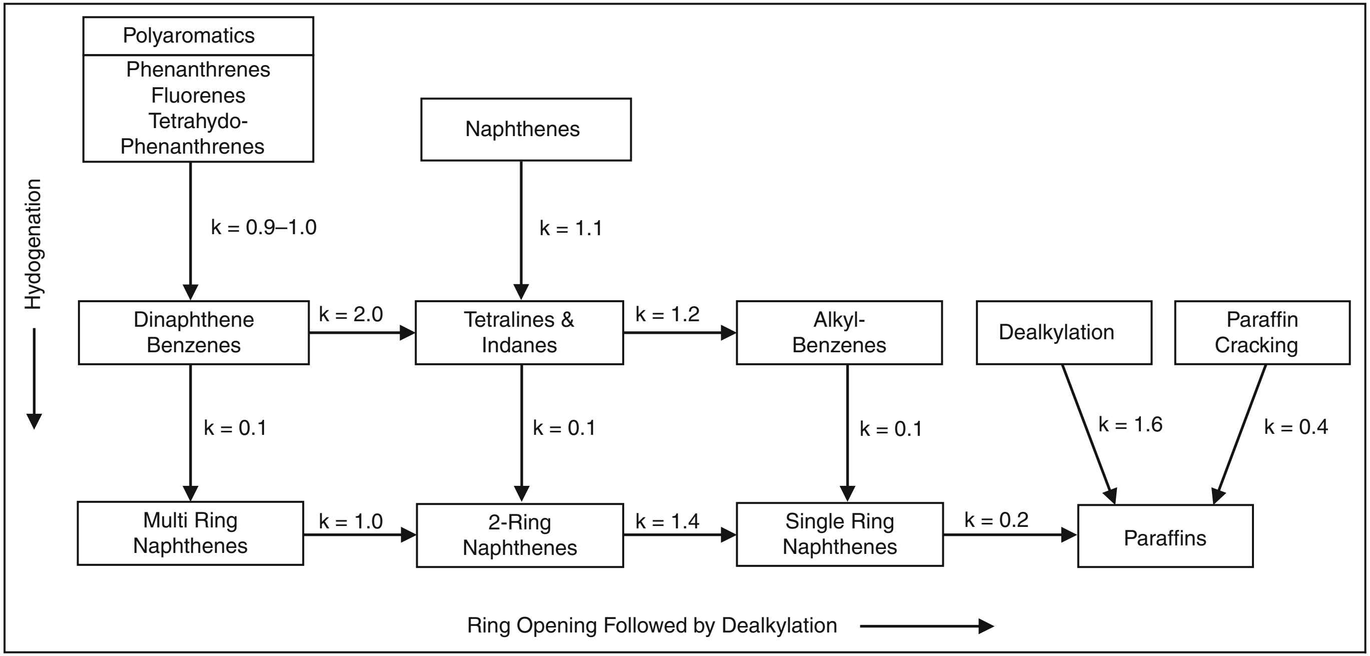


Figure 7.12 Relative rates of reactions under hydrocracking conditions (Filimonov et al., 1972)

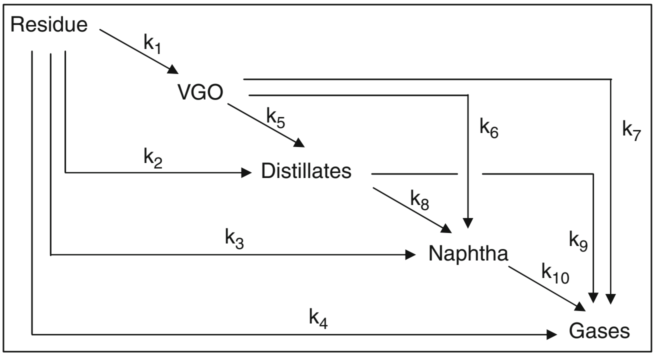


Figure 7.13 Proposed kinetic model for the hydrocracking of heavy oils

7.3.7. Process Configuration

The one-stage process shown in Figure 7.14 can be used for light feeds with once through or recycle process. In commercial hydrocrackers, a conversion of 40–80% of the feed can be achieved. However if high conversion is required the product from the bottom of the distillation tower is recycled back to the reactor for complete conversion. This configuration can be used to maximize a diesel product, and it employs an amorphous catalyst.

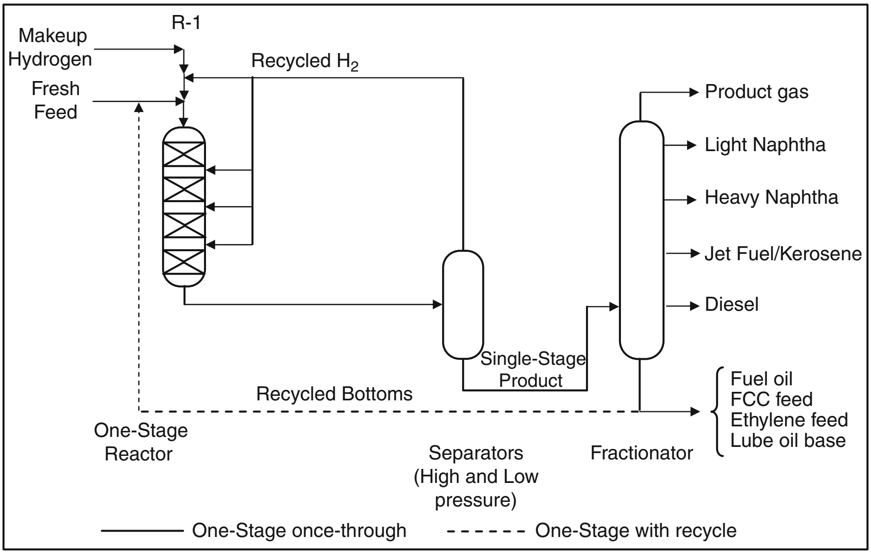


Figure 7.14 Simplified flow diagram of one-stage hydrocracking process with and without recycle

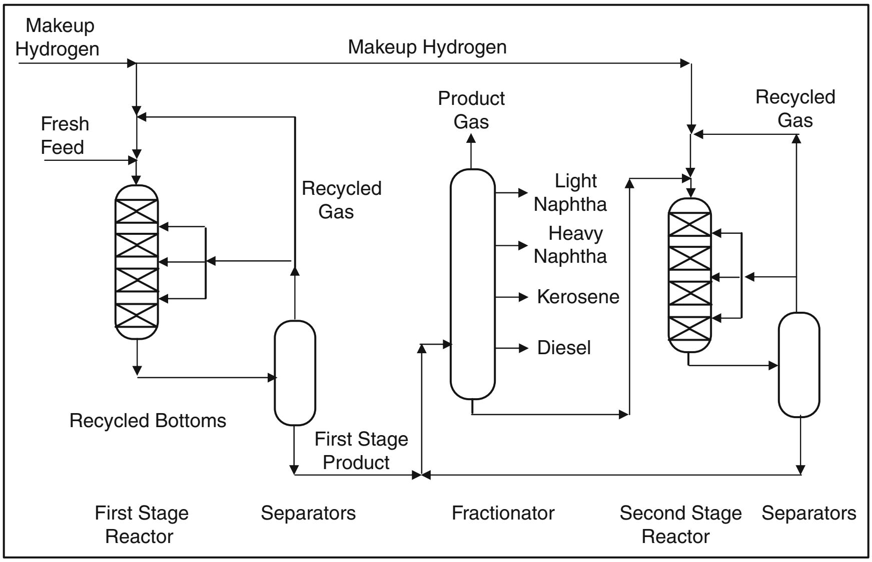


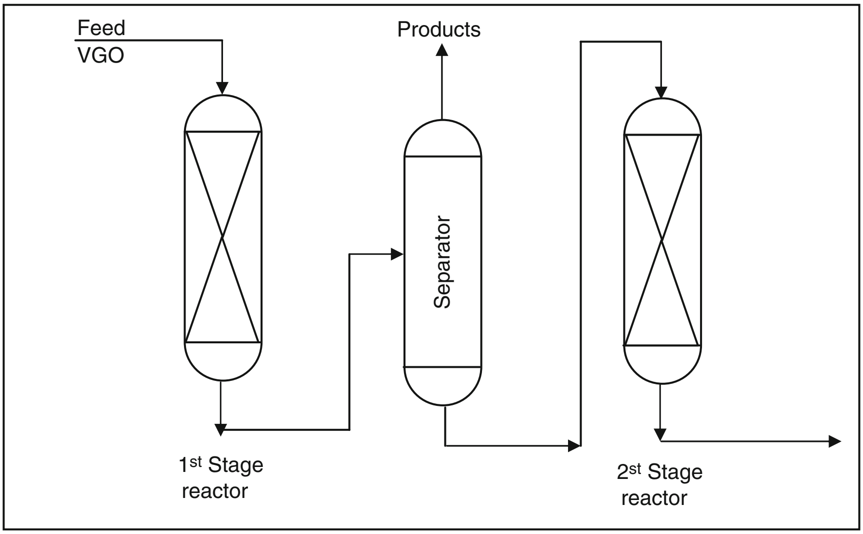
Figure 7.15 Conventional two-stage hydrocracker

The two-stage operation is shown in Figure 7.15. The effluent from the first stage reactor is sent to a separator and fractionator. The fractionator bottoms are sent to the second reactor. In both configurations, the hydrogen is separated in the high pressure separator and recycled back to the reactor. The hydrocracking catalyst in the first stage has a high hydrogenation/acidity ratio, causing sulphur and nitrogen removal. In the second reactor, the catalyst used is of a low hydrogenation/acidity ratio in which naphtha production is maximized. The main reactions taking place in each reactor are shown in Figure 7.16.

However, if middle distillate, kerosene, diesel and jet fuel are to be maximized, a high hydrogenation/acidity ratio is used. A hydrotreatment reactor may be added before the first hydrocracker to help in removing sulphur and nitrogen compounds from the feed. Since H_2S and NH_3 are separated before entering the second hydrocracker, this allows the selection of special catalysts in the second reactor without the poisoning effect of sour gases. This will allow deep hydroconversion. The two-stage configuration offers more flexibility than the single stage scheme. It is better suited for heavy feedstocks (Secherzer and Gruia, 1996).

7.3.8. Hydrocracking Severity

There are two levels of hydrocracking severity: mild and conventional. In mild hydrocracking the process is run at less severe operating conditions similar to desulphurization (hydrotreating) conditions (Secherzer and Gruia, 1996). A comparison of hydrotreating, mild hydrocracking and conventional



Main Reaction	Main Reaction
HDS Hydrodesulfurization	HDA Aromatic Hydrogenation
HDN Hydrodenitrogenation	HDI Hydroisomerization
HDA Aromatic Hydrogenation	HDC Hydrocracking
Control parameter: nitrogen specification	Control parameter: yields specification

Figure 7.16 Main reactions in two-stage hydrocracking

hydrocracking operating conditions are given in Table 7.16. A one-stage reactor without recycle is used in mild hydrocracking. The major characteristics of this process are the production of a high yield of fuel oil and a savings of hydrogen, since the process is operated at almost half of the hydrogen pressure used in conventional hydrocracking. A comparison of the products in each process is shown in Figure 7.17.

Usually mild hydrocracking is used to produce LSFO (Secherzer and Gruia, 1996) as shown in Figure 7.17.

7.3.9. Catalytic Dewaxing

Catalytic dewaxing is a particular hydrocracking process used to improve cold flow properties of middle distillates and lubricants by cracking normal paraffins. Dewaxing can be achieved by isomerization, as carried out by Chevron's isodewaxing process. Isoparaffins have lower melting points than normal paraffins. The properties targeted for improvement are pour point and viscosity of middle distillates and lubricants, the cloud point of diesel fuel, and the freeze point of jet fuel.

Table 7.16 Comparison of operating conditions of mild hydrocracking, hydrotreating and conventional hydrocracking (Secherzer and Gruia, 1996).

Operating conditions	Hydrotreating	Mild hydrocracking	Hydrocracking
Conversion (%)	–	20–70	70–100
H_2 pressure (bars)	25–50	35–70	85–140
H_2 flow (L/min)	300	300–1000	1000–2000
Temperature (°C)	360–400	350–440	350–450
LHSV (h^{-1})	0.5−2.5	0.3−1.5	0.5−2.0
Catalyst			
Hydrogen transfer	Co/Mo	Ni/Mo	Ni/Mo
(Metal)	Ni/Mo	Co/Mo	Ni/W Pd
Support	Alumina	Alumina	Si–Al
Cracking (acid)	–	Si–Al	Zeolite

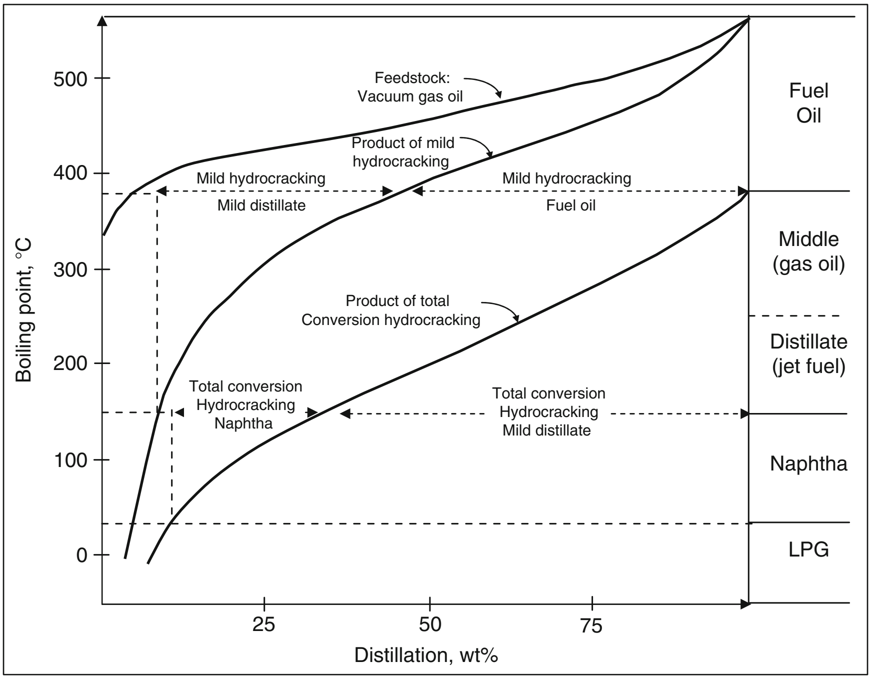


Figure 7.17 Comparison of products obtained by mild and conventional hydrocracker (Secherzer and Gruia, 1996)

Due to their high melting points, long-chain normal paraffins have the most detrimental effect on low temperature properties of middle distillates and lube oils. By reducing the amount or chain length of normal and minimally branched paraffins in these fuels and lubricants, their cold flow properties are improved. This can be accomplished by using a catalytic dewaxing process. Such a process can also be used to improve the flow properties of gas oils.

A single-stage, once through hydrocracking process can be used for catalytic dewaxing, with or without hydrotreating, depending on the sulphur and nitrogen content of the feedstock. The catalytic process is carried out as a trickle bed reactor over a bifunctional zeolite catalyst under hydrogen flow. A non-noble metal (e.g. nickel) supported on a medium-pore zeolite, such as ZSM-5 can be used. The medium-pore zeolite ZSM-5 appears to be particularly suitable to obtain a high selectivity.

7.3.10. Hydrocracking Correlations

7.3.10.1. Yield Correlations

The yield correlations in conventional hydrocracking depend on feed properties, hydrogen severity and mode of operation. There are three modes of operation: maximum gasoline mode, maximum ATK mode (jet fuel) and maximum diesel fuel. In all these modes, gasoline yield is used to correlate other yields. Using mild hydrocracking (low severity) will add a fourth mode of operation, maximum low sulphur fuel oil (LSFO). The hydrogen severity ranges between (1.5 – 4) wt% of feed. In mild hydrocracking it can be assumed as 1.5 wt% and in conventional hydrocracking as 3.0 wt%. In high severity (high aromatic feeds) it can be assumed as 4.0 wt% of feed. ATK mode is frequently used because of the high demand for aviation fuels, and it is presented here from data compiled by (Maples, 1993). Table 7.17 lists typical hydrocracking yields.

7.3.10.2. Maximum ATK Correlations

The ATK mode yield correlations are given here as an example. These correlations are developed from plant data. The following is the calculation procedure for ATK yields:

Table 7.17 Typical hydrocracking yields (Baral and Miller, 1982)

	Naphtha	Jet	Diesel
Yields on coker gas oil and FCC decanted oil (vol% on feed)			
Butanes	17	8	5
C_5–180 °F	32	15	9
180–380 °F	81	24	20
Jet or diesel	–	74	84
Total	130	121	118

- Hydrocracking severity H where

  $$\text{H wt\%} = \frac{\text{lb Hydrogen}}{\text{lb of feed}} \times 100$$

  For maximum ATK, assume H = 3 wt%

  $$\text{In this case } V_H = \frac{\text{thousands of ft}^3 \text{ hydrogen}}{\text{bbl feed}}$$

  And is related to hydrocracking severity as

  $V_H = 0.6621 \times H \times SG$
- Calculate liquid volume% (LV%) of gasoline

  $$\text{Gasoline LV\%} = -0.03734\ \text{API}_f^2 + 1.57575\ \text{API}_f + 0.014923\ \text{K} \\ -1.36473\ V_H - 0.16324\ V_H/\text{K}$$

  Where $K = (T_B)^{1/3}/SG$
- Butanes (iC_4 and nC_4)

  $$C_4\ \text{LV\%} = 0.020359\ (\text{LV\% Gasoline})^2 + 0.04888\ (\text{LV\% Gasoline}) \\ + 0.108964\text{API}_f$$
- Heavy naphtha (HN) (180–380 °F)

  $$\text{HN LV\%} = -0.10322\ (\text{LV\% Gasoline})^2 + 2.981215\ (\text{LV\% Gasoline}) \\ - 0.07898\ \text{API}_f$$
- ATK

  Calculated by mass difference between feed and products
- The following equation is used to convert LV% to wt% of hydrocarbon products

  $\text{Product wt\%} = 0.8672 \times \text{Product LV\%} - 0.9969$

Example E7.7

A feed of VGO of 37,500 BPCD is hydrocracked to maximize the ATK production. The API of the feed is 20 and the mean average boiling point T_B = 575 °F. Make material balance around this hydrocraker.

Solution:

From feed API of 20 the SG is 0.934

Assume H = 3 wt% then

$V_H = 0.6621 \times 3 \times 0.934 = 1.855\ \text{ft}^3/\text{bbl}$

$K = (575+460)^{1/3}/(0.934) = 10.83$

$$\text{Gasoline LV\%} = -0.03734(20)^2 + 1.57575 \times 20 + 0.014923 \times 10.83 \\ - 1.36473 \times 1.855 - 0.16324\ (1.855/10.83) = 14.18$$

$\text{Gasoline wt\%} = 0.8672 \times 14.18 - 0.9969 = 11.30$

C_4 LV% $= 0.020359\ (14.18)^2 + 0.04888\ (14.18) + 0.108964 \times 20 = 6.96$

C_4wt% $= 0.8672 \times 6.96 - 0.9969 = 5.04$

HN LV% $= -0.10322\ (14.18)^2 + 2.981215\ (14.18) - 0.07898 \times 20 = 19.94$

HN wt% $= 0.8672 \times 19.94 - 0.9969 = 16.29$

ATK wt% = 100 + 3 − 11.30 − 5.04 − 16.29 = 70.37

Summary of material balance:

Feed	VGO	100
	Hydrogen	3.00
		103.00
Products		
	C_4	5.04
	Gasoline (C_5-180 °F)	11.3
	HN (180 – 400 °F)	16.29
	ATK (+400 °F)	70.37
	Total	103.0

7.3.11. Simulation of Hydrocracking Units

Hydrocracking of VGO is carried out with a bifunctional catalyst and thus, two types of reactions take place the hydrogenation of sulphur and nitrogen compounds and the hydrocracking of heavy paraffins to lower molecular weight paraffins and olefins.

Example E7.8

A VGO feed containing 950 lb mol/h n-C_{16} and 30 lb mol C_2H_6S (ethyl mercaptane) and 20 lb mol/h C_5H_5N (pyridine) available at 500 °F and 100 psia needs to be hydrocracked. This feed is pumped to raise its pressure up to 900 psia before mixing with hydrogen stream that also need to be compressed from 150 psia to 900 psia. The hydrogen is available at 400 °F. The mixed stream of oil feed and hydrogen is then heated to 600 °F before entering the hydrocracking reactor.

The reactions involved are listed in Table E7.8.1:

Table E7.8.1 Reactions in the hydrocracking unit

Rxn #	Reaction	Reaction type	Conversion (%)
1	$C_2H_6S + H_2 \rightarrow C_2H_6 + H_2S$	Conversion	100
2	$C_5H_5N + 5H_2 \rightarrow C_5H_{12} + NH_3$	Conversion	100
3	$C_{16}H_{34} + H_2 \rightarrow C_6H_{14} + C_{10}H_{22}$	Conversion	50
4	$C_{16}H_{34} + H_2 \rightarrow 2C_8H_{18}$	Conversion	50

The reactor products are then cooled and enter a distillation column to separate the gases and light components at the top. C_8 is withdrawn in a side stream from the column. Furthermore, heavier hydrocarbons are coming from the bottom of the distillation column. Perform a material and energy balance for the hydrocracking process using UNISIM simulator. Utilize the flowsheet in Figure E7.8.1.

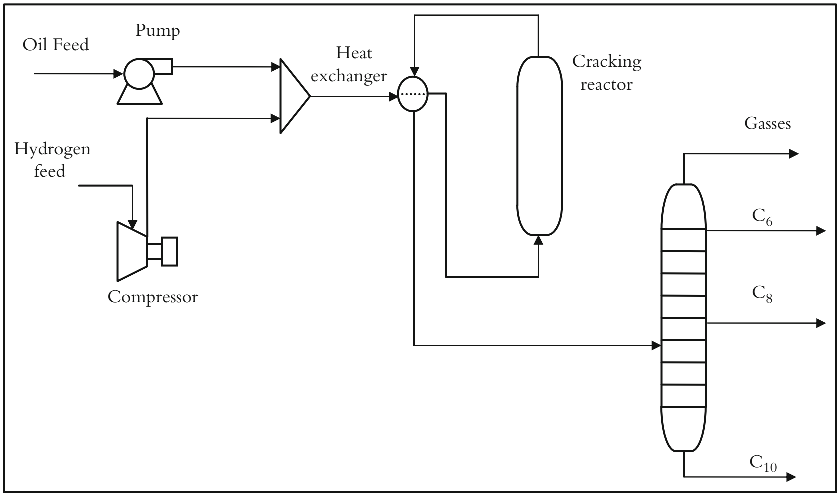


Figure E7.8.1 Flow chart of hydrocracking process

Solution:

1. Enter Simulation Basis Environment in UNISIM
2. Add all the components as shown in Table E7.8.2
3. Select Peng–Robinson as Fluid package
4. Insert Reaction-1 stoichiometry and conversion, do the same for the consequent reactions, Reaction-2, Reaction-3 and Reation-4
5. Enter simulation environment
6. Insert the first unit for the oil feed as shown in the flow chart with compositions, temperature and pressure
7. Continue inserting units as shown in the chart
8. The reactor is conversion reactor
9. The distillation column is 10 trays with partial reflux. The active specifications to run the distillation column are: C_{10} recovery of 80%, C_8 recovery of 80%, C_6 recovery 99% and draw rate is 226.8 kg mol/h. The pressure drop from top to bottom is 344.7 to 482.6 kPa, respectively

Table E7.8.2 lists summary of results.

Table E7.8.2 Energy and material balance results

Stream name	Oil feed	Hydrogen feed	Pump out	Compressor out	Mixed feed	Heated feed	Reactor product	Cooled product	Gases	C_6 stream	C_8 stream	C_{10} stream
Temperature (°F)	500	400	505.4	1157	529.34	600	705.71	643.31	95.5	95.5	376	466.28
Pressure (psia)	100	150	900	900	900	898	873	871	50	50	63.33	70
Total molar flow (lb mol/h)	1000	1081.3	1000	1081.3	2081.3	2081.3	2001.3	2001.3	21.38	621.86	858.11	500
n-$C_{16}H_{34}$ (lb mol/h)	950	0	950	0	950	950	0	0	0	0	0	0
Hydrogen (lb mol/h)	0	1081.3	0	1081.3	1081.3	1081.3	1.34	1.34	1.25	0	0	0
C_2H_6S (lb mol/h)	30	0	30	0	30	30	0	0	0	0	0	0
C_5H_5N (lb mol/h)	20	0	20	0	20	20	0	0	0	0	0	0
H_2S (lb mol/h)	0	0	0	0	0	0	30	30	7.06	22.93	0	0
NH_3 (lb mol/h)	0	0	0	0	0	0	20	20	2.87	17.13	0	0
C_2H_6 (lb mol/h)	0	0	0	0	0	0	30	30	8.33	21.67	0	0
n-C_5H_{12} (lb mol/h)	0	0	0	0	0	0	20	20	0.21	19.78	0	0
n-C_6H_{14} (lb mol/h)	0	0	0	0	0	0	475	475	1.62	470.25	3.11	0
n-C_8H_{18} (lb mol/h)	0	0	0	0	0	0	950	950	0	69.98	760	120

QUESTION AND PROBLEMS

7.1. Classify hydrogen-consuming refinery processes.

7.2. Find the catalyst volume needed for hydrotreating a gas oil containing 1.5 wt% sulphur to a final residual sulphur of 0.05 wt%. The reaction rate can be expressed as:

$$k = 3.7 \times 10^9 \exp\left(\frac{-13,200}{T}\right)$$

The desulphurization reaction temperature is 350 °C, and the pressure is 2.1 MPa. The reaction order is 1.5. The feed flow rate is 150,000 kg/h and has a density of 850 kg/m^3.

7.3. Coker naphtha is hydrotreated to remove 80% of the sulphur, 60% of the nitrogen and all the olefins. Sulphur is present as thiophene and nitrogen as pyrrole. The naphtha has the following properties: Specific gravity: 0.763, sulphur: 1.7 wt%, nitrogen: 200 wppm, propylene: 0.2 wt%, butanes: 3.5 wt% and butadienes: 0.3 wt%.

- **(a)** Find the chemical hydrogen requirement for one barrel of naphtha.
- **(b)** Make a material balance around the hydrotreater and find the hydrotreated naphtha API.

7.4. The atmospheric residue desulphurization unit (ARDS) is running under the following conditions: Feed (AR) API: 13, sulphur content: 4 wt%, nitrogen content: 0.25 wt% and metal contents 110 wppm. Make a material balance around this unit.

7.5. In a two-stage conventional hydrocracker, it is required to maximize the production of ATK for the following feed: Feed API: 24, S: 0.5 wt %, N: 850 wppm. T_B = 800 °F. Assume the required hydrogen is 3.5 wt% of feed. Calculate all the product yields.

7.6. Classify bifunctional catalysts strength and functions in hydrocracking.

7.7. For a one-stage hydrocracking reactor, what would be the best catalyst composition to maximize the production of kerosene?

7.8. Hydroconversion unit is used to upgrade vacuum residue at a flow rate of 16,000 bbl/d. Under the following specifications: Catalyst pore volume = 0.5 ml/g, carbon content of coke deposits = 82% and density = 1350 kg/m^3. Vanadium is removed as V_2S_3 (density = 4700 kg/m^3), and nickel is removed as NiS (density – 5500 kg/m^3). Vacuum residue properties: API = 2.2, sulphur 4.5 wt% and nitrogen = 4700 wppm, nickel = 120 wppm, vanadium = 310 wppm.

Removal efficiency in the process: De-sulphurization, wt% is 80, vanadium is 75 wppm, nickel is 70 wppm. The spent catalyst contains 15% carbon.

What is the minimum catalyst consumption in (kg/h) when the catalyst pores are completely filled with carbon and metal sulphide deposits?

7.9. Make a comparison between the various hydroconversion processes and reactor technology used.

7.10. Explain product conversion behaviour in the fixed bed desulphurization reactor.

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CHAPTER EIGHT

FLUIDISED CATALYTIC CRACKING

8.1. INTRODUCTION

The fluidised catalytic cracking (FCC) unit is the heart of the refinery and is where heavy low-value petroleum stream such as vacuum gas oil (VGO) is upgraded into higher value products, mainly gasoline and C_3/C_4 olefins, which can be used in the alkylation unit for production of ultra-clean gasoline (C_7–C_8 alkylates). The FCC process has been in operation for over 60 years during which, a great deal of developments has occurred. Major developments have occurred in two areas: new catalysts and new reactor and regenerator designs.

Recently, new processes have been developed, such as petro-FCC, residue FCC (RFCC) and olefin production, by a variety of means, including deep catalytic cracking (DCC). The original FCC has also been developed to improve yield, emission control and adaptability for different crude. The FCC unit mainly depends on circulating a zeolite catalyst with the vapour of the feed into a riser-reactor for a few seconds. The cracked products are disengaged from the solids and taken out to a distillation column for separation of the desired products. The catalyst is circulated back into the regenerator where coke is burned and the catalyst regenerated. The combustion of the coke generates the heat required to carry out the generally endothermic reaction in the riser.

8.2. ROLE OF FCC IN THE REFINERY

A block diagram of a typical refinery is shown in Figure 8.1. This figure shows how the FCC plays a central role when feedstocks, such as hydrotreated VGO (HT VGO) and atmospheric residue desulphurised (ARDS) oil, are used (Tominaga and Tameki, 1997). More recently, vacuum residues are desulphurised and used as feed. In this case, the unit is called a residue FCC (RFCC unit). The basic processing principles are the same for both units.

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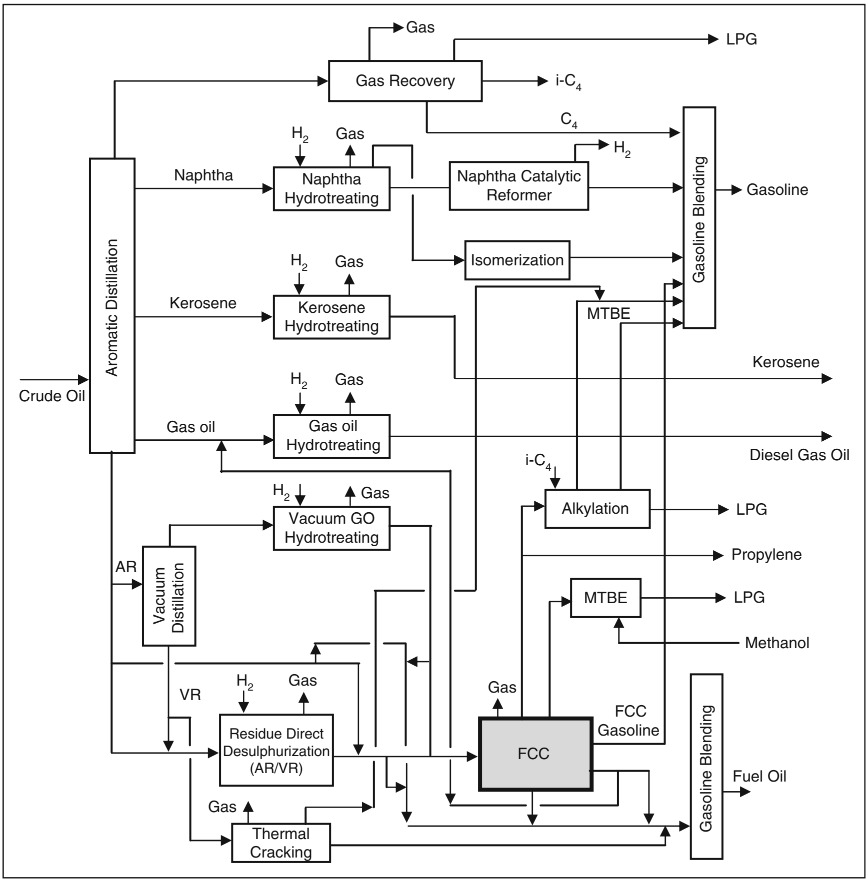


Figure 8.1 Role of FCC in refining operation

The role of the FCC is to take heavy desulphurised feedstock and crack it into lighter, mainly high octane gasoline. In a typical refinery, a FCC is installed mainly to produce gasoline. The FCC also produces olefins ($C_5^=$ and $C_4^=$) and LPG. Olefins can be utilised for alkylation and MTBE production. In fact, some FCC units can be dedicated for the production of petrochemicals, as in the UOP petro-FCC process.

8.3. FEEDSTOCK AND PRODUCTS

The main feedstock used in a FCC unit is the gas oil boiling between 316 °C and 566 °C (600 °F and 1050 °F). This gas oil can be considered mixtures of aromatic, naphthanic and paraffinic molecules. There are also varying amounts of contaminants such as sulphur, nitrogen and metals particularly in the higher boiling fractions. These differences in feed composition and in contaminants affect the operating conditions required to obtain desired yields. To protect the catalyst, feed pre-treatment by hydrotreating is required in order to remove contaminants and improve cracking characteristics and yields.

Gas oil from residue and conversion processes (predominantly coking) can be fed to catalytic cracking units. They must be hydrotreated before catalytic cracking to separate aromatics and remove sulphur. The principal limitation on charge stocks are the Conradson Carbon Residue (CCR) and metal contaminants. The effect of Conradson carbon is to form a deposit on the catalyst. This deposit could be beyond the burning capacity in the regenerator. For atmospheric residue, it is desulphurised first in the ARDS unit. Vacuum residue must also desulphurised and may be deasphalted before used in the FCC. Special RFCCs are designed to handle such heavy feeds.

The presence of organometalic compounds tends to deposit metals in the desulphurisation process; therefore a guard reactor should be used. Nitrogen tends to poison the catalyst by neutralising its acid sites. However, the FCC process is unaffected if the nitrogen content level is controlled below 0.2%. Some possible feedstocks are atmospheric distillates, coking distillates, visbreaking distillates, VGO, atmospheric residue (desulphurised) and vacuum residue (desulphurised, deasphalted). Typical feedstock properties are given in Table 8.1. In addition, products with their corresponding yields and characteristics are shown in Table 8.2.

Table 8.1 Feedstock properties of FCC unit (Tominaga and Tameki, 1997)

	Desulphurised vacuum gas oil	Atmospheric residue
Specific gravity (15/4 °C)	0.896	0.889
API	26.3	27.5
Gas oil fraction (GO), wt% (boiling point < 343 °C)	7	4
VGO fraction (VGO), wt% (boiling point 343–538 °C)	88.5	52.5
Vacuum residue fraction (VR), wt% (boiling point > 538 °C)	4.5	43.5
Conradson Carbon Residue (CCR), wt%	0.2	4.2
Sulphur, wt%	0.4	0.11
Nitrogen, wt%	0.064	0.19
Nickel (Ni), wppm	0.26	17
Vanadium (V), wppm	0.15	0.5

Table 8.2 FCC products

Products	Characteristics	Yield (wt%)
Dry gas + H_2S ($C_1 + C_2 + C_3 + H_2$) + H_2S	H_2S must be removed	3–5
LPG: C_3, $C_3^=$. C_4, $C_4^=$	Petrochemical feedstock	8–20
Gasoline	Main product, good octane number	35–60
Light cycle oil (LCO)	Rich in aromatics, high sulphur content, diluent for fuel	12–20
Heavy cycle oil (HCO) + slurry	Very rich in aromatics, slurry of solids, (mainly catalyst coke)	10–15
Coke	Consumed in regenerator	3–5

8.4. FLUIDISATION

When a fluid flows upward through a packed bed of catalyst particles at low velocity, the particles remain stationary. As the fluid velocity increases, the pressure drop increases. Upon further increases in velocity, a balance of pressure drop times the cross-sectional area equals the gravitational forces on the particles' mass. Then the particles begin to move. This is the minimum fluidisation velocity as shown in Figure 8.2. The stable fluidisation starts at a certain pressure drop. As the velocity increases, the bed expands and bed porosity increases while the pressure drop remains practically unchanged. This is the practical region which includes all modes of fluidisation such as bubbling, slugging and pneumatic transport (Bonifay and Marcilly, 2001). These modes are shown in Figure 8.2.

8.5. FCC REACTIONS

The main reaction in the FCC is the catalytic cracking of paraffin, olefins, naphthenes and side chains in aromatics. A network of reactions occurring in the FCC is illustrated in Figure 8.3. The VGO undergoes the desired 'primary cracking' into gasoline and LCO. A secondary reaction also occurs, which must be limited, such as a hydrogen transfer reaction which lowers the gasoline yield and causes the cycloaddition reaction. The latter could lead to coke formation (needed to provide heat for catalyst regeneration).

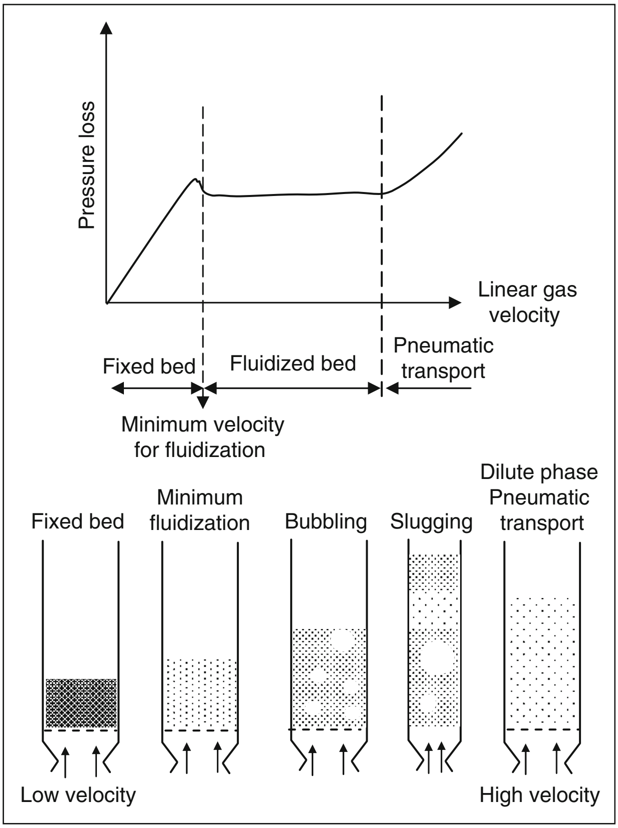


Figure 8.2 Modes of fluidisation

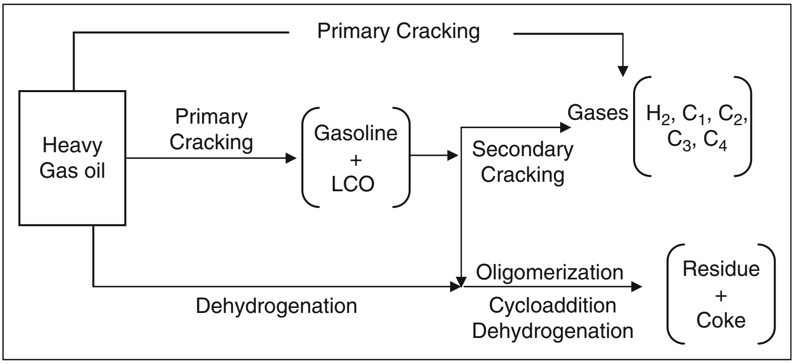


Figure 8.3 FCC reactions network

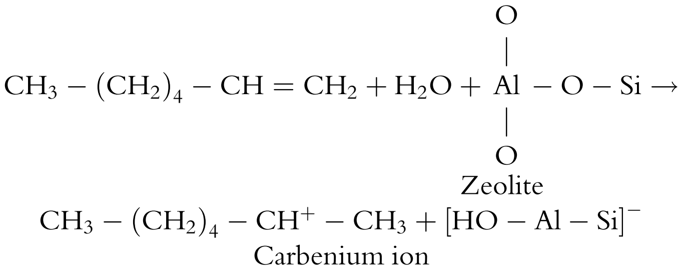
8.5.1. Primary Reactions

Primary cracking occurs by the carbenium ion intermediates in the following steps:

(a) Olefin is formed first by the mild thermal cracking of paraffin:

$$nC_8H_{18} \rightarrow CH_4 + CH_3 - (CH_2)_4 - CH = CH_2 \tag{8.1}$$

(b) Proton shift:



$$\begin{gathered} CH_3 - (CH_2)_4 - CH = CH_2 + H_2O + \underset{\substack{|\\ O\\ \text{Zeolite}}}{\overset{\substack{O\\ |}}{Al}} - O - Si \rightarrow \\ \underset{\text{Carbenium ion}}{CH_3 - (CH_2)_4 - CH^+ - CH_3} + [HO - Al - Si]^- \end{gathered} \tag{8.2}$$

(c) Beta scission:

Carbon–carbon scission takes place at the carbon in the position beta to the carbenium ions and olefins.

$$\begin{gathered} CH_3 - (CH_2)_4 - CH^+ - CH_3 \rightarrow CH_3 - CH = CH_2 + \\ CH_2^+ - CH_2 - CH_2 - CH_3 \end{gathered} \tag{8.3}$$

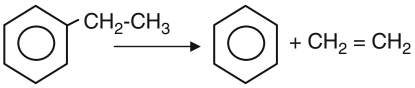
The newly formed carbenium ion reacts with another paraffin molecule and further propagates the reaction.

The chain reaction is terminated when (a) the carbenium ion losses a proton to the catalyst and is converted to an olefin; or (b) the carbenium ion picks up a hydride ion from a donor (e.g. coke) and is converted to paraffin. Beside paraffins, other hydrocarbons which are formed by primary cracking include the following:

1. Olefins – smaller olefins

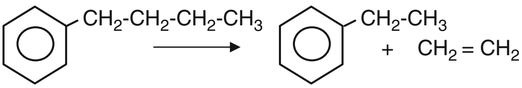
$$\begin{gathered} CH_3 - CH = CH - CH_2 - CH_2 - CH_2 - CH_3 \rightarrow \\ CH_3 - CH = CH - CH_3 + CH_2 - CH = CH_2 \end{gathered} \tag{8.4}$$

2. Alkylaromatics – Dealkylation



(8.5)

3. Alkylaromatics – Side chain cracking



(8.6)

Hydrogen transfer plays a key role in the gas oil cracking process. It reduces the amount of olefins in the product, contributes to coke formation, and thereby influences the molecular weight distribution of the product. Through intermolecular (bimolecular) hydrogen transfer, highly reactive olefins are converted to more stable paraffins and aromatics as in the following reaction:

$$\underset{\text{Olefin}}{3C_nH_{2n}} + \underset{\text{Naphthene}}{C_mH_{2m}} \rightarrow \underset{\text{Paraffin}}{3C_nH_{2n+2}} + \underset{\text{Aromatic}}{C_mH_{2m-6}} \tag{8.7}$$

Further loss of hydrogen to olefins by aromatics or other hydrogen-deficient products results in more paraffins and coke

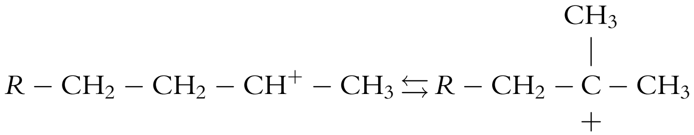
$$\underset{\text{Aromatics}}{C_nH_{2n-6}} \quad \text{or} \quad \underset{\text{Cyclo-olefins}}{C_mH_{2m-2}} \quad \xrightarrow[\substack{\text{Alkylation, condensation}\\ \text{Polymerization}}]{\text{H loss}} \quad \text{Coke} \tag{8.8}$$

$$\underset{\text{Olefins}}{C_nH_{2n}} \xrightarrow{\text{H addition}} \underset{\text{Paraffins}}{C_nH_{2n+2}} \tag{8.9}$$

8.5.2. Secondary Reactions

Gasoline formed from primary cracking can undergo further secondary cracking, which is generally caused by hydrogen transfer mechanisms such as isomerisation, cyclisation and coke formation.

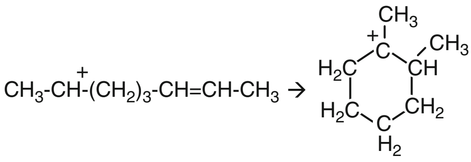
Isomerisation



$$\underset{\substack{\text{Secondary}\\ \text{Carbenium ion}}}{R - CH_2 - CH_2 - CH^+ - CH_3} \leftrightarrows \underset{\substack{\text{Tertiary}\\ \text{Carbenium ion}}}{R - CH_2 - \underset{+}{\overset{\overset{\displaystyle CH_3}{|}}{C}} - CH_3} \tag{8.10}$$

The final product is the transformation of paraffins and olefins to iso-paraffins.

Cyclisation



(8.11)

The final result would be the cyclisation of olefins to naphthenes and possibly further cyclisation to coke.

The main reactions in the FCC reactor can be summarised as follows:

- Paraffins
  Thermal catalytic cracking
  Paraffin cracking → Paraffins + Olefins
- Olefins
  The following reaction can occur with olefins:
  Olefin cracking → LPG olefins
  Olefin cyclisation → Naphthenes
  Olefin isomerisation → Branched olefins + Branched paraffins
  Olefin H-transfer → Paraffins
  Olefin cyclisation → Coke
- Naphthenes
  Naphthene cracking → Olefins
  Naphthene dehydrogenation → Aromatics
  Naphthene isomerisation → Restructured naphthenes
- Aromatics
  Aromatics (side chain) → Aromatics + Olefins
  Aromatic transalkylation → Alkylaromatics
  Aromatic dehydrogenation → Polyaromatics → Coke

8.6. THERMODYNAMICS OF FCC REACTIONS

The key reaction in cracking is β-scission, which is not equilibrium limited; therefore, thermodynamics are of limited value in either estimating the extent of a reaction or adjusting the operating variables. Cracking of relatively long-chain paraffins and olefins can go up to 95% completion at cracking conditions.

Certain hydrogen transfer reactions act in the same way. Isomerisation, transalkylation, dealkylation and dehydrogenation reactions are intermediate in attaining equilibrium. Condensation reactions, such as olefin polymerisation and paraffin alkylation, are less favourable at higher temperatures. Examination of the equilibrium constants and heat of reaction of these reactions are shown in Table 8.3 (Sadeghbeigi, 2000). It is apparent that the type and magnitude of these reactions have an impact on the heat balance of the unit. For example, a catalyst with less hydrogen transfer characteristics will cause the net heat of reaction to be more endothermic. Consequently, this will require a higher catalyst circulation and possibly a higher coke yield to maintain the heat balance.

Table 8.3 Typical thermodynamic data for idealised reactions of importance in catalytic cracking

		Log K_E equilibrium constant			Heat of reaction BTU/mole
		850 °F	950 °F	980 °F	950 °F
Cracking	$n\text{-}C_{10}H_{22} \rightarrow n\text{-}C_7H_{16} + C_3H_6$	2.04	2.46	–	32,050
	$1\text{-}C_8H_{16} \rightarrow 2C_4H_8$	1.68	2.1	2.23	33,663
Hydrogen transfer	$4C_6H_{12} \rightarrow 3C_6H_{14} + C_6H_6$	12.44	11.09	–	109,681
	$\text{cyclo-}C_6H_{12} + 3\ l\text{-}C_5H_{10} \rightarrow 3n\text{-}C_5H_{12} + C_6H_6$	11.22	10.35	–	73,249
Isomerisation	$l\text{-}C_4H_8 \rightarrow \text{trans-2-}C_4H_8$	0.32	0.25	0.09	−4,874
	$n\text{-}C_6H_{10} \rightarrow \text{iso-}C_6H_{10}$	−0.2	−0.23	−0.36	−3,420
	$o\text{-}C_6H_4(CH_3)_2 \rightarrow m\text{-}C_6H_4(CH_3)_2$	0.33	0.3	–	−1,310
	$\text{cyclo-}C_6H_{12} \rightarrow CH_3\text{-cyclo-}C_5H_9$	1	1.09	1.1	6,264
Transalkylation	$C_6H_6 + m\text{-}C_6H_4(CH_3)_2 \rightarrow 2C_6H_5CH_3$	0.65	0.65	0.65	−221
Cyclisation	$l\text{-}C_7H_{14} \rightarrow CH_3\text{-cyclo-}C_6H_{11}$	2.11	1.54	–	−37,980
Dealkylation	$\text{iso-}C_3H_7\text{-}C_6H_5 \rightarrow C_6H_6 + C_3H_6$	0.41	0.88	1.05	40,602
Dehydrogenation	$n\text{-}C_6H_{14} \rightarrow l\text{-}C_6H_{12} + H_2$	−2.21	−1.52	–	56,008
Polymerisation	$3C_2H_4 \rightarrow l\text{-}C_6H_{12}$	–	–	−1.2	–
Paraffin alkylation	$l\text{-}C_4H_8 + \text{iso-}C_4H_{10} \rightarrow \text{iso-}C_8H_{18}$	–	–	3.3	–

The occurrence of both exothermic and endothermic reactions contributes to the overall heat balance. Overall, the reaction is quite endothermic, and heat must be supplied to the system by the combustion of coke during catalyst regeneration.

The high volume of products caused by the cracking of larger molecules, requires low operating pressure (1–5 bars). The high endothermic nature of cracking reactions requires that the reactor operates at high temperatures 480–550 °C (869–1022 °F).

8.7. FCC CATALYST

The main catalyst which is used in a FCC reactor is the zeolite type. It is in a powderform with an average particle size of 75 μm and an average surface area of 800 m^2/g. It has a crystalline structure of aluminosilicates. A matrix is added to the zeolite which acts as a binder and filler.

8.7.1. Zeolite

The main active component in the catalyst is the Y-Zeolite. It is a crystalline structure of aluminosilicates which has the Y-faujasite structure (Figure 8.4). The highest pore size in the Y-faujasite structure is 8 °A, which is called the super cage. It can allow some C_{18}–C_{25} mono-, di- and tri-nuclear aromatics present in the VGO to pass.

In the cracking of long chain paraffins, another type of high silica zeolite is added. This zeolite is called ZSM-5 and is used to improve octane number

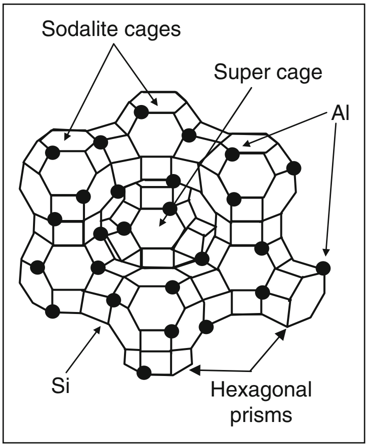


Figure 8.4 Structure of Y-faujasite

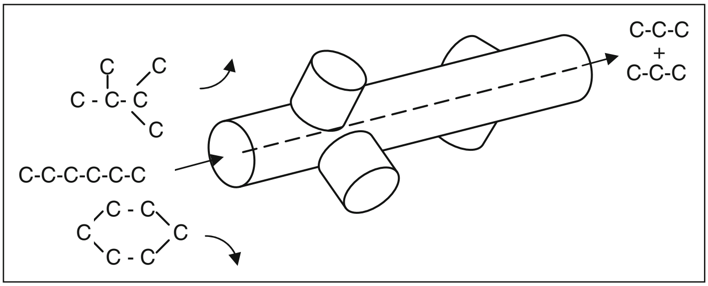


Figure 8.5 Schematic representation of shape-selective cracking with ZSM-5 zeolite (Scherzer, 1990)

and it is composed of zig-zag channel systems (Scherzer, 1990). Figure 8.5 shows how hexane will easily enter the catalyst pore. Then hexane cracks into propane, while iso-hexane and benzene do not enter the pores. Thus the unreacted stream is enriched with iso-paraffins and aromatics, which contribute to an increase in the octane number.

8.7.2. Matrix

The matrix is added to the zeolite to increase the body of the catalyst and add some improved properties. Three types of substances constitute the matrix:

1. A binder is added as a glue which is then added to the catalyst to provide cohesion for zeolite particles.
2. A filler is added to make up the body of the catalyst. It is usually a clay (Kaoline). The function of the filler and binder is to provide physical integrity (density and attrition resistance).
3. Additives, such as a small amount (ppm) of metal, are added to the catalyst to promote the combustion of CO to CO_2 in the regenerator. Metallic oxides are added to fix SO_x on the catalyst. The sulphur is recovered as H_2S in the reactor. An addition of 5% ZSM-5 zeolite will lead to an increase of one research octane number (RON).

8.8. FCC CONFIGURATION

The basic configuration of the FCC unit is a reactor (riser) and a regenerator. The catalyst is circulated between them where it is deactivated in the riser and regenerated in the regenerator. There are two basic types of FCC units in use today. The 'Side-by Side' type is one in which the reactor

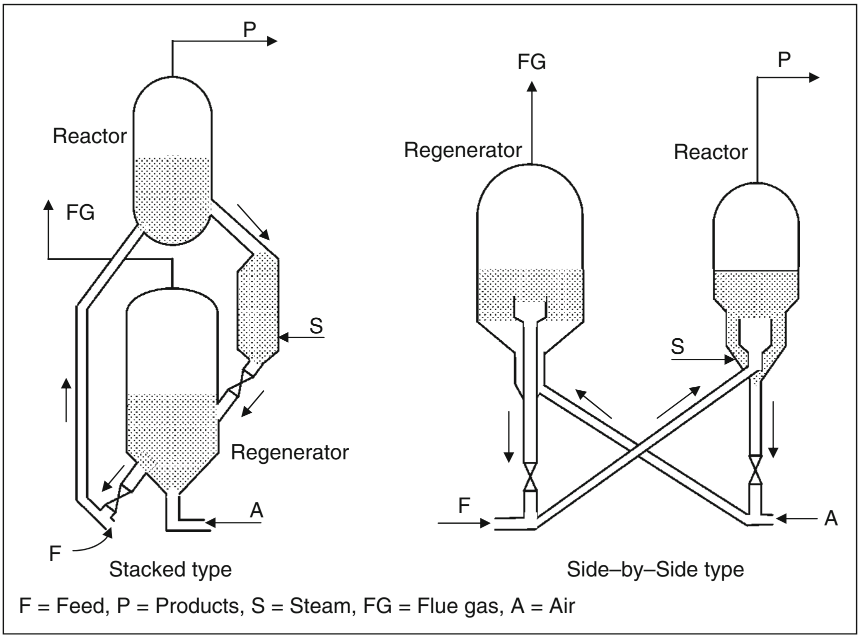


Figure 8.6 FCC type configuration

and regenerator are separate vessels adjacent to each other. The Stacked or Orthoflow type reactor is mounted on the top of the regenerator. There have been many developments and modifications over the last few years to improve both performance and/or efficiency, or to develop special purpose FCCs. The basic two types of FCC are shown in Figure 8.6.

8.9. PROCESS DESCRIPTION

The process flow diagram for the side-by-side FCC unit is shown in Figure 8.7. Steam and VGO heated up to 316–427 °C (600–800 °F) are fed to the bottom of the riser, which is a long vertical pipe. The regenerated hot catalyst at 649–760 °C (1200–1400 °F) is also fed to the bottom of the riser. The riser is the main reactor in which the endothermic reactions take place. The residence time in the riser is 2–10 s. At the top of the riser, the gaseous products flow into the fractionator, while the catalyst and some heavy liquid hydrocarbon flow back in the disengaging zone. Steam is injected into the stripper section, and the oil is removed from the catalyst with the help of some baffles installed in the stripper. The oil is stripped in this way from the catalyst and the spent catalyst is sent to the regenerator at a temperature of

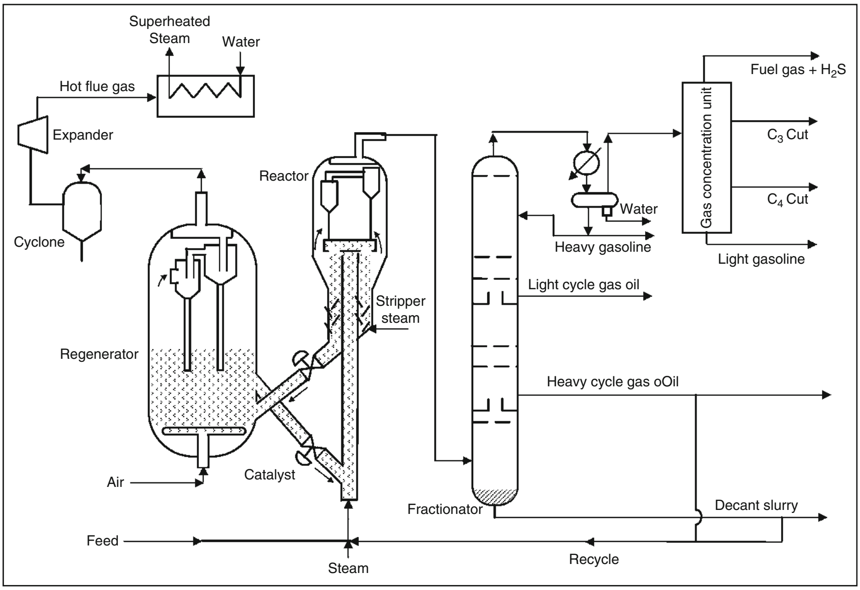


Figure 8.7 Fluid catalytic cracking process flow sheet

482–538 °C (900–1000 °F). The coke in the spent catalyst, produced in the cracking reaction, is burned off in the regenerator by introducing excess air, which is used to ensure the efficient combustion of coke. The produced flue gas exits at the top of the regenerator. The hot flue gas contains carbon dioxide, carbon monoxide water and excess air at the regenerator temperature. These gases are sent to the power recovery unit to produce superheated steam. The operation of the FCC remains in a steady state as long as a heat balance exists between the heat produced in the regenerator and the heat consumed in the reactor.

In both the reactor and the regenerator, hydrocyclones are installed to catch any solid particles carried out in the overheated stream. The product gases from the reactor are sent to the fractionator which produces light gases, heavy gasoline (main product), light cycle gas oil (LCO), heavy cycle gas oil (HCO) and decant slurry. The light gases are sent to the gas concentration unit where flue gas, propane, butane, LPG and light gasoline are produced. The operating conditions are usually adjusted to produce the maximum amount of gasoline from the VGO as shown in Table 8.4 (Parkash, 2003).

The decant slurry from the bottom of the fractionator is a mixture of heavy aromatics and fine catalyst particles. These particles are formed during the circulation of the catalyst and are carried out to the fractionator. The filtered decant can be used as an aromatic solvent or recycled back to the riser with the HCO.

Table 8.4 Reactor and regenerator operating condition for max gasoline production (Parkash, 2003)

Variable	Value
Reactor Feed Rate, MBPSD	40
Feed Temperature, °F	446
Catalyst/Oil Ratio	5.4
Catalyst Circulation Rate, tons/min	21.7
Catalyst Makeup Rate, tons/day	2.5
Riser Outlet Temperature, °F	991
Dispersion Steam, wt% feed	0.9
Stripping Steam, tons/ton catalyst	0.0213
Reactor Pressure, psig	30
Regenerator Pressure, psig	33
Regenerator Temperature, °F	1341
Flue Gas Temperature, °F	1355

8.10. MODES OF FLUIDISATION IN FCC UNIT

The modes of fluidisation are used to operate the different parts of the FCC unit (Tominaga and Tameki, 1997). The regenerator is run at the higher velocity of the stable turbulent fluidisation. The line connecting the regenerator to the riser is carried out at the 'bubbling fluidisation' zone. The riser is operated at the 'pneumatic transport' zone, where the catalyst and products are carried out from the riser. In the stripper section, where steam is injected, the mode is 'bubbling fluidisation'. The regenerated catalyst is transported back in the left line in a 'pneumatic transport' mode. The fluidisation modes are summarised in Table 8.5.

8.11. FCC YIELD CORRELATIONS

The yields of the products involved in fluid cracking are obtained by the regression of plant data compiled by Maples (1993) using a zeolite catalyst. The correlations given in Table 8.6 require target conversion (LV%), feed API and sulphur in the feed. Conversion is defined as the percentage of the oil fed that has been cracked into lighter fractions than gasoline and lighter products:

$$\text{CONV\%} = \left(\frac{\text{volume of oil feed} - \text{volume of cycle stock}}{\text{volume of oil feed}}\right) \times 100 \quad (8.12)$$

Table 8.5 Modes of fluidisation in FCC

Location in FCC	Mode of fluidisation
Regenerator	Turbulent fluidisation: to attain uniform burning temperature in bed.
Line for catalyst transport from regenerator to riser	Bubbling fluidisation
Riser	Pneumatic transport: Catalyst and products are carried out from riser. Plug flow has a few seconds of residence time.
Stripper	Bubbling fluidisation: Steam is injected in the stripper to vaporise and recover heavy oil and reduce coke formation.
Lift line from regenerator to reactor	Pneumatic transport

Table 8.6 FCC yield correlations

Products	Correlation
Coke wt%	0.05356 × CONV – 0.18598 × API + 5.966975
LCO LV%	0.0047 × CONV^2 – 0.8564 × CONV + 53.576
Gases wt%	0.0552 × CONV + 0.597
Gasoline LV%	0.7754 × CONV – 0.7778
iC_4 LV%	0.0007 × CONV^2 + 0.0047 × CONV + 1.40524
nC_4 LV%	0.0002 × CONV^2 + 0.019 × CONV + 0.0476
$C_4^=$ LV%	0.0993 × CONV – 0.1556
C_3 LV%	0.0436 × CONV – 0.8714
$C_3^=$ LV%	0.0003 × CONV^2 + 0.0633 × CONV + 0.0143
HCO	100 – CONV – (LCO LV%)
Wt% S in Gases	3.9678 × (wt% S in feed) + 0.2238
Wt% S in LCO	1.04994 × (wt% S in feed) + 0.00013
Wt% S in HCO	1.88525 × (wt% S in feed) + 0.0135
S in Coke[a]	wt% S in feed – wt% S in gases – wt% S LCO – wt% S HCO
Gasoline API	−0.19028 × CONV + 0.02772 × (Gasoline LV%) + 64.08
LCO API	−0.34661 × CONV + 1.725715 × (Feed API)

[a] Assuming no sulphur in gasoline

The recycle stock is the portion of the feedstock which is not cracked to fractions lighter than gasoline. For example, for 75% conversion, the cycle stock is 25%.

Example E8.1

A feed of 20,000 BPD of AGO (650–850 °F) having an API of 24 and a sulphur content of 0.2 wt%, is mixed with another of feed of 15,000 BPD of VGO (850–1050 °F) that has an API of 15 and a sulphur content of 0.35 wt%. They are used as a feed to FCC unit. Use the FCC correlations to find the material balance around the reactor unit. Assume a conversion of 75 LV%. Figure E8.1 shows the reactor input and output streams.

Solution:

AGO = 20000 (bbl/day) × 318.6 (lb/bbl) × (1 day/24 h) = 265,000 lb/h
VGO = 15000 (bbl/day) × 338 (lb/bbl) × (1 day/24 h) = 211250 lb/h
S in AGO = 265000 × 0.2/100 = 530 lb/h
S in VGO = 211250 × 0.35/100 = 739 lb/h
S in feed = 1269/476250 × 100 = 0.266%
Conversion = ((Vol. of feed – Vol. of cycle stock)/Vol. of feed) × 100 = 75%
Cycle stock = unconverted portion below gasoline = (LCG + HCGO) = 25

API of mixture:
Total feed = 476,250 lb/h
SG for AGO = 0.9099 and SG for VGO = 0.9659

$$\text{Then SG for mixed feed} = \frac{20000}{20000+15000}(0.9099) + \frac{15000}{20000+15000}(0.9659)$$
$$= 0.9339$$

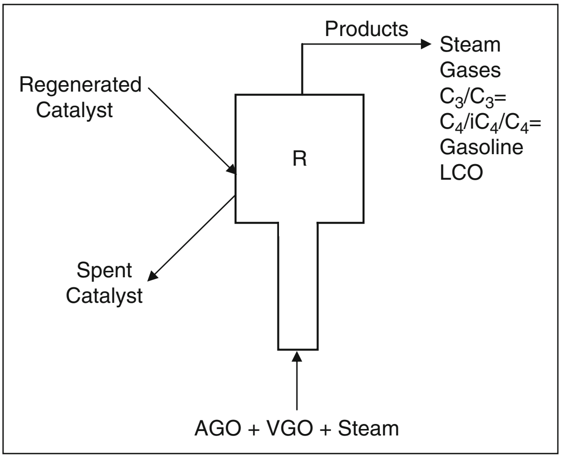


Figure E8.1 Reactor input and output streams

This gives feed API = 20.02

A summary of the feed mixture is shown in Table E8.1.1.

Using the above data and the yield correlations from Table 8.6, the material balance and product properties can be calculated as shown in Table E8.1.2

Table E8.1.1 Feed properties

Stream	BPD	API	lb/h	wt% S	lb S/h
AGO	20,000	24	265,000	0.2	530
VGO	15,000	15	211,250	0.35	739
		20.02	476,250		1269

Table E8.1.2 Yields and properties of products

			lb/h
Coke wt%	$0.05356 \times (75) - 0.18598 \times (20.02) + 5.966975$	6.3	30,004
LCO LV%	$0.0047 \times (75)^2 - 0.8564 \times (75) + 53.576$	15.8	81,337
Gases wt%	$0.0552 \times (75) - 0.597$	4.7	22,574
Gasoline LV%	$0.7754 \times (75) - 0.7778$	57.4	226,816
iC_4 LV%	$0.0007 \times (75)^2 + 0.0047 \times (75) + 1.40524$	5.7	16,375
nC_4 LV%	$0.0002 \times (75)^2 + 0.019 \times (75) + 0.0476$	2.6	7735
$C_4^=$ LV%	$0.0993 \times (75) - 0.1556$	7.3	22,356
C_3 LV%	$0.0436 \times (75) - 0.8714$	2.4	6230
$C_3^=$ LV%	$0.0003 \times (75)^2 + 0.0633 \times (75) + 0.0143$	6.4	16,987
HGO wt%	$100 - 75 - 15.8$	9.7	46,027
S in H_2S wt%	$3.9678 \times (0.266) + 0.2238$	1.28	289
S in LCO wt%	$1.04994 \times (0.266) + 0.00013$	0.278	226
S in HCO wt%	$1.88525 \times (0.266) + 0.0135$	0.515	237
S in Coke wt%	$(1269 - 289 - 226 - 237)/29{,}813$	1.734	517
Gasoline API	$-0.19028 \times (75) + 0.02772 \times (59.1) + 64.08$	51.4	
LCO API	$-0.34661 \times (75) + 1.725715 \times (20.02)$	8.5	

8.12. MATERIAL AND ENERGY BALANCES

The material and energy balance around the reactor and regenerator can be calculated by defining the input and output streams.

8.12.1. Material Balance

8.12.1.1. Reactor Material Balance

The input and output streams to the reactor (Figure 8.8) are:
Reactor input:

- Oil feed (VGO) to the riser: F (BPD) or m_f (lb/h)
- Injection steam: S_{in} (lb/h)
- Regenerated catalyst: m_{cat} (lb/h)

Reactor output:

- Masses of products m_i, as calculated from FCC yield correlations. These correlations require some feed properties such as: API, sulphur content and degree of severity expressed as conversion.
- Spent catalyst circulation rate m_{scat} (lb/h)
- Steam present in cracked products, S_{out} (lb/h)

Thus, a material balance around the reactor is

$$m_f + S_{in} + m_{cat} = \sum_{i=1}^{p} m_i + S_{out} + m_{scat} \tag{8.13}$$

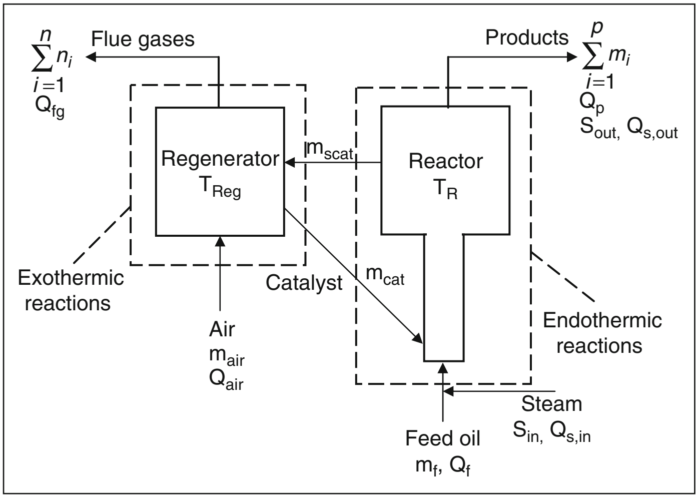


Figure 8.8 Input and output streams for reactor and regenerator in FCC unit

where p is the total number of vapour products and assuming S_{in} does not condense and is present in the exiting vapour products at the same rate ($S_{\text{in}} = S_{\text{out}}$). m_{i} is the mass of each product that can be calculated using the FCC correlations. The produced coke is present in spent catalyst. Thus

$$m_{\text{coke}} = m_{\text{scat}} - m_{\text{cat}}$$

Equation (8.13) can be rewritten as follows:

$$m_f = \sum_{i=1}^{F} m_i + m_{\text{coke}} \tag{8.14}$$

8.12.1.2. Regenerator Material Balance

Regenerator input:

- Spent catalyst circulation rate m_{scat} (lb/h)
- Air for coke burning m_{air} (lb/h)

Regenerator output:

- Flue gases n_{i} (lb/h)
- Regenerated catalyst m_{cat} (lb/h)

Thus, the material balance around the regenerator produces:

$$m_{\text{air}} + m_{\text{scat}} = \sum_{i=1}^{N} n_i + m_{\text{cat}} \tag{8.15}$$

where n_{i} is the mass of each gas produced from the coke burning which may contain CO_2, CO, H_2O, SO_2, N_2 and O_2 (from excess air).

8.12.2. Energy Balance

8.12.2.1. Reactor Heat Balance

Heat input:

- Heat of feed oil Q_{F} (Btu/h) at inlet feed temperature (T_{f})
- Heat of steam injected Q_{S} (Btu/h) at T_{s}
- Heat of regenerated catalyst Q_{cat} (Btu/h) at regenerator outlet temperature (T_{Reg})

Heat output:

- Heat in vapour products, Q_{p} (Btu/h) at reactor outlet temperature (T_{R})
- Heat of spent catalyst Q_{scat} (Btu/h) at T_{R}

- Heat of exit steam $Q_{s,out}$ (Btu/h) at T_R

Then the energy balance can be expressed as

$$\begin{aligned} & m_f C_{p,f}(T_f - T_o) + m_f(-\Delta H_R) + m_{cat} C_{P,cat}(T_{Reg} - T_o) + S_{in} C_{ps}(T_s - T_o) \\ & \quad = (T_R - T_o)\sum m_i C_{P,i} + m_{scat} C_{P,scat}(T_R - T_o) + S_{out} C_{ps}(T_R - T_o) \end{aligned} \tag{8.16}$$

Since, $m_{coke} = m_{scat} - m_{cat}$ and $S_{in} = S_{out}$, then equation (8.16) becomes

$$\begin{aligned} & m_f C_{p,f}(T_f - T_o) + m_f(-\Delta H_R) + m_{cat} C_{P,cat}(T_{Reg} - T_R) + S_{in} C_{ps}(T_s - T_R) \\ & \quad = (T_R - T_o)\sum m_i C_{P,i} + m_{coke} C_{P,coke}(T_R - T_o) \end{aligned} \tag{8.17}$$

8.12.2.2. Regenerator Heat Balance

Heat input:

- Heat of spent catalyst Q_{scat} (Btu/h) at T_R
- Heat of input air for coke burning Q_{air} (Btu/h) at T_{air}
- Heat of coke combustion q_{coke} (Btu/h)

Heat output:

- Heat of flue gas Q_{fg} (Btu/h) at T_{Reg}
- Heat of regenerated catalyst Q_{cat} (Btu/h) at T_{Reg}

Thus the heat balance around the regenerator can expressed as

$$\begin{aligned} & m_{air} C_{p,air}(T_{air} - T_o) + m_{coke} C_{P,coke}(T_R - T_o) + q_{coke} \\ & \quad = (T_{Reg} - T_o)\sum n_i C_{P,gi} + m_{cat} C_{P,cat}(T_{Reg} - T_R) \end{aligned} \tag{8.18}$$

Example E8.2

Find the catalyst circulation rate for the FCC unit used in example E8.1 by carrying out a heat balance around the regenerator. A sketch of the stream flows and temperatures around the regenerator is presented in Fig. E8.2.1

Data:

Heat of combustion of coke, $\Delta H_C = -0.393 \times 10^6$ kJ/kmol,
$C_{P,cat} = 1.11$ kJ/kg.K,
$C_{P,air} = 29.6$ kJ/kmol.K, $C_{P,N_2} = 32.6$ kJ/kmol.K, $C_{P,CO_2} = 46.9$ kJ/kmol.K,
$C_{P,coke} = 21.1$ kJ/kg.K

Solution:

Coke produced = 29,813 lb/h = 13,551 kg/h (from example E8.1)
Coke = 13,551 kg/h = 1129 kmol/h
$q_{coke} = 1129\ (\text{kmol/h}) \times 0.393 \times 10^6\ (\text{kJ/kmol}) = 443.8 \times 10^6\ (\text{kJ/h})$

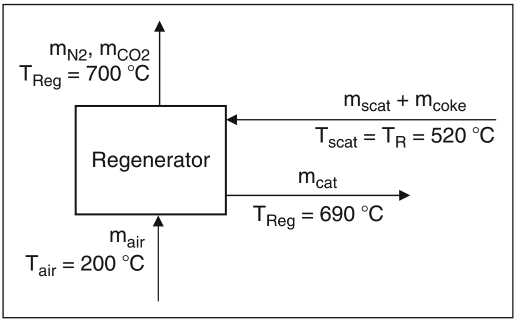


Figure E8.2.1 Regenerator

Air required = O_2 required/0.21
O_2 required:
$C + O_2 \rightarrow CO_2$
$m_{O2} = O_2 \text{ required} = 1129 \text{ kmol/h}$
$m_{CO2} = 1129 \text{ kmol/h}$
$m_{air} = \text{air required} = 1129/0.21 = 5376 \text{ kmol/h}$
$m_{N2} = 5379 \times 0.79 = 4247 \text{ kmol/h}$
Thus, the heat balance from equation (8.18) gives

$$\begin{aligned}&5376 \times 29.6(200-15) + m_{cat} \times 1.11 \times (520-15) + 13551 \times 21.1 \times (520-15)\\&\quad + 443.8 \times 10^6 = (700-15)[1129 \times 46.9 + 4247 \times 32.6] + m_{cat} \times 1.11(690-15)\end{aligned}$$

$m_{cat} = 2.58 \times 10^6 \text{ kg/h} = 43.0 \text{ t/min} = 0.717 \text{ t/s}$

8.13. Kinetic Model for FCC Reactor

The FCC process involves a network of reactions producing a large number of components. Therefore, lumping models can be used to describe the reaction system in terms of the feed and a defined number of products. Three, four and up to over ten lumps can be used theoretically. A three lump model (Figure 8.9) assumes that VGO produces two products: gasoline and a combined product of gas and coke, where y refers to the mass fraction of each lump and k is the reaction rate constant.

A more realistic model is the four-lump model (Figure 8.10) in which VGO produces gasoline, gas and coke.

Assuming that the VGO cracking rate is second order and gasoline rate is first order. The three and four lump models in Figures 8.9 and 8.10, respectively, are shown below. In these models the catalyst deactivation rate ϕ is considered equal for all reactions.

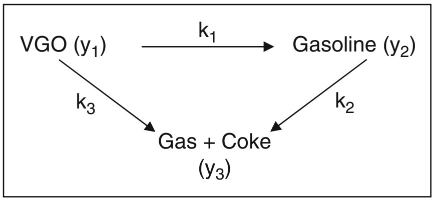


Figure 8.9 Three-lump model

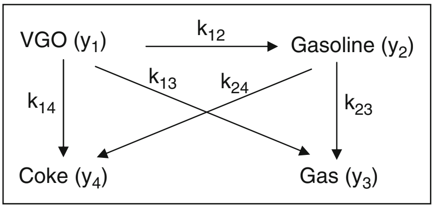


Figure 8.10 Four-lump model

Three-lump model:
for VGO

$$r_1 = \frac{\mathrm{d}y_1}{\mathrm{d}t} = -k_1 y_1^2 \phi - k_3 y_1^2 \phi = -(k_1 + k_2) y_1^2 \phi \tag{8.19}$$

for gasoline

$$r_2 = \frac{\mathrm{d}y_2}{\mathrm{d}t} = k_1 y_1^2 \phi - k_2 y_2 \phi = \left(k_1 y_1^2 - k_2 y_2\right) \phi \tag{8.20}$$

for gas + coke

$$r_3 = \frac{\mathrm{d}y_3}{\mathrm{d}t} = \left(k_3 y_1^2 + k_2 y_2\right) \phi \tag{8.21}$$

Four-lump model:
for VGO

$$r_1 = \frac{\mathrm{d}y_1}{\mathrm{d}t} = -k_{12} y_1^2 \phi - k_{13} y_1^2 \phi - k_{14} y_1^2 \phi \tag{8.22}$$

for gasoline

$$r_2 = \frac{\mathrm{d}y_2}{\mathrm{d}t} = k_{12} y_1^2 \phi - k_{23} y_2 \phi - k_{24} y_2 \phi = \left(k_{12} y_1^2 - k_{23} y_2 + k_{24} y_2\right) \phi \tag{8.23}$$

for gas

$$r_3 = \frac{\mathrm{d}y_3}{\mathrm{d}t} = \left(k_{23} y_2 + k_{13} y_1^2\right) \phi \tag{8.24}$$

Table 8.7 Experimental data at 548.9 °C and catalyst to oil ratio (C/O) = 4 (Ancheyta-Juarez and Murillo-Hernandez, 2000)

Space velocity (h^{-1})	Conversion (wt%)	VGO (wt%)	Gasoline (wt%)	Gas (wt%)	Coke (wt%)
10	82.38	17.62	54.16	21.08	7.14
20	71.18	28.82	48.65	16.81	5.72
30	62.04	37.96	43.85	13.6	4.59
60	49.26	50.74	37.67	8.85	2.74

for coke

$$r_4 = \frac{dy_4}{dt} = \left(k_{14}y_1^2 + k_{24}y_2\right)\phi \tag{8.25}$$

Experimental data reported by Ancheyta-Juarez and Murillo-Hernandez (2000), which are shown in Table 8.7, can be used to evaluate the reaction rate constants.

Example E8.3

Use the experimental data given in Table 8.7 with ϕ equal to 1.0. Estimate the reaction rate constants for the three-lump model.

Solution:

For a three-lump model and $\phi = 1$

$$\frac{dy_1}{dt} = -(k_1 + k_3)y_1^2 \tag{E8.3.1}$$

$$\frac{dy_2}{dt} = \left(k_1 y_1^2 - k_2 y_2\right) \tag{E8.3.2}$$

$$\frac{dy_3}{dt} = \left(k_3 y_1^2 + k_2 y_2\right) \tag{E8.3.3}$$

Initial conditions at $t = 0$ are at $y_1 = 1$, $y_2 = 0$ and $y_3 = 0$. Initial guesses for k_1, k_2 and k_3 are assumed. Equations (E8.3.1), (E8.3.2) and (E8.3.3) are solved numerically in the Excel worksheet. The resulted values for y_1, y_2 and y_3, at time corresponding to the space velocity in Table 8.7, are compared with the experimental composition listed in Table 8.7. The Solver in the Excel worksheet is used to minimise the difference by changing the values of k_1, k_2 and k_3. The resulting k values are
$k_1 = 23\ h^{-1}$, $k_2 = 3.1\ h^{-1}$ and $k_3 = 7.5\ h^{-1}$
Predicted yields are plotted as solid lines versus conversion in Figure E8.3. The experimental data are also plotted from Table 8.7 as symbols in the same figure.

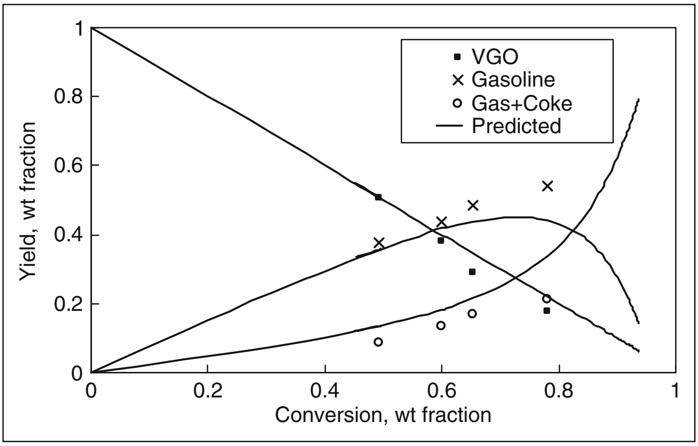


Figure E8.3 Experimental and predicted gasoline, gas and coke yields

8.14. CONCENTRATION AND TEMPERATURE PROFILES IN THE RISER

It is possible to calculate the concentration profile for each component in the riser reactor by differential material balance in the riser. If the four-lump model discussed earlier is considered, it is possible to derive the following equation for each lump VGO, gasoline, gases and coke (Jia *et al.*, 2003):

For VGO

$$\frac{dy_1}{dz} = -\frac{A_r \varepsilon_g \phi \rho_g}{m_g}[k_{12} + k_{13} + k_{14}]y_1^2 \tag{8.26}$$

For gasoline

$$\frac{dy_2}{dz} = -\frac{A_r \varepsilon_g \phi \rho_g}{m_g}\left[-k_{12}y_1^2 + (k_{24} + k_{23})y_1\right] \tag{8.27}$$

For gases

$$\frac{dy_3}{dz} = \frac{A_r \varepsilon_g \phi \rho_g}{m_g}\left[k_{13}y_1^2 + k_{23}y_2\right] \tag{8.28}$$

For coke

$$\frac{dy_4}{dz} = \frac{A_r \varepsilon_g \phi \rho_g}{m_g}\left[k_{14}y_1^2 + k_{24}y_2\right] \tag{8.29}$$

Where

A_r = Cross-sectional area of the riser

ε_g = Hydrocarbon gases void fraction

m_g = Hydrocarbon gases mass flow rate in the riser (kg/s)

ϕ = Catalyst activity

ρ_g = Density of gas phase in the riser (kg/m^3)

z = Axial distance in the riser (m)

Numerical integration of equation (8.26) to (8.29) will give the yield profile of each component along the length of the riser. The value ε, ϕ, ρ_g and m_g have to be updated along the length of the riser.

Updating these values along the riser length can be carried out using the following equations:

$$\varepsilon_g = \frac{\rho_{\mathrm{cat}} m_g}{\rho_g m_{\mathrm{cat}} \psi + \rho_{\mathrm{cat}} m_g} \tag{8.30}$$

where $\psi = u_g/u_p$, u_g is the velocity of the gas (m/s) which is gas flow rate divided by riser cross-sectional area, u_p is the particle velocity in the riser and is defined as

$$u_p = \frac{m_{\mathrm{cat}}}{A_r \rho_{\mathrm{cat}} (1 - \varepsilon_g)} \tag{8.31}$$

The hydrocarbon gases flow rate is calculated from

$$m_g = m_{\mathrm{VGO}}(y_1 + y_2 + y_3) \tag{8.32}$$

The density ρ_g has to be updated as a function of temperature change in the riser, which is calculated from a temperature profile generated from the energy balance equation.

The coke content of the catalyst C_c, varies with coking time according to

$$C_c = 2.43 \times 10^{-3} t_c^{0.2} \tag{8.33}$$

And the deactivation function with respect to coke content can be determined:

$$\phi = \frac{1}{1 + 69.47(100C_c)^{3.8}} \tag{8.34}$$

Coking time t_c can be calculated at each riser interval as

$$\frac{dt_c}{dz} = \frac{A_r \rho_{\mathrm{cat}} \psi}{m_{\mathrm{cat}} \psi + \left[\sum_1^3 \frac{y_i}{MW_i}\right] m_g (1 - y_4) \rho_{\mathrm{cat}} \frac{RT_r}{P}} \tag{8.35}$$

The energy balance equation gives

$$\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}z} = -\frac{A_\mathrm{r}\varepsilon_\mathrm{g}\rho_\mathrm{g}\phi}{(m_\mathrm{cat}C_\mathrm{pcat} + m_\mathrm{g}C_\mathrm{pg})}\begin{bmatrix}(k_{12}\Delta H_{12} + k_{14}\Delta H_{14} + k_{13}\Delta H_{13})y_1^2 \\ + (k_{24}\Delta H_{24} + k_{23}\Delta H_{23})y_2\end{bmatrix} \tag{8.36}$$

The boundary conditions are at $z = 0$, $y_1 = 1$, $y_2 = y_3 = y_4 = 0$, $T_\mathrm{r} = T_0$ and $t_\mathrm{c} = 0$.

Example E8.4

The cracking of gas oil is carried out through a 33 m riser height with an 0.8 m inside diameter. Typical industrial FCC riser data (Ali and Corriou, 1997) are listed in Table E8.4.1.

Kinetic and energy data (Abul-Hamayel, 2003) are listed in Table E8.4.2.

Typical molecular weights and heat capacities (Ahari et al., 2008) are given in Table E8.4.3.

Solve the riser material and energy balance equations and plot the concentration and temperature profile versus riser height.

Table E8.4.1 Typical FCC riser data

I.D. (m)	Height (m)	Catalyst flow rate (kg/s)	Feed flow rate (kg/s)	Catalyst temperature (K)	Feed temperature (K)	Riser pressure (atm)
0.8	33	144	20	960	494	2.9

Table E8.4.2 Kinetic constants and energies for four-lump model at 823 K

k_{12} (wt frac h)$^{-1}$	k_{13} (wt frac h)$^{-1}$	k_{14} (wt frac h)$^{-1}$	k_{23} (h)$^{-1}$	k_{24} (h)$^{-1}$
121	35	21	12	3
H_{12} (kcal/mol)	H_{13} (kcal/mol)	H_{14} (kcal/mol)	H_{23} (kcal/mol)	H_{24} (kcal/mol)
28	19	15	34	30

Table E8.4.3 Kinetic constants and energies for four-lump model at 823 K

	Molecular weight (kg/kmol)	C_p (kJ/kg K)
Gas oil	333	3.3
Gasoline	106.7	3.3
Gases	40.0	3.3
Coke	14.4	1.087
Catalyst	–	1.087

Solution:

Utilising the operating data the ρ_g was calculated at initial conditions of temperature and pressure

$$\rho_g = \frac{P(Mw)}{RT} = \frac{2.9(333)}{0.082(494)} = 23.84\ \text{kg/m}^3$$

Gas velocity u_g was then calculated at ρ_g

At $z = 0$ of the riser

$y_1 = 1,\ y_2 = y_3 = y_4 = 0$

$m_g = 20\ (1 + 0 + 0) = 20\ \text{kg/s}$

$$u_g = \frac{m_g}{\rho_g A_r} = \frac{20}{23.84(0.5)} = 1.67\ \text{m/s}$$

Then u_p and ε_g are calculated simultaneously as follows:

$$u_p = \frac{144}{0.5(8)\left(1 - \varepsilon_g\right)} = \frac{36}{1 - \varepsilon_g}$$

$$\varepsilon_g = \frac{8(20)}{23.84(144)\left(36/\left(1 - \varepsilon_g\right)\right)/1.67 + 8(20)}$$

The catalyst activity can be determined as

$$\phi = \frac{1}{1 + 69.47\left(0.243 t_c^{0.2}\right)^{3.8}}$$

Coking time t_c can be calculated from equation (8.35) as

$$\frac{dt_c}{dz} = \frac{0.5(8)\left(1.67/u_p\right)}{144\left(1.67/u_p\right) + \left[\frac{y_1}{333} + \frac{y_2}{106.7} + \frac{y_3}{40}\right](20)(1 - y_4)(8)\frac{0.082 T_r}{2.9}} \quad \text{(E8.4.1)}$$

Simple energy balance on the catalyst and the feed is performed to calculate the riser inlet temperature at $z = 0,\ T_r = T_0 = 821.8\ \text{K}$

At $y_1 = 1$ and $y_2 = 0$

$$\frac{dT_r}{dz} = -\frac{0.5\varepsilon_g(23.84)(\phi)}{144(1.887 + 20(3.3))}\left[\left(k_{12}\Delta H_{12} + k_{14}\Delta H_{14} + k_{13}\Delta H_{13}\right)\right] \quad \text{(E8.4.2)}$$

Equations E8.4.1 and E8.4.2 should be solved numerically at boundary conditions of y and values of k and H from Table E8.4.2. Gas density is then calculated at the estimated riser temperature. Then the differential equations (8.26) to (8.29) are solved in Excel, using the Euler method. The procedure is repeated to calculate T_r and t_c then the product compositions.

Figure E8.4.1 shows the FCC riser composition profiles as a function of riser height. The temperature and activity of catalyst profiles are shown in Figure E8.4.2.

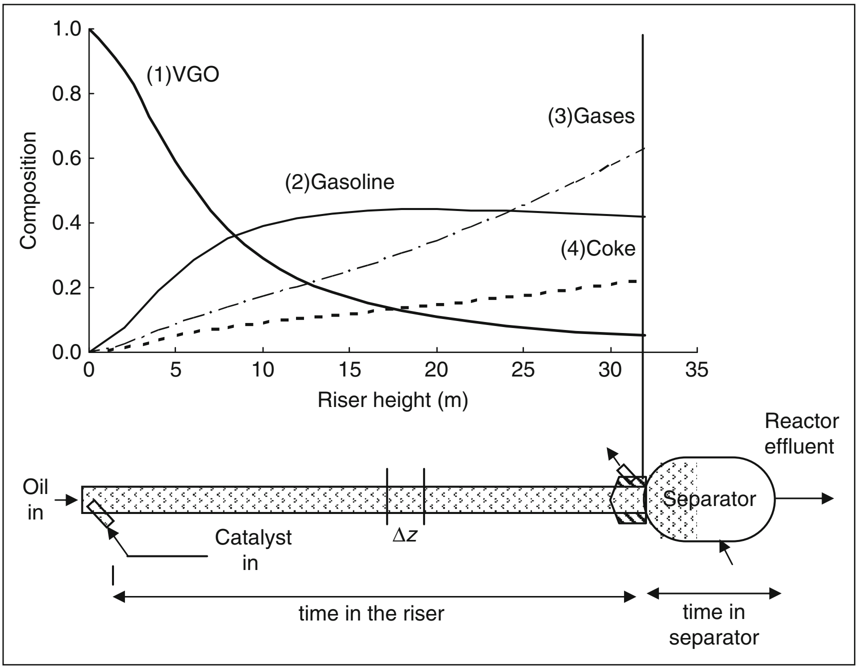


Figure E8.4.1 Product concentration profiles along the riser

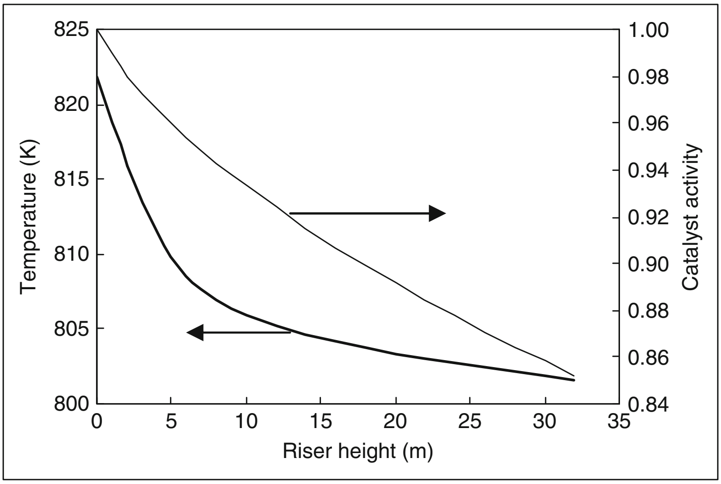


Figure E8.4.2 Temperature and catalyst activity profile in the riser

8.15. SIMULATION OF FCC UNIT

The FCC unit is basically composed of the reactor and the regenerator. At least three types of reactions take place in the riser of the reactor. The basic equation takes place in the regenerator where coke is burned by air to form CO_2 and water vapour. A UNISIM (2007) simulator is used in the following example which is composed of a conversion reactor where cracking, hydrogen transfer and coke formation reactions take place. The outcome of the reactor is split into coke and products streams. Products are sent to a fractionation unit and coke is sent to another conversion reactor (regenerator) where all the coke is burned with 7% excess air.

Example E8.5

A VGO feed of 78,428 lb/h is fed to the riser of a FCC unit at 900 °F and 20 psia. Assume that the feed is composed of 94 mol% $C_{26}H_{54}$ paraffin and 6 mol% *n*-butyl naphthalene ($C_{14}H_{16}$). Perform a UNISIM simulation on the FCC unit shown in Fig. E8.5.1.

The following reactions occur in the riser:

Cracking reaction (90% Conversion)

$$nC_{26}H_{54} \rightarrow C_6H_{12} + C_6H_{14} + C_{10}H_{20} + C_4H_{10} \qquad \text{(E8.5.1)}$$

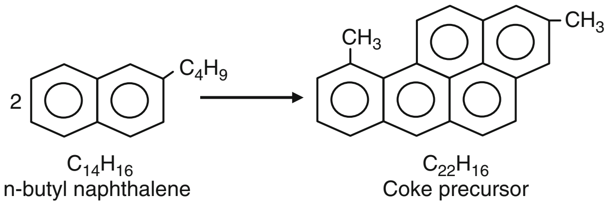
$C_{10}H_{20}$ is further cracked (95% Conversion)

$$C_{10}H_{20} \rightarrow C_6H_{12} + iC_4H_8 \qquad \text{(E8.5.2)}$$

Hydrogen transfer reaction (100% Conversion)

$$C_6H_{12} + 3iC_4H_8 \rightarrow 3C_4H_{10} + C_6H_6 \qquad \text{(E8.5.3)}$$

Condensation reaction of coke (100% Conversion)



(E8.5.4)

In the UNISIM simulation define the coke as a hypothetical component (hypo2000) with a UNIFAC structure of $[(ACH)_{10}(AC)_8(ACCH_3)_2]$ (Hsu and Robinson, 2006).

Coke coming out from the reactor is further burned in the regenerator using air according to the following reaction (100% Conversion):

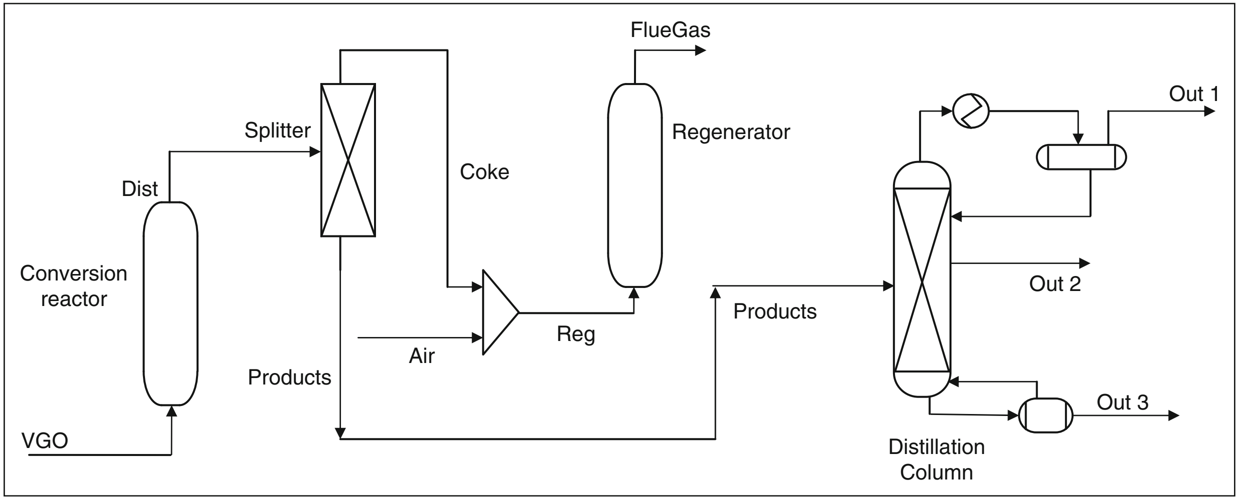


Figure E8.5.1 UNISIM flowchart for the FCC unit

Table E8.5.1 Summary of UNISIM results

			Stream composition (mole %)													
Stream	Feed rate (lb/h)	Temp. (°F)	C_3	$C_{14}H_{16}$	$C_{26}H_{54}$	$C_{10}H_{20}$	C_6H_{14}	C_6H_{12}	Benz	nC_4	Coke	$C_4^=$	O_2	CO_2	H_2O	N_2
VGO	78430	900.0	0	6.0	94	0	0	0	0	0	0	0	0	0	0	0
Dist	78428	891.7	1.37	0	2.15	0.97	19.35	25.16	12.58	37.24	6.9	0	0	0	0	0
Products	76578	896.1	1.38	0	2.17	0.97	19.49	25.33	12.67	38.0	0	0	0	0	0	0
Coke	1854	896.1	0	0	0	0	0	0	0	0	1.0	0	0	0	0	0
Air	86551	100	0	0	0	0	0	0	0	0	21.0	0	0	0	0	79.0
Reg	88405	133.7	0	0	0	0	0	0	0	0	0.22	0	20.95	0	0	78.83
Flue gas	88405	1456	0	0	0	0	0	0	0	0	0	0	15.13	4.81	1.75	78.31
Out 1	18551	42.3	4.1	0	0	0	0	0	0	95.9	0	0	0	0	0	0
Out 2	34953	153	0	0	3.2	1.4	29	37	18	11.4	0	0	0	0	0	0
Out 3	23074	161.3	0	0	3.3	1.5	29.5	38.6	19.3	7.7	0	0	0	0	0	0

$$\text{Hypo}-2000 + 26O_2 \rightarrow 22CO_2 + 8H_2O \qquad \text{(E8.5.5)}$$

Solution:

1) A conversion reactor is used to carry out reactions (E8.5.1) to (E8.5.3) at 900 °F and 20 psia. The product stream is called Dist (Figure E8.5.1).
2) The Dist stream is split into Hypo-2000 as a coke stream and the other products.
3) Air is injected at 100 °F and 20 psia.
4) The mixed stream (reg) is sent to the regenerator reactor where coke is combusted producing hot flue gases.
5) The product stream is sent to a fractionator.

A summary of the results for all streams is shown in Table E8.5.1.

8.16. NEW TECHNOLOGY

The major drive for FCC process improvements is the demand for higher gases (LPG and olefins) and the decline in demand for residual oils. Replacement of diesel fuels to gasoline will also drive FCC technology to reduce its production in favour of lighter products. Environmental aspects are being observed in developing new FCC unit. The following processes have been developed and some have already been commercialised.

8.16.1. Deep Catalytic Cracking

DCC is a new FCC process using a new catalyst for heavy feed stocks to give light olefins. The yield of olefins depends greatly on the type of feedstock. Paraffenic feeds give the lightest propylene yield of 23 wt% and 6.9 wt% isobutylene (Hsu and Robinson, 2006).

8.16.2. Catalytic Pyrolysis Process

The catalytic pyrolysis process (CPP) is an extension of DCC but with increased ethylene yield. The ratio of $C_3^=/C_2^=$ can be adjusted by controlling the operating conditions. $C_3^=$ can be produced up to around 20 wt% while $C_2^=$ can be adjusted between 10 and 20 wt%. It is suggested to optimise the use of crude oil as a petrochemical feedstock by using a combination of steam cracking (SC) and catalytic pyrolysis (CPP) as shown in Figure 8.11 (Hsu and Robinson, 2006).

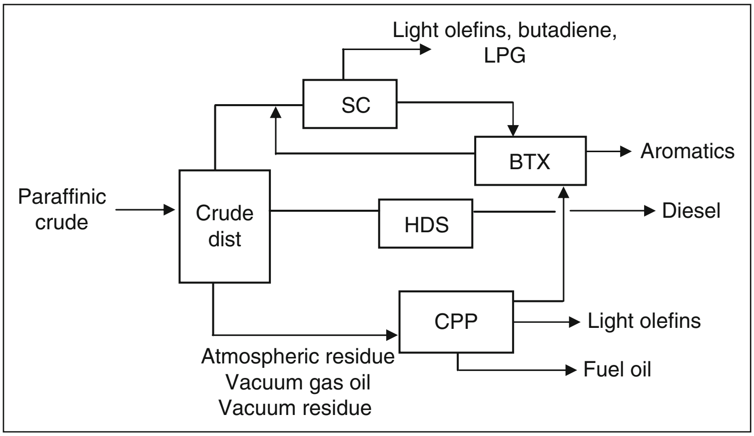


Figure 8.11 Flowchart for crude to petrochemical

8.16.3. Petro-FCC

The Petro-FCC process is licensed by UOP. The process gives the highest yield of propylene, lighter olefins and aromatics for petrochemical operation from feedstocks which can include conventional FCC feeds and residual feeds. The feed comes in contact with the blended catalyst in the riser under sever condition. A schematic diagram of the process is shown in Figure 8.12.

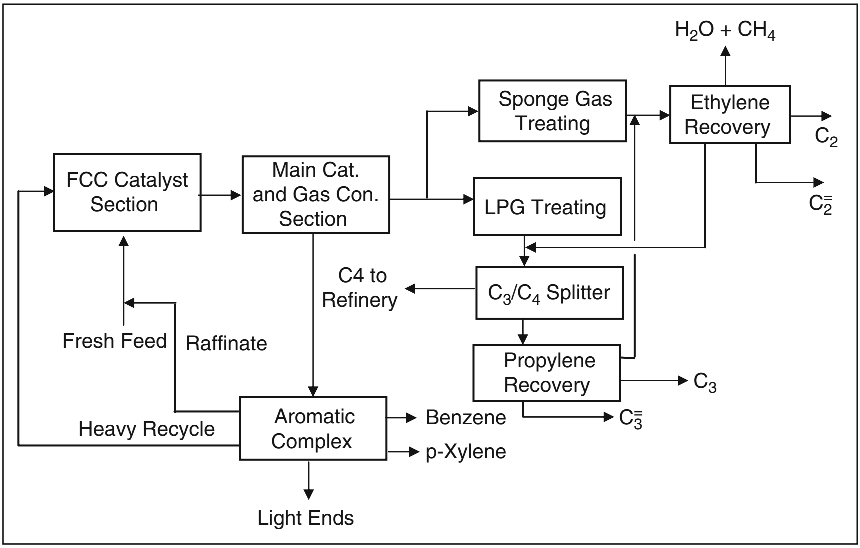


Figure 8.12 UOP Petro-FCC complex (PetroFCC, 2008)

Table 8.8 Yield patterns of conventional FCC and Petro-FCC units

Component	Conventional FCC wt%	Petro-FCC wt%
H_2S, H_2,C_1 & C_2	2	3
Ethylene	1	6
Propane	1.8	2
Propylene	4.7	22
Butane	4.5	5
Butene	6.5	14
Naphtha	53.5	28
Distillate	14	9.5
Fuel oil	7	5
Coke	5	5.5

The process starts with a uniquely designed FCC unit and is capable of producing a product of 18 LV% $C_3^{=}$, 7 LV% $C_2^{=}$, 10 LV% $C_4^{=}$ and 20 LV% benzene and paraxylene. A complete comparison of conventional and Petro-FCC yields is given in Table 8.8 (Hsu and Robinson, 2006).

QUESTIONS AND PROBLEMS

8.1. Use a feed composed of AGO and VGO coming out from a distillation unit with a conversion of 70% in a once-through operation with a zeolite catalyst.

	BPD	Ton/day	Sulphur Ton/day
Atmospheric gas oil	7451.65	1050.78	21.169
Light vacuum gas oil	4662.92	666.143	27.888
Heavy vacuum gas oil	24635.5	3674.16	169.032
Total	36750.07	5391.083	218.089

8.2. If the HCGO in the above problem is recycled to extinction, by how much will the gasoline production be increased? How much coke will lay down?

8.3. For the following conditions, calculate (a) the wt% hydrogen in coke, (b) the coke yield, and (c) the catalyst-to-oil ratio.
Carbon on spent catalyst: 1.50 wt%

Carbon on regenerated catalyst: 0.80 wt%
Air from blower: 155,000 lb/h
Hydrocarbon feed to reactor: 295,000 lb/h
Flue gas analysis (Orsat) vol%: CO = 12.0, $CO_2 = 6.0$, $O_2 = 0.7$, $N_2 = 81.3$

8.4. The following operating data were obtained from an FCC unit which is now in operation. Operating data:

- Combustion air to the regenerator (dry basis: excluding water fraction)
  Flow rate: 120,000 kg/h, Temperature: 200 °C
- Composition of the regenerator flue gas (dry basis)
  O_2 0.5 vol% SO_2 0.2 vol%
  CO 3 vol% N_2 81.3 vol%
  CO_2 15 vol%
- Regenerator flue gas temperature 720 °C
- Regenerator catalyst bed temperature 700 °C
- Spent catalyst temperature 550 °C
  (1) With a coke combustion balance calculation around the regenerator, estimate the coke yield as wt% on the basis of fresh feed oil.
  (2) Estimate the flow rate of the circulating catalyst (t/min).

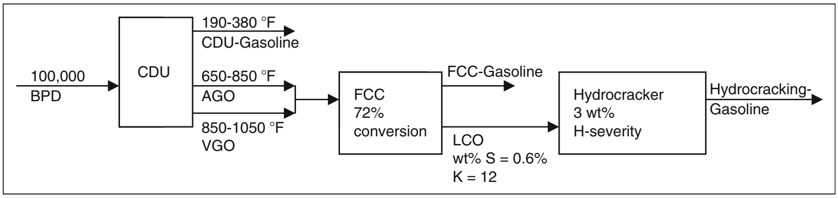
Note: The capacity of the FCC unit is 40,000 BPSD, and the specific gravity of the feed oil is 0.915 (15/4 °C).

8.5. 100,000 BPD crude oil, with an API of 24, is fed to a distillation column. The crude TBP and API as a function of accumulated volume% (LV%) are as follows:

$$\mathrm{TBP}(^{\circ}\mathrm{R}) = \left\{ \left(1.5 \ln\left(\frac{100}{100 - \mathrm{LV\%}} \right) \right)^{2.7} + 1 \right\} 486$$

$$\mathrm{API} = -0.0004\,\mathrm{LV\%}^3 + 0.05\,\mathrm{LV\%}^2 - 2.4\,\mathrm{LV\%} + 72$$

A gasoline cut is produced from the CDU unit as well as AGO and VGO cuts which are fed to the FCC unit as shown in the flowchart. Gasoline is also produced from the FCC as well as LCO, which is then fed to a hydrocracking unit to produce gasoline. Calculate the total amount of gasoline (lb/h) that is produced from all units.



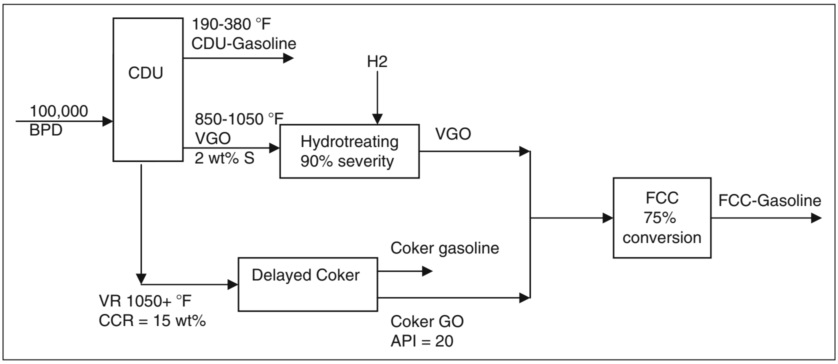
8.6. 100,000 BPD crude oil, with 3 wt% sulphur, is fed to a distillation column. The crude TBP and API as a function of accumulated volume % (LV%) are as follows:

$$\mathrm{TBP}(^\circ\mathrm{R}) = \left\{\left(2\ln\left(\frac{100}{100-\mathrm{LV\%}}\right)\right)^{2.5} + 1\right\}490$$

$$\mathrm{API} = -0.0004\ \mathrm{LV\%}^3 + 0.05\ \mathrm{LV\%}^2 - 2.4\ \mathrm{LV\%} + 72$$

A gasoline cut is produced from the CDU unit as well as a VGO cut which is fed to the coker unit as shown in the flowchart. Gasoline is also produced from the FCC. Calculate the following:

- **a)** CDU gasoline
- **b)** Coker gasoline
- **c)** Feed to FCC
- **d)** FCC gasoline



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CHAPTER NINE

PRODUCT BLENDING

9.1. INTRODUCTION

Refining processes do not generally produce commercially usable products directly, but rather semi-finished products which must be blended in order to meet the specifications of the demanded products.

The main purpose of product blending is to find the best way of mixing different intermediate products available from the refinery and some additives in order to adjust the product specifications. For example, gasoline is produced by blending a number of components that include alkylate, reformate, FCC gasoline and an oxygenated additive such as methyl tertiary butyl ether (MTBE) to increase the octane number.

The final quality of the finished products is always checked by laboratory tests before market distribution. Gasolines are tested for octane number, Reid vapour pressure (RVP) and volatility. Kerosenes are tested for flash point and volatility. Gas oils are tested for diesel index, flash point, pour point and viscosity.

Product qualities are predicted through correlations that depend on the quantities and the properties of the blended components. In this chapter, various mixing rules along with correlations are used to estimate the blend properties such as specific gravity, RVP, viscosity, flash point, pour point, cloud point and aniline point. The octane number for gasoline is correlated with corrections based on aromatic and olefin content.

The desired property P_{Blend} of the blended product may be determined using the following mixing blend rule:

$$P_{\text{Blend}} = \frac{\sum_{i=1}^{n} q_i P_i}{\sum_{i=1}^{n} q_i} \tag{9.1}$$

where P_i is the value of the property of component i and q_i is the mass, volume or molar flow rate of component i contributing to the total amount of the finished product. For example, q_i can be volume fraction x_{vi}, therefore, the denominator in equation (9.1) will equal 1.

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Table 9.1 Typical properties for gasoline blending components (Gary and Handwerk, 2001)

Component	RVP (psi)	MON	RON	API
iC_4	71.0	92.0	93.0	
nC_4	52.0	92.0	93.0	
iC_5	19.4	90.8	93.2	
nC_5	14.7	72.4	71.5	
iC_6	6.4	78.4	79.2	
LSR gasoline	11.1	61.6	66.4	78.6
HSR gasoline	1.0	58.7	62.3	48.2
Light hydrocracker gasoline	12.9	82.4	82.8	79.0
Heavy hydrocracker gasoline	1.1	67.3	67.6	49.0
Coker gasoline	3.6	60.2	67.2	57.2
FCC Light gasoline	1.4	77.1	92.1	49.5
FCC gasoline	13.9	80.9	83.2	51.5
Reformate 94 RON	2.8	84.4	94.0	45.8
Reformate 98 RON	2.2	86.5	98.0	43.1
Alkylate $C_3^=$	5.7	87.3	90.8	
Alkylate $C_4^=$	4.6	95.9	97.3	70.3
Alkylate $C_5^=$	1.0	88.8	89.7	

The blending mixing rule expressed by equation (9.1) assumes that the given property is additive (or linear). Additive properties include specific gravity, boiling point and sulphur content. However, properties like viscosity, flash temperature, pour point, aniline point, RVP and cloud point are not additive. Table 9.1 lists typical properties of pure components and petroleum cuts that can be blended for gasoline to meet market specifications.

9.2. Reid Vapour Pressure Blending

RVP is the vapour pressure at 100 °F of a product determined in a volume of air four times the liquid volume. RVP is not an additive property. Therefore, RVP blending indices are used. A commonly used RVP index is based on an empirical method developed by Chevron Oil Trading Company (1971).

$$\mathrm{BI}_{\mathrm{RVP}i} = \mathrm{RVP}_i^{1.25} \tag{9.2}$$

where $\mathrm{BI}_{\mathrm{RVP}i}$ is the RVP blending index for component i and RVP_i is the RVP of component i in psi.

Using the index, the RVP of a blend is estimated as

$$\mathrm{BI}_{\mathrm{RVP,Blend}} = \sum_{i=1}^{n} x_{\mathrm{v}i}\mathrm{BI}_{\mathrm{RVP}i} \qquad (9.3)$$

where $x_{\mathrm{v}i}$ is the volume fraction of component i.

Example E9.1

Calculate the RVP of a blend of LSR gasoline, HSR gasoline, Reformate and FCC gasoline. Properties and available quantities of the components are given in Table E9.1.1.

Solution:

As illustrated in Table E9.1.2, the RVP of the blend is calculated through the following steps:

- The volume fraction of each component $x_{\mathrm{v}i}$ is calculated and listed in Table E9.1.2.
- The RVP index of each component is calculated. For example, the calculation of LSR gasoline gives $\mathrm{BI}_{\mathrm{RVP}i} = 11.1^{1.25} = 20.26$
- The volume fraction is multiplied by the index for each component (Table E9.1.2)

From the summation, $\mathrm{BI}_{\mathrm{RVP,Blend}} = 14.305$, then

$$\mathrm{RVP}_{\mathrm{Blend}} = (14.305)^{1/1.25} = 8.4 \text{ psi}$$

Hence, the RVP of the blended product is 8.4 psi.

Table E9.1.1 Quantities and RVP values of the blending components

Component	Quantity (BPD)	RVP (psi)
LSR gasoline	5000	11.1
HSR gasoline	4000	1.0
Reformate 94 RON	6000	2.8
FCC gasoline	7000	13.9

Table E9.1.2 Summary of RVP calculations

Component	Quantity (BPD)	$x_{\mathrm{v}i}$	$\mathrm{BI}_{\mathrm{RVP}i}$	$x_{\mathrm{v}i} \times \mathrm{BI}_{\mathrm{RVP}i}$
LSR gasoline	5000	0.227	20.26	4.599
HSR gasoline	4000	0.182	1.0	0.182
Reformate 94 RON	6000	0.273	3.62	0.989
FCC gasoline	7000	0.318	26.84	8.535
Sum	22,000	1.0		14.305

Additives, such as propane, *i*-butane and *n*-butane can be added to the gasoline blend to adjust the RVP requirements. Example E9.2 illustrates how the amount of an additive is calculated using the method of RVP index.

Example E9.2

Determine the amount of *n*-butane required to produce a gasoline blend with RVP = 10 psi from the components listed in Table E9.1.1. The RVP of *n*-butane is 52 psi.

Solution:

Assume V_{Butane} is the volume flow rate (BPD) of *n*-butane needed to be added to the blend. RVP indices are calculated for all components including *n*-butane and listed in Table E9.2.1.

Table E9.2.1 Summary of calculations

Component	Quantity V_i(BPD)	$\mathrm{BI}_{\mathrm{RVP}i}$	$V_i \times \mathrm{BI}_{\mathrm{RVP}i}$
LSR gasoline	5000	20.26	101,300
HSR gasoline	4000	1.0	4000
Reformate 94 RON	6000	3.62	21,732
FCC gasoline	7000	26.84	187,880
n-Butane	V_{Butane}	139.64	139.64 V_{Butane}
Sum	22,000 + V_{Butane}		314,912 + 139.64 V_{Butane}

The volume is first multiplied by the index and then divided by the total volume. The summation yields the RVP index for the blend.

$$\mathrm{BI}_{\mathrm{RVP,Blend}} = 10^{1.25} = \frac{314,912 + 139.64\,V_{\mathrm{Butane}}}{22,000 + V_{\mathrm{Butane}}}$$

The above equation is solved for V_{Butane} to be 625.7 BPD, which is the amount of *n*-butane needed to adjust the RVP of the blend to 10 psi.

9.3. FLASH POINT BLENDING

The flash point is the lowest temperature at which vapours arises from oil ignites. It indicates the maximum temperature at which a fuel can be stored without serious hazard. If the flash point of a petroleum product does not meet the required specifications, it can be adjusted by blending this product with other fractions. Flash point is not an additive property and flash point blending indices are used, which blend linearly on a volume basis. The flash point of a blend is determined using the following equation:

$$\mathrm{BI}_{\mathrm{FP,Blend}} = \sum_{i=1}^{n} x_{\mathrm{v}i}\mathrm{BI}_{\mathrm{FP}i} \tag{9.4}$$

where $x_{\mathrm{v}i}$ is the volume fraction of component i, and $\mathrm{BI}_{\mathrm{FP}i}$ is the flash point index of component i that can be determined from the following correlation (Riazi, 2005):

$$\mathrm{BI}_{\mathrm{FP}i} = \mathrm{FP}_i^{1/x} \tag{9.5}$$

FP_i is the flash point temperature of component i, in K, and the best value of x is -0.06.

Another relation to estimate the flash point blending index is based on the flash point experimental data reported by Gary and Handwerk (2001).

$$\mathrm{BI}_{\mathrm{FP}i} = 51708 \times \exp[(\ln(\mathrm{FP}_i) - 2.6287)^2/(-0.91725)] \tag{9.6}$$

FP_i is the flash point temperature of component i, in °F. The flash point blending index is blended based on wt% of components.

Example E9.3

Calculate the blend flash point of the components listed in Table E9.3.1. If the resulted temperature is lower than 130 °F, component D is added to the blend to increase the flash point. Knowing that the flash point of D is 220 °F, calculate the amount (BPD) of component D (SG = 0.95) to be added to adjust the flash point.

Solution:

The flash point indices are calculated using equation (9.6) and listed in Table E9.3.2.

The mass flow rates are calculated for each component based on the given specific gravity and BPD.

For component A $\left(2500\,\frac{\mathrm{bbl}}{\mathrm{day}}\right)\left(\frac{5.6\ \mathrm{ft}^3}{1\ \mathrm{bbl}}\right)\left(\frac{0.8 \times 62.4\ \mathrm{lb}}{\mathrm{ft}^3}\right)\left(\frac{\mathrm{day}}{24\ \mathrm{h}}\right) = 29,120\ \mathrm{lb/h}$

The weight fractions ($x_{\mathrm{w}i}$) are then calculated and listed in Table E9.3.2.

Table E9.3.1 Quantities and flash points of the blending components

Component	BPD	SG	Flash point (°F)
A	2500	0.80	120
B	3750	0.85	100
C	5000	0.90	150

Table E9.3.2 Summary of calculations

Component	x_{wi}	BI_{FPi}
A	0.207	321.36
B	0.329	731.07
C	0.465	106.47

$$BI_{FP,Blend} = \sum_{i=1}^{n} x_{wi} BI_{FPi} = 356.55$$

$$FP_{Blend} = \exp\left(\left[(-0.91725) \times \ln\left(\frac{356.06}{51708}\right)\right]^{0.5} + 2.6287\right) = 117.36\ ^{\circ}F$$

The calculated flash point is less than 130 °F therefore, component D need to be added.
The flash point index for component D is
$BI_{FPi} = 51708 \exp[(\ln(220) - 2.6287)^2/(-0.91725)] = 12.41$
The blend flash point index is
$BI_{FPi} = 51708 \exp[(\ln(130) - 2.6287)^2/(-0.91725)] = 218.94$
If W_D is the mass flow rate for component D, then
29,120 (321.36) + 46,410 (731.07) + 65,520 (106.47) +
12.41 W_D = (141,050 + W_D) 218.94
W_D = 93,843 lb/hr
The volumetric flow rate of component D is 6785 BPD.
Using the other flash point index correlation (equation 9.5) gives a blend flash point of 119.6 °F which is comparable with the one calculated above.

9.4. POUR POINT BLENDING

The pour point is the lowest temperature at which oil can be stored and still capable of flowing or pouring, when it is cooled without stirring under standard cooling conditions. Pour point is not an additive property and pour point blending indices are used, which blend linearly on a volume basis. The pour point of a blend is determined using the following equation:

$$BI_{PP,Blend} = \sum_{i=1}^{n} x_{vi} BI_{PPi} \tag{9.7}$$

where x_{vi} is the volume fraction of component i, and BI_{PPi} is the pour point index of component i that can be determined from the following correlation (Hu and Burns, 1970):

$$BI_{PPi} = 3,262,000 \times (PP_i/1000)^{12.5} \tag{9.8}$$

where PP_i is the pour point of component i, in °R.

The pour point of the product, PP_{Blend}, is then evaluated using the reverse form of equation (9.8).

Another relation to estimate the pour point blending index is the same formula for the flash point reported by Riazi (2005) with different value of the exponent:

$$BI_{FPi} = PP_i^{1/x} \tag{9.9}$$

PP_i is the pour point temperature of component i, in K, and the best value of x is 0.08.

Example E9.4

What is the pour point of the following blend?

Component	BPD	Pour Point (°C)
Catalytic cracked gas oil	2000	−15
Straight run gas oil	3000	−3
Light vacuum gas oil	5000	42
Heavy vacuum gas oil	1000	45

Solution:

The given pour point temperatures are converted to Kelvin then the pour point indices are calculated for each component and listed in Table E9.4. The blend pour point is calculated from the blend index shown in Table E9.4:

$$PP_{Blend} = \left((1697.2/3,262,000)^{1/12.5}\right) \times 1000 = 546\ ^\circ R$$

$PP_{Blend} = 86\ ^\circ F = 30\ ^\circ C$

Table E9.4 Summary of calculations

Component	x_{vi}	BI_{ppi}	$x_{vi} \times BI_{ppi}$
Catalytic cracked gas oil	0.1818	227.3	41.32
Straight run gas oil	0.2727	461.0	125.7
Light vacuum gas oil	0.4545	2748	1249
Heavy vacuum gas oil	0.0909	3093	281.2
Sum	1		1697.2

9.5. CLOUD POINT BLENDING

Cloud point is the lowest temperature at which oil becomes cloudy and the first particles of wax crystals are observed as the oil is cooled gradually under standard conditions. Cloud point is not an additive property and cloud point blending indices are used, which blend linearly on a volume basis using the following:

$$\mathrm{BI}_{\mathrm{CP,Blend}} = \sum_{i=1}^{n} x_{vi}\mathrm{BI}_{\mathrm{CP}i} \tag{9.10}$$

where x_{vi} is the volume fraction of component i, and $\mathrm{BI}_{\mathrm{CP}i}$ is the cloud point blending index of component i that can be determined from the following correlation (Hu and Burns, 1970; Riazi, 2005):

$$\mathrm{BI}_{\mathrm{CP}i} = \mathrm{CP}_i^{1/x} \tag{9.11}$$

CP_i is the cloud point temperature of component i, in K and the value of x is 0.05.

Example E9.5

Calculate the cloud point of the following blend

Component	BPD	Cloud point (°F)
A	1000	–5
B	2000	5
C	3000	10

Solution:

The given cloud point temperatures are converted to Kelvin then the cloud point indices are calculated for each component and listed in Table E9.5.1. The blend cloud point is calculated from the summation as
$CP_{\mathrm{Blend}} = (1.8098 \times 10^{48})^{0.05} = 258.75\ \mathrm{K} = -14.25\ °\mathrm{C} = 6.35\ °\mathrm{F}$

Table E9.5.1 Summary of calculations

Component	x_{vi}	CP (K)	$\mathrm{BI}_{\mathrm{cp}i} \times 10^{48}$	$x_{vi} \times \mathrm{BI}_{\mathrm{cp}i} \times 10^{48}$
A	0.167	252.4	1.101	0.1839
B	0.333	258.0	1.701	0.5664
C	0.500	260.8	2.119	1.0595
Sum	1.0			1.8098

9.6. ANILINE POINT BLENDING

The aniline point indicates the degree of aromaticity of a petroleum fraction. It is the minimum temperature at which equal volumes of the aniline and the oil are completely miscible. Aniline point is not an additive property, and aniline point blending indices are used, which blend linearly on a volume basis. The aniline point of a blend is determined using the following formula:

$$\mathrm{BI}_{\mathrm{AP,Blend}} = \sum_{i=1}^{n} x_{\mathrm{v}i}\mathrm{BI}_{\mathrm{AP}i} \tag{9.12}$$

where $x_{\mathrm{v}i}$ is the volume fraction of component i, and $\mathrm{BI}_{\mathrm{AP}i}$ is the aniline point index of component i that can be determined from the following correlation (Baird, 1981):

$$\mathrm{BI}_{\mathrm{AP}i} = 1.124[\exp(0.00657\mathrm{AP}_i)] \tag{9.13}$$

AP_i is the aniline point of component i, in °C.

Example E9.6

What is the aniline point of the following blend?

Component	BPD	Aniline point (°C)
Light diesel	4000	71.0
Kerosene	3000	60.7
Light cycle gas oil	3000	36.8

Solution:

The volume fractions and aniline point indices are calculated and listed in Table E9.6.

$\mathrm{BI}_{\mathrm{AP,Blend}} = 0.4(1.792) + 0.3(1.675) + 0.3(1.432) = 1.6468$

$$\mathrm{AP}_{\mathrm{Blend}} = \ln(1.6468/1.124)/0.00657 = 58.17°\mathrm{C}$$

Table E9.6 Summary of calculations

Component	$x_{\mathrm{v}i}$	$\mathrm{BI}_{\mathrm{AP}i}$
Light diesel	0.4	1.792
Kerosene	0.3	1.675
Light cycle gas oil	0.3	1.432
Sum	1.0	

9.7. SMOKE POINT BLENDING

The smoke point is the maximum flame height in millimetre at which the oil burns without smoking when tested at standard specified conditions. The smoke point of a blend is determined using the following formula (Jenkis and Walsh, 1968):

$$\begin{aligned} \mathrm{SP_{Blend}} = {} & -255.26 + 2.04\ \mathrm{AP_{Blend}} - 240.8\ \ln(\mathrm{SG_{Blend}}) \\ & + 7727(\mathrm{SG_{Blend}}/\mathrm{AP_{Blend}}) \end{aligned} \tag{9.14}$$

where SP_{Blend} is the blend smoke point in mm, AP_{Blend} and SG_{Blend} are the aniline point and specific gravity of the blend, respectively. Aniline point for the blend is calculated as discussed in section 9.6. Specific gravity is an additive property and can be blended linearly on a volume basis. The specific gravity of a blend is estimated using the mixing rule:

$$\mathrm{SG_{Blend}} = \sum_{i=1}^{n} x_{\mathrm{v}i}\mathrm{SG}_i \tag{9.15}$$

where $x_{\mathrm{v}i}$ is the volume fraction of component i, and SG_i is the specific gravity of component i. It must be stated here that, API is not an additive property, and it does not blend linearly. Therefore, API is converted to specific gravity, which can be blended linearly.

Example E9.7

What is the smoke point of the following blend?

Component	BPD	Aniline point (°C)	SG
Kerosene A	4000	50	0.75
Kerosene B	3000	60	0.8
Kerosene C	3000	55	0.85

Solution:

The volume fractions and aniline point indices are calculated and listed in Table E9.7.

$\mathrm{SG_{Blend}} = 0.4(0.75) + 0.3(0.8) + 0.3(0.85) = 0.805$

$\mathrm{BI_{AP,Blend}} = 0.4\ (1.561) + 0.3(1.667) + 0.3(1.613) = 1.6296$, gives $AP_{\mathrm{Blend}} = 56.54\ ^\circ\mathrm{C}$

$\mathrm{SP_{Blend}} = -255.26 + 2.04(56.54) - 240.8\ \ln(0.805) + 7727(0.805/56.54) = 22.33\ \mathrm{mm}$

Table E9.7 Summary of calculations

Component	x_{vi}	BI_{APi}
Light diesel	0.4	1.561
Kerosene	0.3	1.667
Light cycle gas oil	0.3	1.613
Sum	1	

9.8. VISCOSITY BLENDING

Viscosity is not an additive property; therefore, viscosity blending indices are used to determine the viscosity of the blended products. A number of correlations and tables are available for evaluating the viscosity indices. The viscosity index of the blended product is determined using the following equation:

$$BI_{vis,Blend} = \sum_{i=1}^{n} x_{vi} BI_{visi} \tag{9.16}$$

where x_{vi} is the volume fraction of component i, and BI_{visi} is the viscosity index of component i that can be determined using the following correlation (Baird, 1989):

$$BI_{visi} = \frac{\log_{10} \nu_i}{3 + \log_{10} \nu_i} \tag{9.17}$$

where ν_i is the viscosity of component i, in cSt.

The viscosity of the blended product is then calculated using

$$\nu_{Blend} = 10^{[3 \times BI_{vis,Blend}/(1 - BI_{vis,Blend})]} \tag{9.18}$$

Example E9.8

Estimate the viscosity of a blend of 2000 barrels of Fraction-1 with a viscosity of 75 cSt, 3000 barrels of Fraction-2 with 100 cSt, and 4000 barrels of Fraction-3 with 200 cSt all at 130 °F.

Solution:

The viscosity index is calculated from equation (9.17).

As shown in Table E9.8, the blend viscosity index is calculated

Table E9.8 Summary of calculations

Component	Quantity (BPD)	x_{vi}	$v_i(cSt)$	BI_{visi}	$x_{vi} \times BI_{visi}$
Fraction-1	2000	0.222	75	0.385	0.0854
Fraction-2	3000	0.333	100	0.400	0.1332
Fraction-3	4000	0.445	200	0.434	0.1931
Sum	9000	1.0			0.4117

The blend viscosity is calculated from the blend index as

$$v_{\text{Blend}} = 10^{[3\times 0.4117/(1-0.4117)]} = 125.73 \text{ cSt}$$

9.9. GASOLINE OCTANE NUMBER BLENDING

The octane number is a characteristic of spark engine fuels such as gasoline. Octane number is a measure of a fuel's tendency to knock in a test engine compared to other fuels. The octane number posted octane number (PON), commercially used for gasoline (referred to as the road octane number), is the average of its research octane number (RON) and motor octane number (MON). The difference between RON and MON is known as fuel sensitivity (S).

There are a number of additives, such as oxygenated ethers or alcohols, that can enhance a gasoline octane number. Tetra-ethyl lead (TEL) which was used for enhancing octane number, has now been phased out and replaced by the oxygenates listed in Table 9.2 with their octane numbers. RONs for selected hydrocarbons are listed in Appendix D.

If the octane number of a blend is calculated by the linear addition of an octane number for each component, the following equation can be obtained:

$$\text{ON}_{\text{Blend}} = \sum_{i=1}^{n} x_{vi}\text{ON}_i \tag{9.19}$$

where x_{vi} is the volume fraction of component i, and ON_i is the octane number of component i.

Many alternative methods have been proposed for estimating the octane number of gasoline blends since the simple mixing rule needs minor corrections. One correction method that uses the octane number index has been reported by Riazi (2005). The following octane index correlations depend on the octane number range as follows:

Table 9.2 Octane numbers of some oxygenates (alcohols and ethers) (Guibet, 1995)

Compound	RON	MON
Methanol	125–135	100–105
Ethanol	120–130	98–103
Methyl-tertiary-butyl ether (MTBE)	113–117	95–101
Ethyl-tertiary-butyl ether (ETBE)	118–122	100–102
Tertiary-butyl alcohol (TBA)	105–110	95–100
Tertiary-amyl-methyl ether (TAME)	110–114	96–100

For $11 \le \mathrm{ON} \le 76$

$$\mathrm{BI}_{\mathrm{ON}i} = \begin{pmatrix} 36.01 + 38.33(\mathrm{ON}/100) - 99.8(\mathrm{ON}/100)^2 + 341.3(\mathrm{ON}/100)^3 \\ -507.02(\mathrm{ON}/100)^4 + 268.64(\mathrm{ON}/100)^5 \end{pmatrix} \tag{9.20a}$$

For $76 \le \mathrm{ON} \le 103$

$$\mathrm{BI}_{\mathrm{ON}i} = -299.5 + 1272(\mathrm{ON}/100) - 1552.9(\mathrm{ON}/100)^2 + 651(\mathrm{ON}/100)^3 \tag{9.20b}$$

For $103 \le \mathrm{ON} \le 106$

$$\mathrm{BI}_{\mathrm{ON}i} = 2206.3 - 4313.64(\mathrm{ON}/100) + 2178.57(\mathrm{ON}/100)^2 \tag{9.20c}$$

The octane number index for a blend can be determined using the following equation:

$$\mathrm{BI}_{\mathrm{ON,Blend}} = \sum_{i=1}^{n} x_{vi}\mathrm{BI}_{\mathrm{ON}i} \tag{9.21}$$

where x_{vi} is the volume fraction of component i, and $\mathrm{BI}_{\mathrm{ON}i}$ is the octane number index of component i that can be determined from equations (9.20a, 9.20b and 9.20c).

Example E9.9

For a blend of alkylate $C_4^=$, coker gasoline, and FCC gasoline. Calculate the RON by

(a) Linear mixing of octane numbers.
(b) Linear mixing of octane number indices.

Properties and quantities of the components are given in Table E9.9.

Table E9.9 Quantities and RON of the blending components

Component	Quantity (BPD)	RON
Alkylate $C_4^=$	6000	97.3
Coker gasoline	4000	67.2
FCC gasoline	5000	83.2

Solution:

(a) Using equation (9.19) for simple mixing rule, the RON for the blend is calculated as

$$\mathrm{RON}_{\mathrm{Blend}} = \frac{1}{6000+4000+5000}[6000(97.3)+4000(67.2)+5000(83.2)] = 84.57$$

(b) Using the index method

$$\mathrm{BI}_{\mathrm{RON,Alkylate}} = -299.5 + 1272(0.973) - 1552.9(0.973)^2 + 651(0.973)^3 = 67.66$$

$$\mathrm{BI}_{\mathrm{RON,coker}} = \begin{pmatrix} 36.01 + 38.33(0.672) - 99.8(0.672)^2 + 341.3(0.672)^3 \\ -507.02(0.672)^4 + 268.64(0.672)^5 \end{pmatrix} = 53.65$$

$$\mathrm{BI}_{\mathrm{RON,FCC}} = -299.5 + 1272(0.832) - 1552.9(0.832)^2 + 651(0.832)^3 = 58.78$$

$$\mathrm{BI}_{\mathrm{RON,Blend}} = 0.4(67.66) + 0.267(53.65) + 0.333(58.78) = 60.98$$

To solve for $\mathrm{RON}_{\mathrm{Blend}}$, equation (9.20b) is solved for RON, when I_{RON} equals 60.98. The resulted $\mathrm{RON}_{\mathrm{Blend}}$ is 88.09.

Example E9.10

It is required to produce gasoline with a RON of 95 from the blending components in Table E9.9 in the previous example. Calculate the amount of the oxygenate MTBE with a RON of 115 to be added in order to adjust the blend RON to 95.

Solution:

Using the index method

$$\mathrm{BI}_{\mathrm{RON,Blend}} = -299.5 + 1272(0.95) - 1552.9(0.95)^2 + 651(0.95)^3 = 65.56$$

$$\mathrm{BI}_{\mathrm{RON,MTBE}} = 2206.3 - 4313.64(1.15) + 2178.57(1.15)^2 = 126.77$$

The RON blending index of alkylate, coker gasoline and FCC gasoline are calculated in Example E9.9. The blend equation (9.21) is then written as

$$65.56(15,000 + V_{\mathrm{MTBE}}) = 6000(67.66) + 4000(53.65) + 5000(58.78) + 126.77\,V_{\mathrm{MTBE}}$$

Solving for $V_{\mathrm{MTBE}} = 1126$ BPD

Depending on the availability of olefin and aromatic contents in the blended components, the octane number of the blend can be calculated using the linear mixing rule method with a correction (Healy et al., 1959; Maples, 1993)

$$\mathrm{RON}_{\mathrm{Blend}} = \overline{R} + 0.03324(\overline{RS} - \overline{R} \times \overline{S}) + 0.00085\left(\overline{O^2} - \overline{O}^2\right) \tag{9.22}$$

$$\mathrm{MON}_{\mathrm{Blend}} = \overline{M} + 0.04285(\overline{\mathrm{MS}} - \overline{M} \times \overline{S}) + 0.00066(\overline{O^2} - \overline{O}^2) - 0.00632\left(\frac{\overline{A^2} - \overline{A}^2}{100}\right)^2 \tag{9.23}$$

where the terms represent volumetric average values of given properties of components as follows:

R = Research octane number (RON)
M = Motor octane number (MON)
S = Sensitivity (RON-MON)
RS = RON × Sensitivity
MS = MON × Sensitivity
O = Volume percent olefins
A = Volume percent aromatics

Example E9.11

Twu and Coon (1998) reported RON of 91.8 for a blend with the composition given in Table E9.11.1.

Table E9.11.1 Composition, RON, MON, olefin and aromatic contents of the blending components (Twu and Coon, 1998)

Component	x_{vi}	RON	MON	Olefin content (%)	Aromatic content (%)
Reformate	0.41	97.8	87	1.4	63.1
Thermally cracked	0.04	70.4	65.1	32.5	9.8
Catalytically cracked	0.32	92.6	80.2	53.3	23.9
Polymerised	0.09	96.8	82.3	100	0
LSR	0.14	58	58	1.3	3.8

(a) Calculate the RON and MON for the blend using equation (9.22) and (9.23), then compare with the reported experimental value.
(b) Calculate the RON of the blend using the blending index method (equation 9.20) and compare with the reported experimental value.

Solution:

(a) All terms in equations (9.22) and (9.23) are calculated and listed in Table E9.11.2.

$$\begin{aligned}\mathrm{RON_{Blend}} &= 89.38 + 0.03324(941.74 - 89.38 \times 9.91)\\ &\quad + 0.00085(1852.38 - 28.11^2) = 92.13\\ \mathrm{MON_{Blend}} &= 79.47 + 0.04285(824.67 - 79.47 \times 9.91)\\ &\quad + 0.00066(1852.38 - 28.11^2)\\ &\quad - 0.00632((1821.11 - 34.44^2)/100)^2 = 81.49\end{aligned}$$

It can be observed from the above calculations that the RON without correction ($\overline{R}$) is 89.38 and with olefin and aromatic corrections, it is 92.13.

The laboratory tested RON for the above blend was 91.8 (Twu and Coon, 1998). Therefore, the correction using the olefin and aromatic contents adjusts the calculations to be closer to the experimental value with a difference of 0.36%.

(b) The blending index method can be used to calculate the RON of the above blend.

Component	BI_{RON}	x_{vi}
Reformate	68.16	0.41
Thermally cracked	54.53	0.04
Catalytically cracked	63.71	0.32
Polymerised	67.17	0.09
LSR	51.52	0.14

$$\begin{aligned}\mathrm{BI_{RON,Blend}} &= 0.41(68.16) + 0.04(54.53) + 0.32(63.71)\\ &\quad + 0.09(67.17) + 0.14(51.52) = 63.77\end{aligned}$$

Then $\mathrm{RON_{Blend}} = 92.69$ with a difference of 0.97%.

Table E9.11.2 Summary of calculations

Component	$\overline{R}$	$\overline{M}$	$\overline{S}$	$\overline{RS}$	$\overline{MS}$	$\overline{A}$	$\overline{O}$	$\overline{A^2}$	$\overline{O^2}$
Reformate	40.10	35.67	4.43	433.06	385.24	25.87	0.57	1632.46	0.80
Thermally cracked	2.82	2.60	0.21	14.92	13.80	0.39	1.30	3.84	42.25
Catalytically cracked	29.63	25.66	3.97	367.44	318.23	7.65	17.06	182.79	909.08
Polymerised	8.71	7.41	1.31	126.32	107.40	0.00	9.00	0.00	900.00
LSR	8.12	8.12	0.00	0.00	0.00	0.53	0.18	2.02	0.24
Sum	89.38	79.47	9.91	941.74	824.67	34.44	28.11	1821.11	1852.38

9.10. LINEAR PROGRAMMING (LP) FOR BLENDING

LP is the most widely applied method for optimising many diverse applications, including refineries and chemical plants. The application of LP has been successfully applied for selecting the best set of variables when a large number of interrelated choices exist. A typical example is in a large oil refinery in which the stream flow rates are very large, and a small improvement per unit of product is multiplied by a very large number. This is done to obtain a significant increase in profit for the refinery.

Optimisation means the action of finding the best solution within the given constraints and flexibilities. LP is a mathematical technique for finding the maximum value of some equation subject to stated linear constraints. The linear in LP stands for the algebraic aspect, which means that all the constraints and objective functions are linear and satisfy two fundamental properties, proportionality and additive. The programming in LP means planning. The implementation of LP involves the development of an integrated LP model representing the refinery operations with all constraints and flexibilities and then solving it to determine the optimum plan.

Refinery optimisation using an LP model has been proven to bring economic gains higher than unit-specific simulation models or advance process control techniques. Once all the data is configured, the model is updated with the variable data. The required variable data includes the following:

- Crude oil or any other raw material prices with minimum and maximum availability
- Selling prices with minimum and maximum demands for the refinery products
- Available process unit capacities
- Available inventory stocks with minimum and maximum storage limits
- Quality specifications, etc.

The following methodology describes how LP is applied to the blending problem. For N independent variables, the objective function (P) that should be maximised is

$$P = a_1X_1 + a_2X_2 + \cdots + a_NX_N \tag{9.24}$$

The objective function is subjected to primary constraint equations such as

$$X_1 \geq 0, X_2 \geq 0, \ldots, X_N \geq 0 \tag{9.25}$$

and

$$\begin{aligned} a_{i1}X_1 + a_{i2}X_2 + \cdots + a_{iN}X_N &\leq b_i \\ a_{j1}X_1 + a_{j2}X_2 + \cdots + a_{jN}X_N &\leq b_j \\ a_{k1}X_1 + a_{k2}X_2 + \cdots + a_{kN}X_N &= b_k \end{aligned} \tag{9.26}$$

can be solved utilising the Excel solver.

The objective function (P) is usually the octane number of the blend that needs to be maximised. Sometimes the objective function can be minimising cost or setting the RVP to a certain value. The primary constraint variables (X_i to X_N) are the volume of each cut for a blend which must be greater than zero. Other constraint can be the capacity of the tank in which the summation of X_is will not exceed. Additional constraints can be any of the blend properties discussed in this chapter. Therefore, a_{i1} to a_{kN} are the properties or their indices for components 1 to N and b_i to b_k are the targeted blending properties or their indices.

In most blending cases, two or more properties are required in order to be adjusted by the addition of some modifiers to the blend. For example, oxygenates are added to enhance gasoline octane number and *n*-butane is added to adjust the RVP. Determining the quantities of the additives becomes more difficult in non-linear property cases. Determining the amounts of these blends is based on solving two (or more) equations with two (or more) unknowns depending on the property equations as discussed above.

Example E9.12

A blend is performed of 3000 barrels of LSR gasoline and 2000 barrels of hydrocracker gasoline. Calculate the amount of FCC gasoline and *n*-butane that must be added to the blend to produce a gasoline of 12 psi RVP and 0.525 cSt viscosity. The properties of all the components are shown in Table E9.12.1.

Solution:

Calculate the RVP index and viscosity index using equations (9.2) and (9.17), respectively. The results are listed in Table E9.12.2

Table E9.12.1 Components amounts and properties for the blend

Component	Barrels	RVP psi	Viscosity cSt
LSR gasoline	3000	12.1	0.2886
Hydrocracker gasoline	2000	15.5	0.4140
FCC gasoline	X	4.8	0.8607
n-Butane	Y	51.6	0.3500

Table E9.12.2 RVP and viscosity indices

Component	BI_{RVP}	BI_{vis}
LSR gasoline	22.56	−0.21936
Hydrocracker gasoline	30.76	−0.14635
FCC gasoline	7.11	−0.0222
n-Butane	138.3	−0.1792

RVP blend is considered as the objective function

$$\begin{aligned}&12^{1.25}(5000+X+Y)-(3000)(22.56)-(2000)(30.76)\\&\quad-(X)(7.11)-(Y)(138.3)=0\end{aligned}\tag{E9.12.1}$$

Viscosity index of the blend is

$$BI_{visi}=\frac{\log_{10}(0.525)}{3+\log_{10}(0.525)}=-0.1028$$

Viscosity blend is considered as the first constraint equation

$$\begin{aligned}&0.1028(5000+X+Y)+(3000)(-0.21936)+(2000)(-0.14635)\\&\quad+(X)(-0.0222)+(Y)(-0.1792)=0\end{aligned}\tag{E9.12.2}$$

Other constraints are added such as $X>0$ and $Y>0$ (E9.12.3)
Solving using the Excel solver with the above objective function and constraints gives
$X = 6025$ barrels
$Y = 640$ barrels
This example can be solved by simultaneous solving of equations (E9.12.1) and (E9.12.2) algebraically.

Example E9.13

A blend is performed for LSR gasoline, hydrocracker gasoline, FCC gasoline and *n*-butane. Calculate the amount of each component that must be added to produce gasoline blend of maximum octane number and 12 psi RVP. The properties of each cut are shown in Table E9.13. The olefin contents in each cut can be assumed to be zero.

Table E9.13 Components properties for the blend

Component	Barrels	RVPpsi	RON	MON
LSR gasoline	X_1	12.1	91	81
Hydrocracker gasoline	X_2	15.5	89.5	85.5
FCC gasoline	X_3	4.8	97	96
n-Butane	X_4	51.6	93	92
Blend	X_T	12	Max	

The maximum blend storage capacity is 15,000 barrels.
Redo the calculation if the available amount of FCC gasoline is 6000 barrels.

Solution:

The objective function is maximising octane number.
Since olefin contents are zero, equation (9.22) becomes

$$\mathrm{RON}_{\mathrm{Blend}} = \overline{R} + 0.03324(\overline{RS} - \overline{R} \times \overline{S}) \tag{E9.13.1}$$

where

$$\overline{R} = \frac{X_1}{X_\mathrm{T}}(91) + \frac{X_2}{X_\mathrm{T}}(89.5) + \frac{X_3}{X_\mathrm{T}}(97) + \frac{X_4}{X_\mathrm{T}}(93)$$

$$\overline{S} = \frac{X_1}{X_T}(91-81) + \frac{X_2}{X_T}(89.5-85.5) + \frac{X_3}{X_T}(97-96) + \frac{X_4}{X_T}(93-92)$$

$$\overline{\mathrm{RS}} = \frac{X_1}{X_T}91(91-81) + \frac{X_2}{X_T}89.5(89.5-85.5) + \frac{X_3}{X_T}97(97-96) + \frac{X_4}{X_T}93(93-92)$$

The following are four constraints:

$$X_1 \geq 0, \quad X_2 \geq 0, \quad X_3 \geq 0, \quad \text{and} \quad X_4 \geq 0 \tag{E9.13.2}$$

An additional constraint is

$$X_1 + X_2 + X_3 + X_4 < 15,000 \text{ barrels} \tag{E9.13.3}$$

The constraint equation for the RVP of the blend can be obtained by calculating the RVP index from equation (9.2)

$$22.56X_1 + 30.755X_2 + 7.105X_3 + 138.3X_4 - 22.33X_\mathrm{T} = 0 \tag{E9.13.4}$$

Using the solver in Excel with the above constrains (equations E9.13.2, E9.13.3, and E9.13.4) and maximising the RON value from equation (E9.13.1), the results are RON equal 96.1 and

$X_1 = 500$, $X_2 = 440$, $X_3 = 12{,}457$ and $X_4 = 1603$ barrels

If the constraint for the amount of FCC gasoline is added, the results will be a RON of 95.7 and

$X_1 = 500$, $X_2 = 440$, $X_3 = 6000$ and $X_4 = 755$ barrels

---

Example E9.14

The following gasoline cuts (Table E9.14.1) are blended to get a RON of 89 and a RVP of 10.2 psi. Calculate X_1 and X_2. Assume that the olefin contents are negligible.

Table E9.14.1 Components properties for the blend

Component	Barrels	RVP(psi)	RON	MON
n-Butane	X_1	51.6	93	92
Isomer gasoline	5735	13.5	83	81.1
Reformer gasoline	14,749	2.2	98.5	86.0
FCC gasoline	20,117	4.4	92.3	86.8
Hydrocracker gasoline	814	12.9	82.8	82.4
Alkylate	4117	4.6	97.3	95.9
Polymer	2071	8.7	96.9	84
MTBE	X_2	9.0	118	101
Blend	$47,603 + X_1 + X_2$	10.2	89	

Solution:

The volume fractions and RVP indices for each component are calculated and listed in Table E9.14.2.

The first equation for the RVP blend is the objective function

$$(10.2^{1.25})(47603 + X_1 + X_2) - 5735(25.9) - 14749(2.7) - 20117(6.4) \\ -814(24.4) - 4117(6.7) - 2071(14.9) - 138X_1 - 15.6X_2 = 0 \tag{E9.14.1}$$

then becomes

$$18.22(47603 + X_1 + X_2) - 394608 - 138X_1 - 15.6X_2 = 0$$

The second equation for octane number is considered as the first constraint

$$\mathrm{RON}_{\mathrm{Blend}} = \overline{R} + 0.03324(\overline{RS} - \overline{R} \times \overline{S}) = 89 \tag{E9.14.2}$$

Table E9.14.2 RVP indices and volume fractions

Component	x_{vi}	Barrels	$\mathrm{BI}_{\mathrm{RVP}}$
n-Butane	$X_1/(47,603 + X_1 + X_2)$	X_1	138
Isomer gasoline	$5735/(47,603 + X_1 + X_2)$	5735	25.9
Reformer gasoline	$14,749/(47,603 + X_1 + X_2)$	14,749	2.7
FCC gasoline	$20,117/(47,603 + X_1 + X_2)$	20,117	6.4
Hydrocracker gasoline	$814/(47,603 + X_1 + X_2)$	814	24.4
Alkylate	$4117/(47,603 + X_1 + X_2)$	4117	6.7
Polymer	$2071/(47,603 + X_1 + X_2)$	2071	14.9
MTBE	$X_2/(47,603 + X_1 + X_2)$	X_2	15.6
Blend	$47,603 + X_1 + X_2$	$47,603 + X_1 + X_2$	18.22

where,

$$\overline{R}(47603 + X_1 + X_2) = 3,927,638 + 93\ X_1 + 118\ X_2$$

$$\overline{S}(47603 + X_1 + X_2) = 181,332.9 + X_1 + 17\ X_2$$

$$\overline{RS}(47603 + X_1 + X_2) = 16,518,930 + 93\ X_1 + 2006\ X_2$$

The other constraints are $X_1 > 0$ and $X_2 > 0$
Using the solver in Excel with the above constraints, the results are
$X_1 = 3927$ barrels
$X_2 = 3984$ barrels

QUESTIONS AND PROBLEMS

9.1. Calculate the number of barrels of *n*-butane that have to be added to a mixture of 1250 barrels of HSR gasoline, 750 barrels of LSR gasoline, and 620 barrels of C_5^+ FCC gasoline to produce a 9 psi RVP. What are the RON and MON of the blend?

Component	Barrels	RVP (psi)	RON	MON	Olefin (%)	Aromatics (%)
HSR gasoline	1250	1	62.3	58.7	0	7
LSR gasoline	750	11.1	66.4	61.6	0	5
C_5^+ FCC	620	13.1	91	80.7	30.6	33.1
n-Butane		51.6	93	92	0	0

9.2. What is the viscosity of a blend of 2000 bbl of oil with a viscosity of 75.5 cSt at 130 °F, 3000 bbl with 225 cSt at 130 °F and 5000 bbl with 6500 cSt at 130 °F?

9.3. What is the flash point of a mixture of 2000 barrels of oil with a flash point of 100 °F, 3000 barrels with a flash point of 80 °F and 5000 barrels with a 150 °F flash point?

9.4. Calculate the pour point of the following mixture:

Component	Barrels	Pour point (°F)
A	5200	10
B	3000	50
C	6500	65
D	3250	45

9.5. Calculate the number of barrels of *n*-butane that have to be added to a mixture of 3000 barrels of LSR gasoline, 2000 barrels of hydrocrakate gasoline, and 6000 barrels of FCC gasoline to produce a 12 psi RVP blend. What is the viscosity of the blend?

Component	Barrels	RVP (psi)	Viscosity (cSt)
n-Butane	X_B	51.6	0.35
LSR gasoline	3000	12.1	0.2886
Hydrocrakate gasoline	2000	15.5	0.414
FCC gasoline	6000	4.8	0.8607

9.6. A blend is performed of 3000 barrels of LSR gasoline and 3000 barrels of hydrocrakate gasoline. Calculate the amount of FCC gasoline and *n*-butane that must be added to the mixture to produce a 12 psi RVP blend with a viscosity of 0.525 cSt.

Component	Barrels	RVP (psi)	Viscosity cSt
n-Butane	X	51.6	0.35
LSR gasoline	3000	12.1	0.2886
Hydrocrakate gasoline	3000	15.5	0.414
FCC gasoline	Y	4.8	0.8607

9.7. A blend is performed for LSR gasoline, hydrocracker gasoline, FCC gasoline and *n*-butane. Calculate the amount of each component that must be added to produce gasoline blend of maximum octane number and 10 psi RVP using the Linear Programming (LP) technique. The properties of each cut are shown in the table below. The olefin contents in each cut can be assumed to be zero. The maximum blend storage capacity is 10,000 barrels.

Component	Barrels	RVP (psi)	RON	MON
LSR gasoline	X_1	12.1	91	81
Hydrocracker gasoline	X_2	15.5	89.5	85.5
FCC gasoline	X_3	4.8	97	96
n-Butane	X_4	51.6	93	92
Blend	X_T	10	Max	

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CHAPTER TEN

ALKYLATION

10.1. INTRODUCTION

Alkylation is the process of producing gasoline range material (alkylates) from olefins such as propylene ($C_3^=$), butylenes ($C_4^=$) and amylene ($C_5^=$), and isobutane. Butylene is the most widely used olefin because of the high quality of the alkylate produced. The current trend toward elimination of methyl tertiary butyl ether (MTBE) has resulted in increased attention to alkylation technology.

An alternative process is the polymerization process in which polymeric materials from unreacted olefins are formed. Reformulated gasoline requires a low olefin content. This makes polymer gasoline undesirable as a blending stock. The motor octane number of a polymer gasoline is much lower than the corresponding values obtained from alkylation. This has resulted in the shutdown of the polymerization units in refineries using alkylation.

10.2. ROLE OF ALKYLATION AND POLYMERIZATION UNITS IN THE REFINERY

Refinery gases produced from different units are collected and sent to the gas plant. Olefins and isobutanes are separated and used as a feed to the alkylation plant (Figure 10.1). Sources of these two components from different refinery units are shown in Table 10.1.

Olefins are sent to the polymerization unit as shown in Figure 10.1. Both alkylation and polymerization units produce gasoline which can be sent to the gasoline pool.

10.3. ALKYLATION PROCESSES

Alkylation is catalysed by a strong acid, either sulphuric (H_2SO_4) or hydrofluoric (HF). In the absence of catalysts, alkylation between isobutane and olefin must be run under severe conditions such as $T = 500\ °C$ (932 °F)

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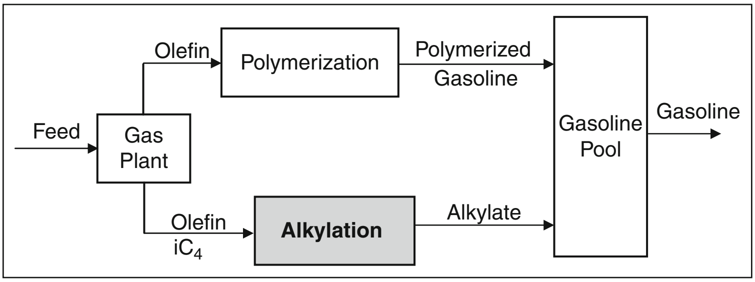


Figure 10.1 Role of alkylation and polymerization units in the refinery

Table 10.1 Olefins and isobutane production from different units

	LV%	
	Isobutane	Olefins
Hydrocracker	3	–
FCC	6	15
Coker	1	15
Hydrotreater	1	–
Reformer	2	–
Isomerization	1	–
Crude unit	0.5	–

and $P = 200$–400 bars (2940–7080 psia). In the presence of an acid catalyst, the reaction temperature will be lower than 50 °C (122 °F), and the pressure will be lower than 30 bars (441 psia). The major difference in using either acid is that isobutane is quite insoluble in H_2SO_4 but reasonably soluble in HF. This requires the use of high isobutane/olefin ratios to compensate for low solubility in H_2SO_4. Furthermore, the reaction must occur at low temperature.

The alkylation process consists of running the hydrocarbons in liquid form (enough pressure is used to ensure that) and at low temperature and with a high isobutane (iC_4) to olefin (such as $C_4^=$) ratio. The reaction products are sent to an acid settler where the acid is recycled back to the reactor. Products are then separated into gaseous LPG propane and *n*-butane and the desired product of alkylate. A block diagram of the process is shown in Figure 10.2.

10.3.1. Sulphuric Acid Alkylation Process

Two sulphuric acid alkylation processes are commonly available. These are the auto-refrigeration process licensed by Exxon and the effluent refrigeration process licensed by Stratford. The major difference between the two

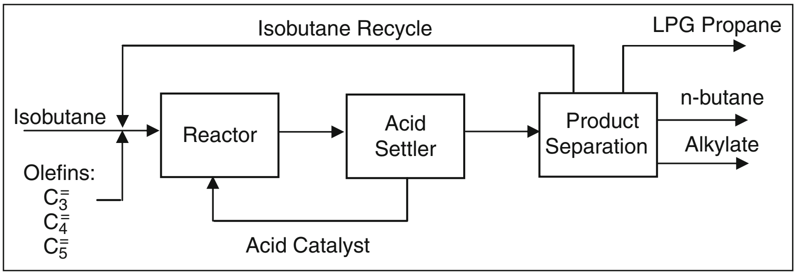


Figure 10.2 Block diagram of alkylation process

processes is in the reactor design. In the auto-refrigeration process, the evaporation of iC_4 and $C_4^=$ induces cooling of the emulsion in the reactor. In the effluent refrigeration process, a refrigeration unit provides cooling to the reactor.

The auto-refrigeration unit is shown in Figure 10.3. The olefin is fed to the first reactor in the cascades, together with the recycled acid and refrigerant. Recycled and make-up isobutanes are distributed to each reactor. Evaporated gases are compressed and fed back to the reactor along with the fresh olefin feed which is also cooled by this stream (Gary and Handwerk, 1994).

The reactor operates at a pressure of 90 kPag (10 psig) and at a temperature of 5 °C (40 °F) for up to 40 min. In the Stratco process, the reactor is operated at a higher pressure of 420 kPag (60 psig), to prevent evaporation of hydrocarbon, and at a temperature of 10 °C (50 °F). A block diagram of the Stratco effluent refrigerated process is shown in Figure 10.4. In this diagram the "effluent treating" section is used to remove free acid and alkyl

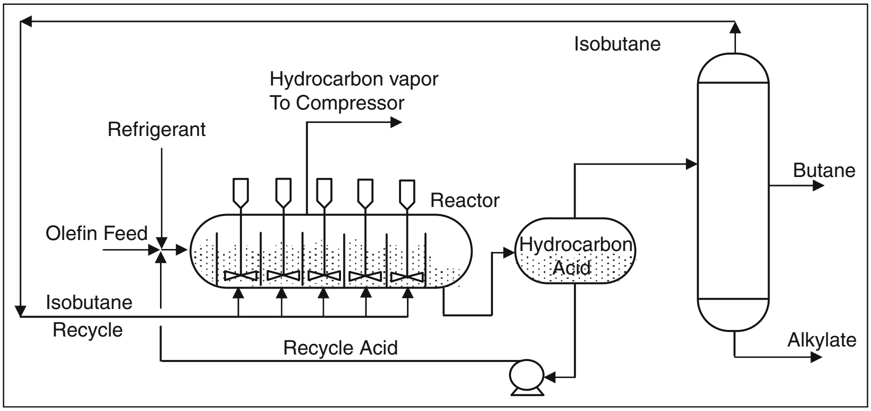


Figure 10.3 Auto-refrigerated sulphuric acid alkylation process

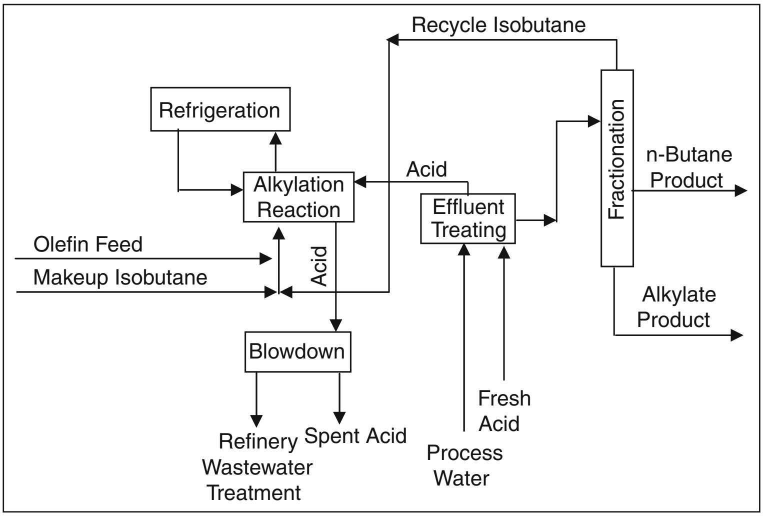


Figure 10.4 Block diagram for Stratco effluent refrigerated sulphuric acid alkylation unit

sulphate to avoid corrosion and fouling. The "blowdown" section is used to purge and neutralized spent acid.

The effluent refrigeration process uses a single Stratco reactor design as shown in Figure 10.5. An impeller emulsifies the hydrocarbon–acid mixture for about 20–35 min.

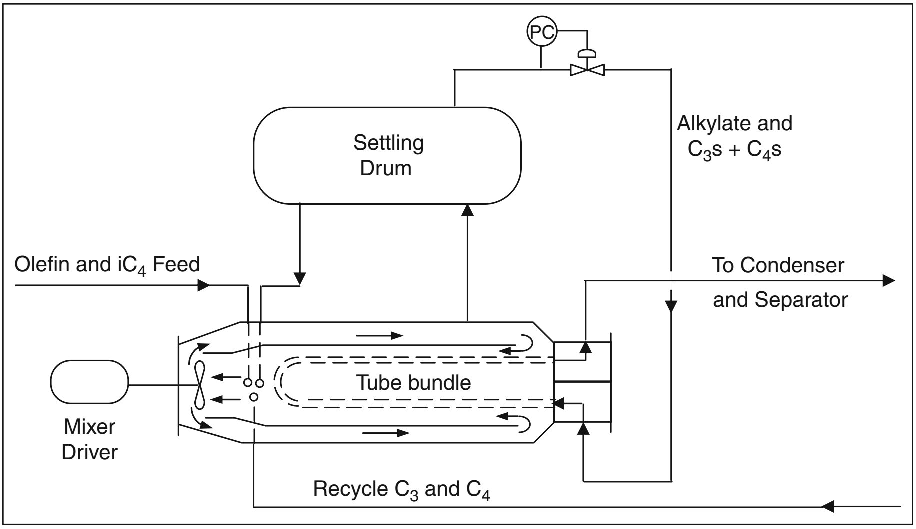


Figure 10.5 Stratco reactor

10.3.2. Hydrofluoric Acid Alkylation

Two hydrofluoric acid (HF) alkylation processes are commonly available. These are the Phillip process and the UOP process. The HF processes have no mechanical stirring as in the sulphuric acid processes. The low viscosity of HF and the high solubility of isobutane in the acid allow for a simpler design. The emulsion is obtained by injecting the hydrocarbon feed into the continuous HF phase through nozzles at the bottom of a tubular reactor. Reaction temperature is about 30 °C (86 °F), allowing for the use of water as a coolant to the reactor.

The two processes are quite similar. The flow diagram of the Phillips process is shown in Figure 10.6. The residence time in the reactor is 20–40 s. The hydrocarbon phase is sent to the main fractionation column to obtain stabilized alkylate. H_2SO_4 alkylation processes are favoured over the HF processes because of the recent concern about the mitigation of HF vapour. HF is a very hazardous material for humans because it can penetrate and damage tissue and bone.

10.3.3. Solid Catalyst Alkylation

Alkylation processes based on solid acids are not yet operated on an industrial scale. However, several companies have developed processes or already offer technology for licensing. The overall process scheme is similar to the liquid acid base process scheme, except for the regeneration section,

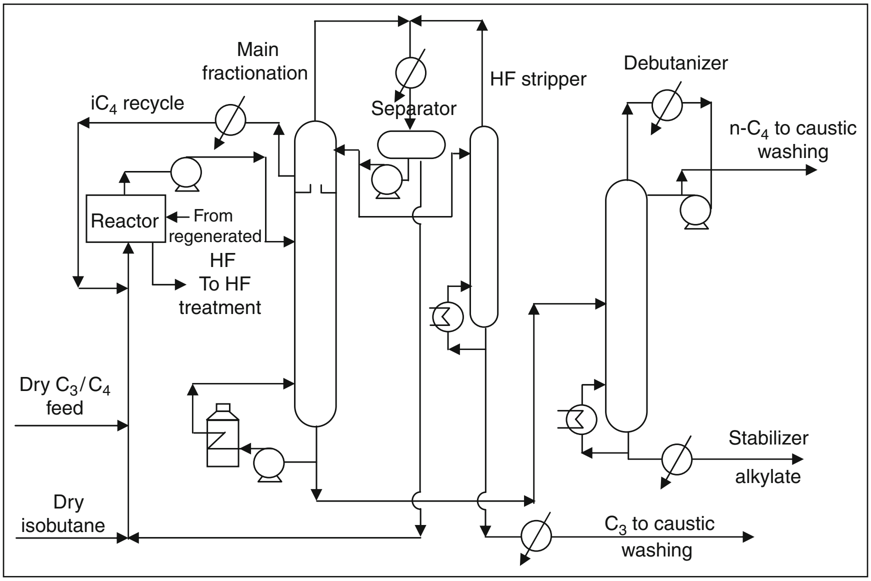


Figure 10.6 Simplified diagram of the Phillip's HF alkyation process

Table 10.2 Solid acid alkylation processes

Process	Reaction temperature (°C)	iC_4/olefin	Catalyst
UOP alkylene	10–40	6–15	HAL-100
Lurgi Eurofuel	50–100	6–12	Faujasite-derived
Haldor Topsoes FBA	0–20		CF_3SO_3H/SiO_2
ABB Lummus AlkyClean	50–90	8–15	Zeolite-derived (SAC)

which is necessary for solid acid catalysts because of rapid deactivation. Hydrogen has proven to be very effective for the regeneration of the catalysts. Examples of solid acid alkylation technologies are shown in Table 10.2.

10.3.4. AlkyClean Process

Lummus technology has developed a solid acid catalyst gasoline alkylation technology (Amico *et al.*, 2006). The AlkyClean process employs a zeolite catalyst coupled with a novel reactor processing to yield a high quality alkylate product. The process shown in Figure 10.7 consists of four main sections: feedstock pretreatment, reaction, catalyst regeneration and product distillation. An olefin feed is preheated and fed with the isobutane recycle to the reactor. The reactor operates at 50–90 °C (122–194 °F) with liquid phase conditions. Multiple reactors are used to allow for the catalyst regeneration cycle. During regeneration, olefin addition is stopped and hydrogen is added to achieve a low reactor concentration of dissolved hydrogen while maintaining liquid phase alkylation reaction conditions. This minimizes

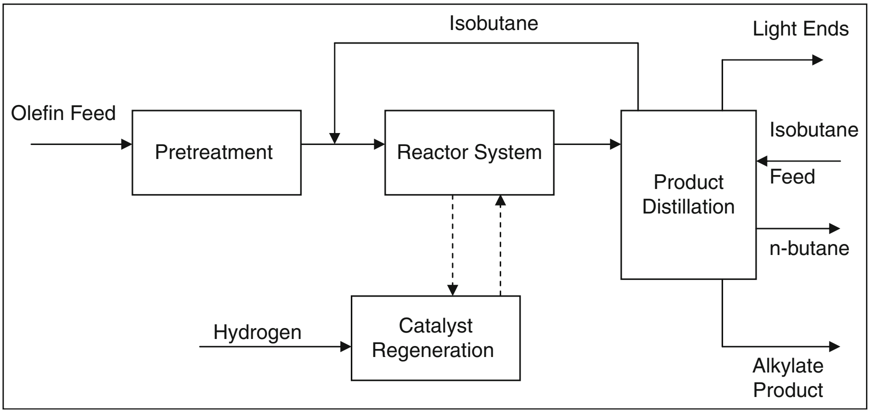


Figure 10.7 AlkyClean process

energy consumption during the switching of the operation. The swing reactor coupled with long catalyst life allows the refiner to work without the need of taking the reactor off-line for moderate temperature regeneration that restores the catalyst activity completely.

10.4. KINETICS AND THERMODYNAMICS OF ALKYLATION

Alkylation is carried out in the liquid, the gas phase or in a mixed gas–liquid system. Consider the simple liquid phase reaction of isobutene (A) and isobutane (B) giving isooctane (A_1).

$$A + B \leftrightarrows A_1 \tag{10.1}$$

If y is considered as the degree of conversion m_{Ao} and m_{Bo} are number moles of A and B in the initial mixture, respectively, and $\delta = m_{Bo}/m_{Ao}$. The number of moles in the reaction system can be expressed by:

$$(m_{Ao} - m_{Ao}y) + (m_{Bo} - m_{Ao}y) + m_{Ao}y = m_{Ao}(1 + \delta - y) \tag{10.2}$$

Accordingly, mole fractions can be expressed as:

$$x_A = \frac{1 - y}{1 + \delta - y}, \quad x_B = \frac{\delta - y}{1 + \delta - y} \text{ and } x_{A1} = \frac{y}{1 + \delta - y} \tag{10.3}$$

Thus, the reaction equilibrium constant can be expressed by:

$$K_{xeq} = \frac{x_{A1}}{(x_A)(x_B)} = \frac{y(1 + \delta - y)}{(1 - y)(\delta - y)} \tag{10.4}$$

And the degree of conversion, y, can be calculated as:

$$y = \frac{(\delta + 1) - \sqrt{(\delta + 1)^2 - \frac{4K_{xeq}\delta}{K_{xeq}+1}}}{2} \tag{10.5}$$

Assuming an ideal solution and applying Raoult's law, the equilibrium constant in the gas phase can be expressed as:

$$K_p = K_{xeq}K_p^o \tag{10.6}$$

where K_p and K_{xeq} are the equilibrium constants of the reaction in the gas and liquid phases, respectively, and K_p^o is the standard gas equilibrium constant which can be calculated using the saturated vapour pressures of the compounds at the temperature of the reaction. K_p^o can be calculated from the equation:

$$K_p^o = \frac{P_{A1}^o}{P_A^o P_B^o} \tag{10.7}$$

The alkylation reactions considered in this chapter are between olefins (butene or isobutene) and isobutane. Typical reactions and values of the equilibrium constants, K_p, at different operating temperatures are given in Table 10.3.

Table 10.3 Equilibrium constant K_p for alkylation reactions at 1 bar in ideal gas phase (Zhorov, 1987)

	K_p (MPa^{-1})					
Reaction	300 K	400 K	500 K	600 K	800 K	Equations
Ethylene + isobutane ↔ 2,3-dimethylpentane	7.7×10^9	5.4×10^5	170.0	39	0.4	(10.8)
Propene + isobutane ↔ 2,3-dimethylpentane	1.3×10^8	2.6×10^5	168.0	6.0	0.1	(10.9)
n-Butene + isobutane ↔ 2,2,4-trimethylpentane	21.7×10^6	2.82×10^3	14.0	0.40	5.2×10^{-3}	(10.10)
1-Pentene + isobutane ↔ 2,2,5-trimethylhexane	55.5×10^6	2.9×10^4	85.0	2.0	1.7×10^{-2}	(10.11)
Isobutene + isobutane ↔ 2,2,4-trimethylpentane	0.11×10^6	76.0	1.0	0.06	1.7×10^{-3}	(10.12)
cis-2-Butene + isobutane ↔ 2,2,4-trimethylpentane	2.4×10^6	662.0	4.0	0.2	4.5×10^{-3}	(10.13)
trans-2-Butene + isobutane ↔ 2,2,4-trimethylpentane	0.77×10^6	303.0	3.0	0.1	3.0×10^{-3}	(10.14)
2-Methyl-2-butene + isobutane ↔ 2,2,5-trimethylhexane	0.23×10^6	105.0	1.0	0.06	1.9×10^{-3}	(10.15)

Example E10.1

Consider an alkylation reaction between isobutene (A) and isobutane (B) to give isooctane (A1) at 300 K. The partial pressures of the reacting species are: $P_A^o = 0.32$ MPa, $P_B^o = 0.37$ MPa and $P_{A1}^o = 0.005$ MPa, respectively. Plot the conversion versus dilution ratio at different equilibrium constants.

Solution:

The standard gas equilibrium constant can be evaluated as:

$$K_p^o = \frac{0.005}{(0.32)(0.37)} = 0.042\ \text{MPa}^{-1}$$

From Table 10.3 the equilibrium constant K_p for isobutene–isobutane at 300 K is 1.1×10^5 MPa^{-1} (reaction 10.12). Thus, the liquid phase equilibrium constant can be evaluated as:

$$\text{K}_{\text{xeq}} = \frac{1.1 \times 10^5}{0.042} = 26.2 \times 10^5$$

Similarly, for 400 K, we have $P_A{}^o = 2.94$ MPa, $P_B{}^o = 3.16$ MPa and $P_{A1}{}^o = 0.16$ MPa, and K_p is 76 MPa^{-1} (Table 10.3). Thus $K_p^o = 0.017$ MPa^{-1} and $K_{xeq} = 4.5 \times 10^3$.

Higher degrees of conversion (close to unity) are obtained when conducting the alkylation reactions in the liquid phase compared with the gas phase reactions at moderate pressures. For this reason, industrial alkylation processes for C_3 and C_4 alkenes and isobutane are conducted in the liquid phase at temperatures between 0–10 °C (32–50 °F) (for the sulphuric acid (H_2SO_4) catalyst) or 30–40 °C (68–104 °F) (for the hydrofluoric acid (HF) catalyst). Figure E10.1

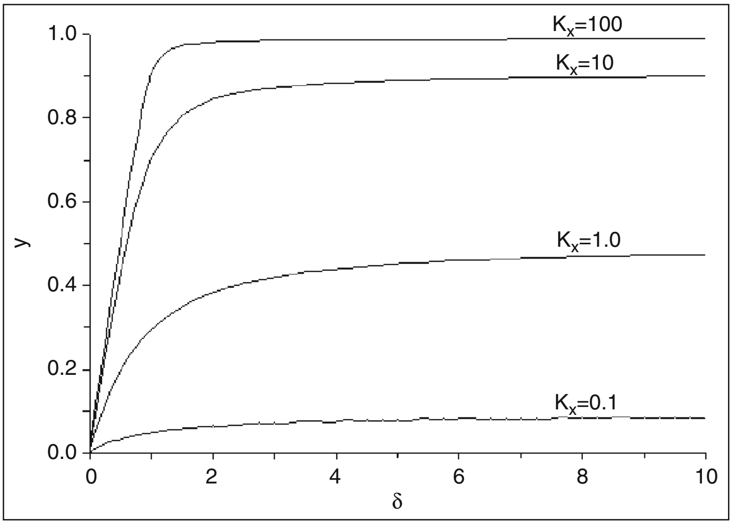


Figure E10.1 Effect of dilution ratio (δ) on conversion for different equilibrium constants (K_{xeq})

shows the relationship of conversion with dilution ratio (δ) for different operating conditions, thus, different values of the equilibrium constants. It is shown that γ becomes close to unity at 300 K (540 R), where $K_{xeq} \geq 100$ and $\delta \geq 1.0$, for reaction (10.12) in Table 10.3.

A series of consecutive reactions leading to the formation of alkylate bottoms and tar can also take place. If solid acid catalyst is used, it requires higher temperatures to ensure favourable thermodynamic conditions. At industrial conditions with temperatures greater than 10 °C (283 K), about 17 side reactions will occur, and the simple model fails to predict the kinetics in liquid phase.

10.4.1. Effect of Operating Conditions

The process conditions that influence the quality of alkylate product and acid consumption rate are the olefin type, dilution ratio δ ($iC_4/iC_4^=$), mixing temperature, impeller speed, space velocity (or residence time) and acid strength.

10.4.1.1. Olefin Type

The presence of propylene or pentene with butane will lower the octane number and increase the acid consumption. The octane number of alkylates produced from light olefins is given in Table 10.4.

Butene in sulphuric acid as a catalyst gives the best octane numbers as shown in Table 10.4. The presence of propylene with butene increases acid consumption and lowers the alkylate octane number. In the case of a $C_3^=/iC_5^=$ feed mixture, the trend is interesting since sulphuric acid consumption decreases up to 82 vol% of the $C_3^=/i\,C_5^=$ mixture. However, the octane number also decreases. This might suggest that at lower acid consumption, it is better to separate the $C_3^=/i\,C_5^=$ mixture from $C_4^=$ and let it react with iC_4 in a separate reactor (Kranz and Graves, 1998).

Table 10.4 Effect of type of olefin on alkylate octane number

	RON		MON	
Types of Olefin	HF	H_2SO_4	HF	H_2SO_4
Propylene	91–93	91–92	89–91	90–92
Butene-1	90–91	97–98	88–89	93–94
Butene-2	96–97	97–98	92–93	93–94
Isobutene	94–95	90–91	91–92	88–89
Amylene	90–92	91–92	88–89	89–91

10.4.1.2. Isobutane Concentration

The $iC_4/C_4^=$ ratio has an important role regarding the quality of alkylate produced and the amount of sulphuric acid consumption. The following reasons explain the behaviour.

- High isobutane concentration ($[iC_4]$) prevents olefin polymerization which results in low quality alkylate and high sulphuric acid consumption.
- Solubility of $iC_4 \ll C_4^=$. Thus high a concentration of iC_4 is required in the mixed hydrocarbons to compensate for its low solubility.
- Equation (10.5) indicates that the conversion to alkylate (y) increases as δ ($iC_4/C_4^=$) is increased.
- The rate of alkylate formation increases while the rate of formation of undesirable heavy alkylates decreases as iC_4 increases, as will be discussed later.
- As isobutane increases, alkylate MON increases and sulphuric acid consumption decreases.

For all these reasons, the $iC_4/C_4^=$ ratio is kept in industrial operation between 5:1 and 15:1 as the external isobutane to olefin (I/O) ratio. Inside a reactor with high circulation, this ratio becomes 100–1000:1.

10.4.1.3. Acid Strength

An optimum value of acid strength of 90 wt% H_2SO_4 is maintained by adding fresh concentrated acid (98–99 wt%). The spent acid is purged out of the system and usually regenerated outside the refinery. As the strength of the acid decreases, the acid consumption increases with the octane number decreases. The minimum acid strength required to operate the system should not be lower than 85 wt%. At lower strength, polymerization occurs and a "runaway" condition prevails. To provide a sufficient margin of safety, acid strength is kept around 90 wt%. Although water lowers the acid activity, 1–2 wt% water is added to ionize the acid. The acid strength decreases because of the formation of gums and other products resulting from the reaction with other impurities. Thus, acid make-up has to be added.

10.4.1.4. Degree of Agitation

When the hydrocarbons (iC_4 and $C_4^=$) are dispersed in sulphuric acid, as shown in Figure 10.8, the speed of the impeller determines the dispersed phase size (droplet diameter) and hence, the interfacial contact area. The reaction rate of iC_4 and $C_4^=$ is quite fast, and the reaction is controlled by mass transfer. Side reactions cause the formation of heavy alkylates as given by the following equation (Rase, 1977):

$$\frac{R_{iC_8}}{R_{\text{heavy alkylate}}} = \frac{(\text{Const})[iC4]_{\text{h}} N^{0.75}(1 - H_{\text{a}})}{(\text{SV})_{\text{o}}} \qquad (10.16)$$

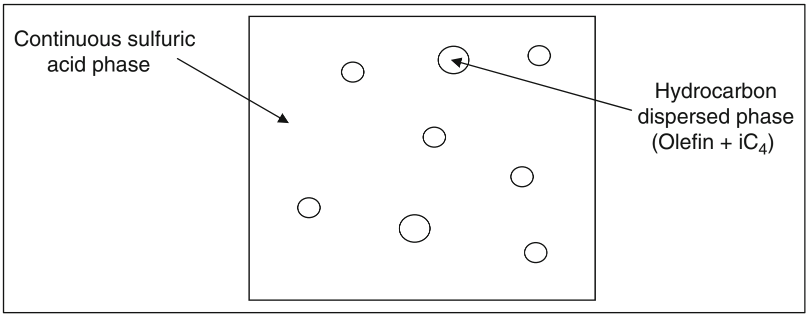


Figure 10.8 Emulsion of hydrocarbon in sulphuric acid

where $[iC_4]_h$ is the concentration of iC_4 in hydrocarbon phase, N is the impeller speed (rpm), H_a is the fractional acid hold-up, $(SV)_o$ is the space olefin velocity (1/h), $R_{\text{Heavy alkylate}}$ is the rate of formation of the undesirable heavy alkylate, and R_{iC8} is the rate of formation of the target alkylate iC_8.

This equation shows that the quality of alkylate produced can be improved by increasing impeller velocity and iC_4 concentration. The rate ratio on the left side of the equation can be maximized by using a low acid hold-up and low olefin space velocity $(SV)_o$.

Since the solubility of iC_4 in the sulphuric acid is lower than that of $C_4^=$, the reaction is controlled by the rate of mass transfer and the dissolution rate of the iC_4 in the acid.

10.4.1.5. Space Velocity

The olefin space velocity is defined as:

$$(SV)_o = \frac{\text{Olefin volumetric rate (bbl/h)}}{\text{Acid volume in contactor (bbl)}} \tag{10.17}$$

The residence time in the reactor is $(1/(SV)_o)$ and is defined as the residence time of the fresh feed and externally recycled isobutane in the reaction mixture. Since the alkylation reaction is very fast, the residence time is not a limiting parameter. However, as the space velocity increases, the octane number tends to decrease while acid consumption tends to increase. Residence time for sulphuric acid is usually from 5 to 40 min, and for hydrofluoric acid, it is 5–25 min.

10.4.1.6. Reaction Temperature

The reaction thermodynamics and kinetics are favoured at low temperatures, as shown before. Sulphuric acid alkylation units are operated at 5–10 °C (40–50 °F). Above 10 °C, oxidation and side reactions are promoted, and the deteriorate-alkylate yield and quality while acid consumption increases. It is impossible to run the reaction below 0 °C (32 °F) because acid viscosity will be too high and agitation becomes difficult. Above 21 °C (70 °F), the polymerization of olefin will occur, and the octane number of alkylate decrease. For HF alkylation, the reaction temperature is less significant and is between 21 and 38 °C (70 and 100 °F).

10.5. PERFORMANCE OF ALKYLATION PROCESS

A schematic diagram of the alkylation process is shown in Figure 10.9. The feed to the reactor consists of olefin V_1 (BPD) and a fresh acid make-up of $m \times 1000$ (lb/day).

The product alkylate yield is V_4 (BPD). Therefore, the external isobutane/olefin ratio $(\mathrm{I/O})_\mathrm{F} = x_1$ which can be expressed as (Edgar and Himmelblau, 1988):

$$(\mathrm{I/O})_\mathrm{F} = x_1 = \frac{V_5 + V_2}{V_1} \tag{10.18}$$

The recycled isobutane (V_2) can be calculated, since $(\mathrm{I/O})_\mathrm{F}$ is assumed to be 5–15. The alkylate yield V_4 can be expressed in term of $(\mathrm{I/O})_\mathrm{F}$ as (Edgar and Himmelblau, 1988):

$$V_4 = V_1(1.12 + 0.13167(\mathrm{I/O})_\mathrm{F} - 0.0067(\mathrm{I/O})_\mathrm{F}^2) \tag{10.19}$$

If we assume a volumetric shrinkage in alkylate formation from olefin and isobutane of 22%, thus:

$$V_4 = V_1 + V_5 - 0.22\,V_4 \tag{10.20}$$

Hence the make-up isobutane (V_5) is:

$$V_5 = 1.22\,V_4 - V_1 \tag{10.21}$$

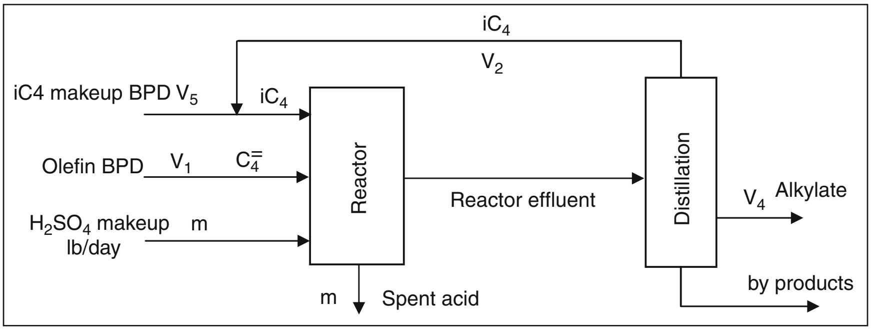


Figure 10.9 Schematic diagram of alkylation process

The acid strength weight percent, x_2, could be derived from the acid addition rate m (strength of 98%), alkylate yield V_4 and the acid dilution factor x_4 as:

$$x_2 = \frac{0.98\,m}{V_4 x_4 + m} \times 100 \tag{10.22}$$

where x_4 is the dilution ratio

$$x_4 = 35.82 - 0.222\ \mathrm{F} \tag{10.23}$$

where F is the performance number and is defined below.

The motor octane number ($x_5 = \mathrm{MON}$) can be expressed in terms of $(\mathrm{I/O})_\mathrm{F}$ and acid strength x_2 as:

$$\mathrm{MON} = 86.35 + 1.098(\mathrm{I/O})_\mathrm{F} - 0.038(\mathrm{I/O})_\mathrm{F}^2 + 0.325(x_2 - 89) \tag{10.24}$$

The performance factor F is calculated as:

$$F = -133 + 3\ \mathrm{MON} \tag{10.25}$$

A higher value of F results in better alkylate quality.

The following steps are taken to calculate alkylate yield and space velocity:

1. Assume $(\mathrm{I/O})_\mathrm{F}$
2. V_1 is given (olefin)
3. V_4 is calculated from $(\mathrm{I/O})_\mathrm{F}$ equation (10.19)
4. V_5 is calculated from V_1 and V_4 from equation (10.21)
5. Neglect acid loss
6. The reactor volume can be calculated

Example E10.2

Find alkylate yield and MON for an alkylate unit having a $C_4^=$ feed of 2000 BPD and an (I/O) ratio = 10. The acid make-up rate is 54,000 lb/day and the acid dilution ratio = 1.5. Assume volume shrinkage = 22% and an olefin residence time of 40 min. Find the reactor volume (ft^3).

Solution:

$x_4 = 1.5$ = dilution ratio lb acid/lb alkylate

$$\begin{aligned} V_4 &= V_1(1.12 + 0.13167(\mathrm{I/O})_\mathrm{F} - 0.0067(\mathrm{I/O})_\mathrm{F}^2) \\ &= 2000(1.12 + 0.13167(10) - 0.0067(100)) = 3533\ \mathrm{BPD} \end{aligned}$$

Make-up iC_4 is:

$$\begin{aligned}
V_5 &= 1.22\ V_4 - V_1\\
V_5 &= 1.22(3533) - 2000 = 2310 \text{ BPD}\\
\text{I/O} &= (V_2 + V_5)/V_1 = (V_2 + 2310)/2000 = 10\\
V_2 &= 17{,}690 \text{ BPD}
\end{aligned}$$

$$\text{Acid strength} = x_2 = \frac{0.98\,m}{V_4x_4 + m} \times 100 = \frac{0.98(54,000)}{3533(1.5) + 54,000} \times 100 = 89.24$$

$$\begin{aligned}
\text{MON} &= 86.35 + 1.098(\text{I/O})_\text{F} - 0.038(\text{I/O})_\text{F}^2 + 0.325(x_2 - 89)\\
&= 86.35 + 1.098(10) - 0.038(100) + 0.325(89.24 - 89)
\end{aligned}$$

$$\text{MON} = 93.6$$

The performance factor F is defined as:

$$F = -133 + 3(93.6) = 147.8$$

Residence time = 40 min. Therefore,

$$(\text{SV})_\text{o} = \frac{60}{40} = 1.5\ \text{h}^{-1}$$

The reactor volume (V_R) can be calculated from the space velocity as:

$$(\text{SV})_\text{o} = 1.5\ \text{h}^{-1} = \frac{2000\ \text{bbl/day}}{V_\text{R}} = \frac{2000\ \text{bbl/day} \times 1\ \text{day/24 h}}{V_\text{R}} = \frac{2000}{24\ V_\text{R}}$$

$$V_\text{R} = \frac{2000\ \text{bbl}}{1.5(24)} \times \frac{5.6\ \text{ft}^3}{1\ \text{bbl}} = 311\ \text{ft}^3(\text{note 1 bbl} = 5.6\ \text{ft}^3)$$

10.6. MATERIAL BALANCE CALCULATIONS USING YIELD FACTORS

Detailed material balance is difficult to perform for industrial alkylation processes. A number of side reactions occur, and it is difficult to determine the volume reduction accurately.

Alkane hydrocarbons such as C_3, C_4 and C_5, can be produced from the reaction of iC_4 with the corresponding olefin. For example C_3 is produced from the following reaction:

$$C_3^{=} + iC_4 \rightarrow C_3 + iC_4^{=}$$

$$iC_4^{=} + iC_4 \rightarrow\ iC_8 \text{ alkylate}$$

$$C_3^{=} + 2iC_4 \rightarrow C_3 + C_8 \text{ alkylate}$$

Table 10.5 Volume and mass factors for alkylation conversions

	$C_3^=$		$C_4^=$		$C_5^=$	
lb iC_4 consumed/lb olefin consumed	1.7132		1.1256		1.2025	
bbl iC_4 consumed/bbl olefin consumed	1.6		1.2		1.4	
Total volume of feed/total volume product	1.234		1.2		1.158	
Product composition %	vol%	wt%	vol%	wt%	vol%	wt%
C_3	14.15	10.71	–	–	–	–
nC_4	–	–	6.93	5.83	–	–
nC_5	3.40	3.14	3.71	3.33	21.80	19.74
Alkylate	75.66	78.34	82.36	83.06	70.23	71.81
Heavy alkylate	5.98	6.70	6.48	7.07	6.95	7.98
Tar	0.811	1.11	0.52	0.71	1.02	1.36

Alternatively, material balances for the alkylation processes are carried out using empirical factors (Gary and Handwerk, 1994). In Table 10.5, volume and mass factors are given for the consumption of isobutane with olefins: propylene ($C_3^=$), butylenes ($C_4^=$) and amylene ($C_5^=$). The volume and weight consumptions of the products are also given for each case.

Example E10.3

A feed stream composed of 3600 BPD isobutane and 4000 BPD butene is introduced into a sulphuric acid alkylation unit. Assuming that all isobutane is consumed in the reaction, calculate the effluent rates. The liquid densities (lb/h/BPD) of components involved in this example are given in Table E10.3.

Solution:

Using the empirical factor for $C_4^=$ listed in Table 10.5 on volume basis,

Amount of $C_4^=$ consumed = 3600/1.2 = 3000 BPD (all iC_4 consumed)

Remaining $C_4^=$ = 4000–3000 = 1000 BPD

Volume of products = volume of feed/1.2 = (3600 + 3000)/1.2 = 5500BPD (volume basis)

If we use mass factors

iC_4 consumed = 3600 (BPD) × 8.22 (lb/h BPD) = 29,592 lb/h

$C_4^=$ consumed = 29592/1.1256 = 26,290 lb/h

$C_4^=$ remaining = 4000 (BPD) × 8.78 (lb/h BPD) − 26,290 = 8750 lb/h

Table E10.3 Summary of component material balance

Feed	BPD	Lb/h	Density Lb/h/BPD
iC_4	3600	29,592	8.22
$C_4^=$	4000	35,040	8.76
Total	7600	64,632	
Products			
nC_4	381.2	3258.0	8.51
nC_5	204.0	1860.8	9.12
Alkylate	4529.8	46,415.6	10.25
Heavy alkylate	356.4	3950.9	11.09
Tar	28.6	396.7	13.87
Remaining $C_4^=$	1000	8750	
Total	6500	64,632	

Total feed consumed = 29,592 + 26,290 = 55,882 lb/h (mass basis)
Total feed consumed = total weight of product
Using composition data of the products in Table 10.5 the effluent flow rates are calculated as shown in Table E10.3.

10.7. SIMULATION OF THE ALKYLATION PROCESS

The alkylation reactors are modeled as three continuous stirred tank reactors (CSTR) in parallel. In the UNISIM simulation of the process a butanizer is used to separate iC_4 from nC_4. A distillation column is used to recover the alkylate from nC_4. Another debutanizer is used to separate and recycle excess iC_4 to the reactors.

Example E10.4

Using the flowsheet of the alkylation unit shown in Figure E10.4.1 for the hydrocarbon feed in Table E10.4.1 and Table E10.4.2, find how much alkylate is formed and perform a complete material balance.

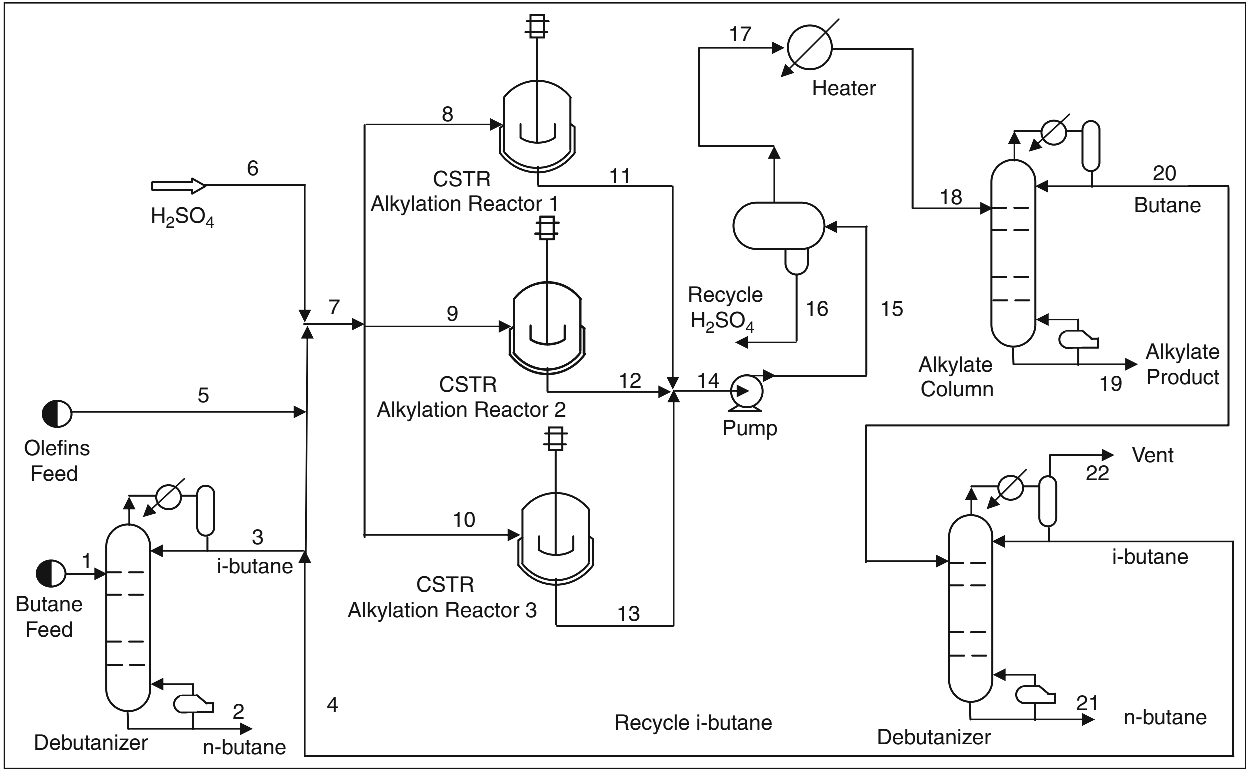


Figure E10.4.1 Alkylation flowsheet (UNISIM, 2007)

Table E10.4.1 Feed conditions

				Composition (mol%)				
Stream	Flow rate (mol/h)	T (°F)	P (psia)	nC_4	iC_4	$iC_4^=$	C_3	iC_5
C_4 feed	348.74	135	130	73.0	25.0	0.0	0.05	1.95
Olefin feed	930.32	104	124	11.46	46.04	42.5	0.0	0.0
H_2SO_4	1925	16	60	Strength = 98.5%				

Solution:

The feed of nC_4 produces some iC_4 which is added to the olefin feed containing mainly iC_4 and $iC_4^=$. A UNISIM simulation has been used. The reactor conditions are given in Table E10.4.2.

Table E10.4.2 Reactor feed conditions

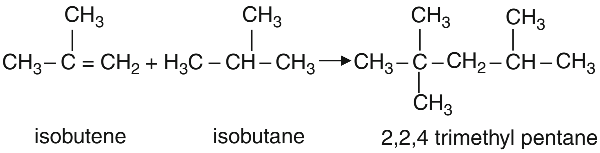
Property	Value
Molar flow rate (lb mol/h)	1046
Pressure (psia)	60
Temperature (°F)	36
Conversion (%)	92
Type of reactor	CSTR

The calculated feed composition is shown in Table E10.4.3.

Table E10.4.3 Feed composition

Component	nC_4	iC_4	$iC_4^=$	H_2O	H_2SO_4
Mole %	3.4	22.1	13.2	0.9	60.4

$iC_4 = 1046 \times 0.221 = 231$ lb mol/h
$iC_4^= = 1046 \times 0.132 = 138$ lb mol/h
iC_4 for three reactors = 693 lb mol/h
$iC_4^=$ for three reactors = 414 lb mol/h
The reaction in each reactor is:



The alkylate produced = 414 × 0.92 = 380 lb mol/h
The condition of each stream is shown in Table E10.4.4

Table E10.4.4 Alkylation process stream data

Stream No.	Flow rate (lb/h)	Temperature (°F)	Pressure (psia)
1	20,363	135	130
2	15,436	169.4	135
3	4927	137.2	122
4	11,650	122.6	100
5	53,277	104	124
6	186,500	16	60
7	256,300	36.11	60
8	85,360	36.11	60
9	85,360	36.11	60
10	85,620	36.11	60
11	85,360	44.6	50
12	85,360	44.6	50
13	85,620	44.6	50
14	256,300	44.6	50
15	256,300	44.67	171
16	186,500	44.67	171
17	69,850	44.67	171
18	69,850	100	171
19	43,450	389.2	129
20	26,400	135.4	111
21	6545	151.5	110
22	8111	122.6	100

QUESTIONS AND PROBLEMS

10.1. Why is sulphuric acid alkylation run in liquid phase and at low temperatures?

10.2. What is the role of alkylation in the refinery?

10.3. Calculate the equilibrium conversion of the reaction: 1-pentane + isobutene → 2,2,5-trimethylpentane at 400 K during sulphuric acid alkylation.

10.4. What are the effects of operating variables in alkylation?

10.5. Calculate the alkylation reactor volume for a butylene feed of 3000 BPD with an isobutane/olefin ratio $(I/O)_F$ of 10 at 10 °C using sulphuric acid.

10.6. Make a complete material balance for the alkylation of 2000 BPD of butylene using $(I/O)_F = 6$. Calculate the effluent rates.

10.7. What is the maximum yield of a pentane-free alkylate that can be produced from 80,000 BPD of isobutane and 2000 BPD propylene, 4000 BPD of butylene and 2000 BPD amylene?

10.8. Make UNISIM simulation as in the case of example E10.4, assuming the following olefin composition as mol%.

nC_4	iC_4	$iC_4^=$	C_3	iC_4
5	40	50	2	3

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CHAPTER ELEVEN

HYDROGEN PRODUCTION

11.1. INTRODUCTION

The increasing demand for clean fuels will be a strong incentive to build new refineries with greater conversion and treating capacity. Hydrogen is needed for the conversion processing of heavy petroleum fractions into lighter products and for removing sulphur, nitrogen and metals from many petroleum fractions. The demand for hydrogen in refineries will also depend on the quality of the processed crude oil. Heavier crude oils will necessitate more demand for hydrogen. The stringent specifications of product quality will also increase hydrogen demand. Synthesis gas, as a mixture of hydrogen, carbon oxides and nitrogen, is also produced in large quantities from the manufacture of ammonia or methanol.

11.2. HYDROGEN REQUIREMENTS IN MODERN REFINERIES

Hydrogen consumption is the result of the chemical reaction of hydrogen with the petroleum fractions, ranging from naphtha to vacuum residue in the following processes (Bourbonneux, 2001):

- Hydrotreating of the various cuts ranging from naphtha to heavy vacuum gas oil, to remove sulphur, nitrogen and metals. Consumption of hydrogen ranges from 0.6 kg (1.32 lb) H_2 per ton (2204 lb) of light distillates to 10 kg (22 lb) H_2 per ton for vacuum distillates.
- Hydrocracking and hydroconversion of gas oil and heavier feedstocks to produce light products. The consumption depends on the quality of the feed and the severity of the process and ranges between 15 and 35 kg (33 and 77 lb) of hydrogen per ton of feed.

It is important to note that these processes require hydrogen of high purity (over 99% purity) and at high pressure to meet process and economic requirements.

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11.3. STEAM REFORMING

11.3.1. Flow Process

The production of hydrogen from light hydrocarbons can be done through two process schemes. The old scheme involves the following stages:

- Steam reforming to produce synthesis gas, a mixture of hydrogen and carbon monoxide.
- Conversion of CO to CO_2 with steam. This is done in two stages, a high-temperature shift converter (HTSC) and a low-temperature shift converter (LTSC).
- The hydrogen rich gas is purified by a CO_2 removal unit where a hot potassium carbonate or amine solution absorbs the CO_2.
- A methanator converts the remaining CO and CO_2 into methane and water.

The final hydrogen purity ranges between 95 and 98%. Figure 11.1 shows the process flow diagram.

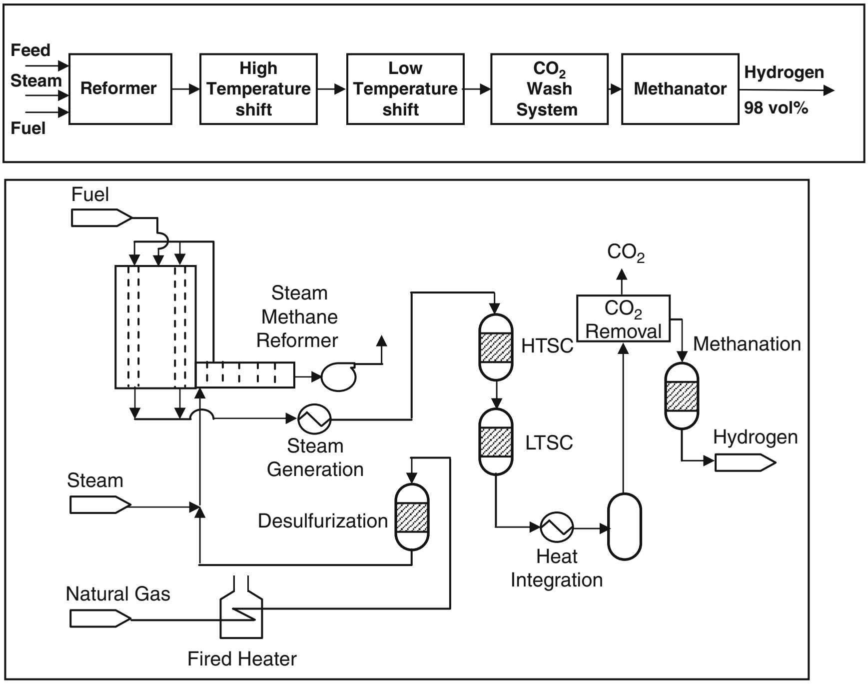


Figure 11.1 Steam reforming with CO_2 absorber and methanator

The newer process scheme differs from the old scheme in CO_2 removal technology. The steps involved in this scheme are as follows:

- Steam reforming to produce synthesis gas, a mixture of hydrogen and carbon monoxide.
- Conversion of CO to CO_2 with steam. This is done in one-stage shift converter.
- A pressure swing adsorption (PSA) unit is used to selectively separate CO_2 through membranes, thus purifying the hydrogen rich product gas stream.

The final product gas is typically 99.9% hydrogen. The higher hydrogen purity is beneficial to the downstream hydrotreating units since it increases the hydrogen partial pressure, lowers the recycle flow, lowers compression costs and increases catalyst life. Figure 11.2 shows the process flow diagram.

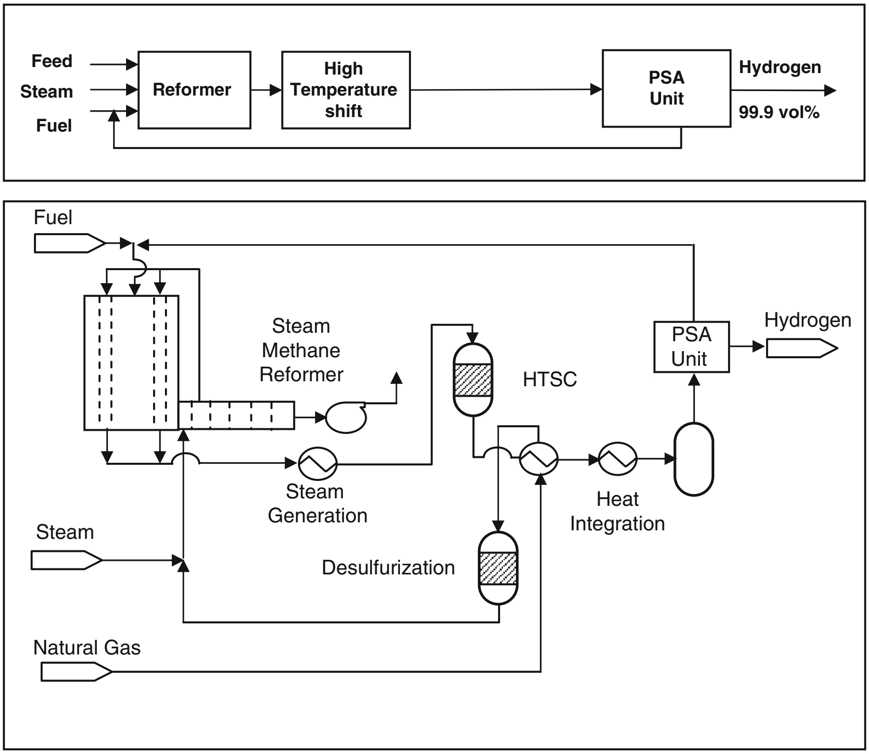


Figure 11.2 Steam reforming with pressure swing adsorber

Details regarding these process schemes will be presented. In any case, since the unit uses catalysts, the feed may contain compounds which can act as poisons to these catalysts. A feed purification step is necessary.

11.3.2. Feed Preparation

The feed to the steam reforming unit is light hydrocarbon streams from the various refinery processes (C_3 to C_7). These streams may contain poisons to the nickel catalyst. Poisons are sulphur compounds such as hydrogen sulphide and mercaptans, and halogenated compounds such as chlorides. Therefore, feed preparation involves the hydrogenation of organic sulphur and chloride into H_2S and HCl respectively, in the presence of a Co–Mo hydrotreating catalyst at 350–400 °C (662–752 °F). The hydrogen sulphide is then adsorbed in a ZnO bed. The treated feed should contain 0.1 ppm sulphur or less, and the chloride content should be limited to 0.5 ppm.

11.3.3. Steam Reforming Reactions

This process produces hydrogen by the chemical reaction of methane and other light hydrocarbons with steam at temperatures of 820–880 °C (1508–1616 °F) and pressures of 20–25 bar (294–368 psi). The catalyst is nickel on alumina support. The feed of light hydrocarbons, mainly methane, is fed to the steam reforming reactor which is essentially tubes filled with a nickel catalyst passing through a furnace. The feed is heated to 540–580 °C (1004–1076 °F) by passing it through the convection section of the furnace. The feed is converted to synthesis gas which is a mixture of H_2, CO, CO_2, CH_4 and H_2O by reaction with excess steam in the radiation section of the furnace. The steam to carbon molar ratio is between 2.5 and 5 (Bourbonneux, 2001).

The reforming reactions are essentially equilibrium reactions meaning that the conversion with the aid of the nickel catalyst approaches the maximum conversion that can be achieved at the reaction temperature and pressure. Therefore, in addition to the catalytic activity of the catalyst, the reaction temperature and pressure, as well as the amount of steam used, will have a great effect on the quality of the hydrogen stream produced from the unit. The main equilibrium reactions are:

$$\begin{gathered} CH_4 + H_2O \leftrightarrows CO + 3H_2, \\ \Delta H = +206\ \text{kJ/mol},\ \Delta G_{298} = -58.096\ \text{kJ/mol} \end{gathered} \tag{11.1}$$

$$\begin{gathered} CO + H_2O \leftrightarrows CO_2 + H_2, \\ \Delta H = -41\ \text{kJ/mol},\ \Delta G_{298} = -28.606\ \text{kJ/mol} \end{gathered} \tag{11.2}$$

$$\begin{gathered} CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2, \\ \Delta H = +165\ \text{kJ/mol},\ \Delta G_{298} = 113.298\ \text{kJ/mol} \end{gathered} \tag{11.3}$$

The first reaction is highly endothermic ($\Delta H^{\circ}_{298} = 206$ kJ/mol) whereas the carbon monoxide conversion is moderately exothermic ($\Delta H^{\circ}_{298} = -41$ kJ/mol). For light hydrocarbons other than methane, the reforming reaction becomes:

$$C_nH_m + nH_2O \leftrightarrows nCO + \left(\frac{m+2n}{2}\right)H_2 \tag{11.4}$$

This reaction occurs through the conversion of the light hydrocarbons to methane followed by the methane reforming reaction. Overall, the reforming reaction (11.4) is also endothermic.

11.3.4. Thermodynamics of Steam Reforming

The steam reforming of methane consists of two reversible reactions: the strongly endothermic reforming reaction (11.1) and the moderately exothermic water-gas shift reaction (11.2). Due to its endothermic character, reforming is favoured by high temperature. Also, because reforming is accompanied by a volume expansion, it is favoured by low pressure. In contrast, the exothermic shift reaction is favoured by low temperature, while unaffected by changes in pressure.

Increasing the amount of steam will enhance the CH_4 conversion, but requires an additional amount of energy to produce the steam. In practice, steam to carbon ratios (S/C) around 2.5–5 are applied. This value for S/C will also suppress coke formation during the reaction.

In calculating the thermodynamic yields, we can apply the standard chemical reaction equilibrium methods which involve calculating the equilibrium constant in the gas phase (K_p) and then solving to obtain the hydrogen yield. Since reforming involves multi-reactions, the method of minimization of the total Gibbs energy at equilibrium is appropriate in this case. In this method, we only specify the species involved in the reactions (reactants and products) and their initial or inlet amounts without necessarily specifying the actual reactions. The total Gibbs energy of the reaction mixture is given by (Elliot and Lira, 1999):

$$G = \sum n_i \overline{G_i} \quad \text{and} \quad \frac{\overline{G_i}}{RT} = \frac{G_i}{RT} + \ln y_i + \ln P \tag{11.5}$$

The standard Gibbs energy G_i is given by Gibbs energy of formation at the reaction temperature and at the standard pressure of 1 bar (14.7 psia).

$$\frac{G_i}{RT} = \frac{\Delta G^{\circ}_{f,i}}{RT} \tag{11.6}$$

The standard Gibbs energy is obtained for each compound from $\Delta G^{\circ}_{f,298}$ and corrected for the temperature of the reaction.

The minimization of the total Gibbs energy of the reaction system is performed, subject to certain constraints which must be satisfied. These constrains are the atomic balances. This means that the number of moles of each atom in the feed must equal the number of moles of that atom in all species at equilibrium. The atomic balances are:

$$\text{O-balance:}\quad 2n_{CO_2} + n_{CO} + n_{H_2O} = n_{H_2O}^{\text{feed}} \tag{11.7}$$

$$\text{H-balance:}\quad 4n_{CH_4} + 2n_{H_2} + 2n_{H_2O} = 4n_{CH_4}^{\text{feed}} + 2n_{H_2O}^{\text{feed}} \tag{11.8}$$

$$\text{C-balance:}\quad n_{CH_4} + n_{CO_2} + n_{CO} = n_{CH_4}^{\text{feed}} \tag{11.9}$$

The minimization process is performed using Solver in the Excel spreadsheet. The temperature and pressure of the reaction as well as the steam-to-methane ratio are entered. A typical example of Gibbs minimization is shown in Example E11.1.

Example E11.1

Feed containing 1 mol CH_4 and 3 mol of H_2O enters a steam reformer at 40 bar and 1073 K. Calculate the composition of the product on a dry basis.

The standard Gibbs free energies of the components are given in the table below

Component	G_i/RT
CH_4	3.193
CO_2	−44.375
CO	−23.164
H_2	0.0
H_2O	−21.146

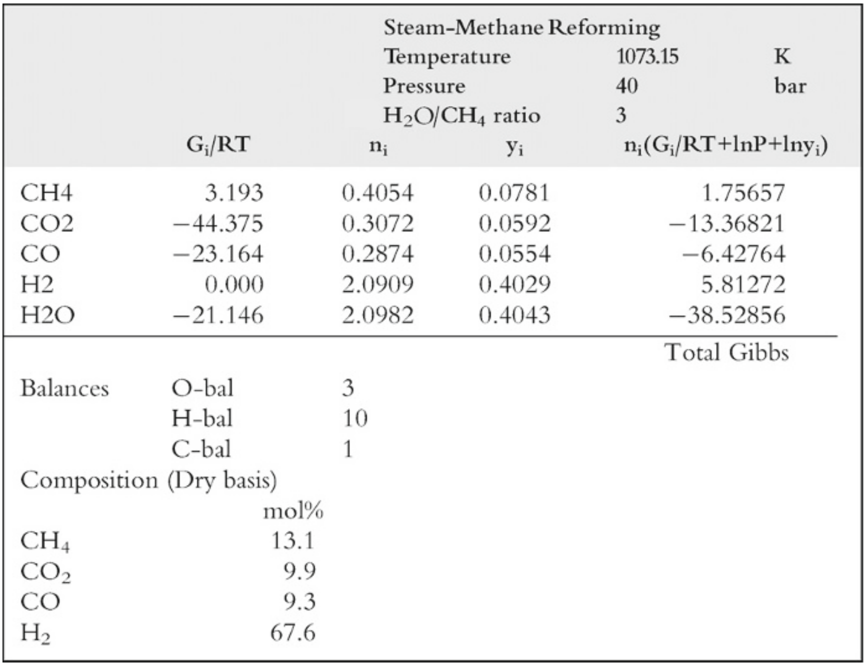
Solution:

Based on the steam-to-methane ratio, the moles of O, H and C atoms are calculated from equations (11.7)–(11.9). Initial guess is inserted for the number of moles of each component in the product stream. Based on this guess, composition is calculated and the Gibbs free energy is calculated from equation (11.5).

The total Gibbs free energy is then summed up. The Excel Solver is used to minimize the total Gibbs free energy cell by changing the number of moles which was initially guessed with the constraints of:

O-bal: $n_{H_2O} = 3$
H-bal: $4n_{CH_4} + 2n_{H_2O} = 4(1) + 2(3) = 10$
C-bal: $n_{CH_4} = 1$

Figure E11.1 shows the results.



Steam-Methane Reforming

Temperature	1073.15	K
Pressure	40	bar
H_2O/CH_4 ratio	3	

	G_i/RT	n_i	y_i	$n_i(G_i/RT+\ln P+\ln y_i)$
CH4	3.193	0.4054	0.0781	1.75657
CO2	−44.375	0.3072	0.0592	−13.36821
CO	−23.164	0.2874	0.0554	−6.42764
H2	0.000	2.0909	0.4029	5.81272
H2O	−21.146	2.0982	0.4043	−38.52856
				Total Gibbs

Balances	O-bal	3
	H-bal	10
	C-bal	1

Composition (Dry basis)

	mol%
CH_4	13.1
CO_2	9.9
CO	9.3
H_2	67.6

Figure E11.1 The reforming reactions spreadsheet

Example E11.2

For a reformer feed of methane and steam at a ratio of 2.5 mol of H_2O to 1 mol CH_4 and at 20 bar, study the effect of the reaction temperature on the hydrogen purity on dry basis in the range 800–900 °C. If the reaction temperature is 850 °C, study the effect of the steam-to-methane ratio in the range 2–5.

Solution:

Using the Excel spreadsheet, vary the temperature and use the solver to get the equilibrium yield. The results are plotted in Figure E11.2.1. As temperature increases, the hydrogen purity increases.

Figure E11.2.2 shows the effect of the H_2O/CH_4 ratio at 850 °C and 20 bar. As this ratio increases, the equilibrium conversion increases and the hydrogen purity increases.

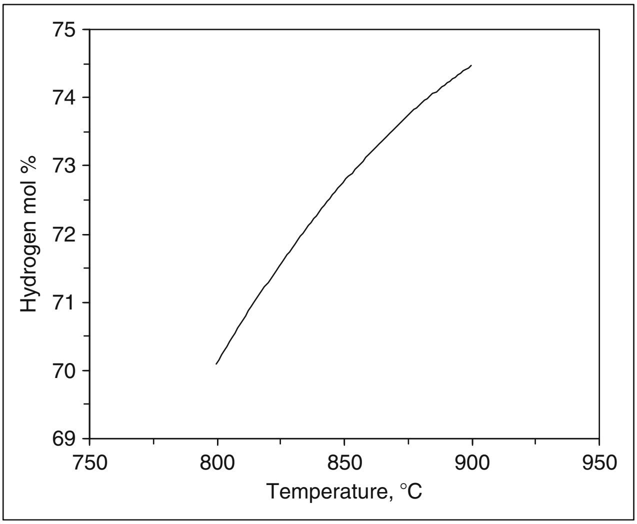


Figure E11.2.1 Effect of reforming reaction temperature on hydrogen purity at 20 bar and 2.5 H_2O/CH_4 ratio

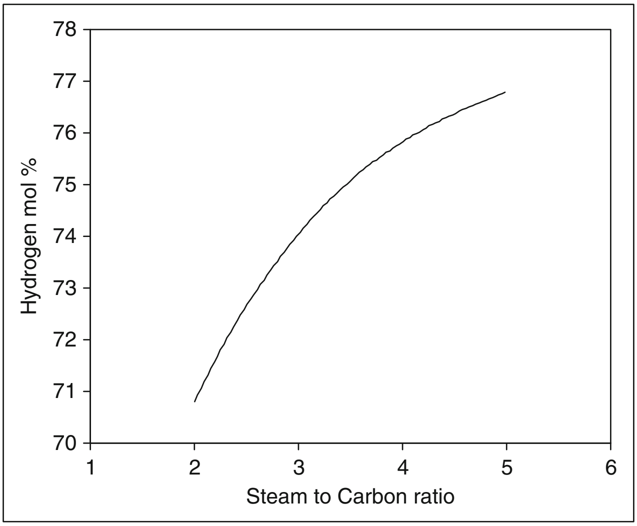


Figure E11.2.2 Effect of feed H_2O/CH_4 ratio on equilibrium hydrogen purity at 850 °C and 20 bar

11.3.5. Operating Variables (Crew and Shumake, 2006)

11.3.5.1. Steam to Carbon Ratio

The steam to carbon ratio is the ratio of moles of steam to moles of carbon in the reformer feed. It is obtained by dividing the molar flow rates of steam and feed. The reformer feed must contain sufficient steam to avoid thermal cracking of the hydrocarbons and coke formation. An excess of steam (over the stoichiometric ratio) is usually used. The higher the steam to carbon ratio, the lower the residual methane will be for a given reformer outlet temperature. Hence, less fuel energy is required in the furnace. The design steam to carbon is typically 3.0 with a range between 2.5 and 5.0.

11.3.5.2. Reformer Inlet Temperature

Since the reforming reaction is endothermic, it is favoured by high temperature. The reformer catalyst tube inlet temperature is maintained at 540–580 °C (1004–1078 °F). The hydrocarbon steam feed is preheated by the hot flue gas in the waste heat recovery (convection) section of the furnace. A higher inlet temperature decreases the amount of fuel required to supply heat to the reaction tubes and decreases the number of tubes and the size of the furnace. Utilization of the hot flue gas to reheat the feed increases the energy efficiency of the process and decreases the steam generation in the waste heat recovery section.

11.3.5.3. Reformer Outlet Temperature

The reformer outlet temperature is the most important process variable that determines the purity of the hydrogen product. The higher the reformer outlet temperature the lower will the residual methane be (higher hydrogen purity) for a given feed rate and steam to carbon ratio. The upper limit of the outlet temperature is governed by the design maximum tube skin temperature which is 1093 °C (2000 °F). High-temperature operation is not necessarily the most economic method taking into consideration the amount of fuel to be burned for an increase in purity. The reformer has been designed for normal operation at outlet temperature in the range of 820–880 °C (1508–1616 °F). The lower feed gas rate will lower the required reformer outlet temperature for the same hydrogen purity. Similarly, the higher steam to carbon ratio will lower the required reformer outlet temperature for the same hydrogen purity.

11.3.5.4. Reaction Pressure

In the reforming reaction, the volume of the products is three times higher than the volume of reactants. Therefore, at a fixed temperature and steam to carbon ratio, lower pressure favours the equilibrium of the reaction. The design outlet pressure of the reformer is in the range 20–25 bar (294–368 psia). The operating pressure of the heater is not fixed locally.

Table 11.1 Reformer outlet composition for different feeds at 850 °C, 24 bar and steam to carbon ratio of 4

Feedstock	Methane	Natural gas	LPG	Naphtha
Composition (vol%)				
CH_4	3.06	2.91	2.39	2.12
CO	12.16	12.62	13.62	14.17
CO_2	9.66	10.40	12.73	14.19
H_2	75.12	73.98	71.86	69.52
N_2	–	0.38	–	–

This is governed by the unit system pressure set by the pressure required at the hydrogen product export header.

11.3.5.5. Feed Type

Light hydrocarbons constitute suitable feed to the steam reformer. Table 11.1 shows the reformer outlet composition (on dry basis) for several feeds.

The light hydrocarbons in the feed are first converted to methane. Then the methane–steam reforming reactions take place. A methane rich feed gives higher hydrogen purity.

11.3.5.6. Space Velocity

Lower space velocity favours the reaction as residence time increases. However, this leads to reduced output gas.

11.3.5.7. Catalyst Activity

Higher catalyst activity favours the reforming reaction. The catalyst is poisoned by sulphur, chloride and arsenic. The catalyst is poisoned by sulphur due to slippage of mercaptan and hydrogen sulphide along with the feed. There is also the possibility of catalyst poisoning due to sulphate carry-over with water mist in steam and dissolved H_2S in impure boiler feed water. The catalyst can also be poisoned by carry-over of arsenic present in ZnO. Chlorine and phosphorous poisoning can come from boiler feed water.

As the steam reforming reaction decreases over time due to catalyst poisoning, the hydrogen purity can be maintained by increasing the furnace outlet temperature and increasing the steam to carbon ratio.

11.3.6. Reformer Process Simulation

Process simulators have become essential tools for the design and performance evaluation of petroleum refining processes and process equipment. In this section the process simulator UNISIM (UNISIM, 2007) will be utilized to simulate the reformer furnace as an equilibrium reactor. This is a reasonable assumption, since the reforming reactions are essentially equilibrium reactions. The following example illustrates such simulation.

Example E11.3

Calculate the outlet reformer temperature, synthesis gas composition and the heat transferred in the reformer furnace for natural gas feed. The composition of the feed is:

	mol%
CH_4	94.1
C_2H_6	4.0
C_3H_8	0.8
CO_2	1.0
N_2	0.1

Inlet temperature is 550 °C. The steam to carbon ratio is 2.5. Steam is available at 600 °C. Pressure is 20 bar. Assume no pressure drop in the furnace. The outlet temperature of the reforming synthesis gas is 850 °C.

Solution:

On the basis of 100 kmol/h of natural gas feed,

Steam flow rate $= (2.5)(100)(0.941 + 2\times0.04 + 3 \times 0.008) = 261.25$ kmol/h Using UNISIM simulator, define the natural gas stream and the steam. Use the Peng–Robinson equation of state as the thermodynamic package. Define the reaction set; that is the reactions involved in the process. Enter the stoichiometric coefficients for each reaction. The process is modelled as a mixer followed by an equilibrium reactor as shown in Figure E11.3.

A summary of the results is presented in Table E11.3.

The heat transferred in the reformer is 2.258×10^7 kJ/h.

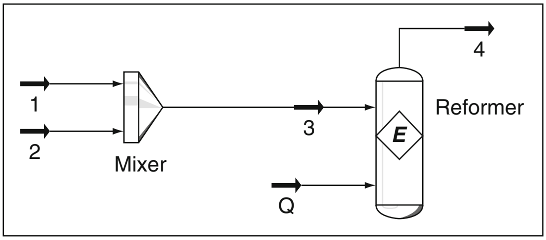


Figure E11.3 Simulation of the reformer

Table E11.3 Summary of results

	Stream 3	Stream 4
Temperature (°C)	579.16	850.00
Molar flow rate (kmol/h)	361.25	529.18
Composition (mol%)		
CH_4	0.26048	0.03880
C_2H_6	0.01107	0.00000
C_3H_8	0.00222	0.00000
CO_2	0.00277	0.05223
N_2	0.00028	0.00019
H_2O	0.72318	0.28468
CO	0.0	0.10833
H_2	0.0	0.51577

11.4. PRODUCT PURIFICATION

The CO in the reformed gas is converted to CO_2 according to reaction (11.2). Due to thermodynamic and kinetic considerations, this is accomplished to two stages: High Temperature Shift Converter (HTSC) and Low Temperature Shift Converter (LTSC), Since the reaction is exothermic the equilibrium yield is favoured by lower temperature; however, the reaction needs a catalyst and the reaction rate favours high temperature.

11.4.1. High-Temperature Shift Converter

Carbon monoxide reacts with steam at high temperature 300–560 °C (572–1040 °F) in the presence of CuO/FeO or Fe_3O_4/Cr_2O_3 catalyst. Most of the CO in the process gas is converted to CO_2. The remaining CO in the outlet gas is between 2 and 3%. The reaction is exothermic and is carried out in a fixed-bed reactor. Temperature affects shift converter operation in two ways: a higher temperature increases the catalyst activity and the reaction proceeds closer to equilibrium. At each catalyst activity level there is an optimum operating temperature. Higher temperature increases CO in the outlet gas due to equilibrium. Lower temperatures also increase CO in the outlet gas due to the decrease in catalyst activity. Multiple catalyst beds with external cooling are used to control the reaction temperature. When the catalyst is new and the catalyst activity is high, the optimum temperature is lower for any given flow and composition. This lower temperature also prolongs the catalyst life. As the catalyst ages, the CO conversion can be maintained by increasing inlet temperature, increasing steam flow or reducing space velocity. Thermodynamically, the shift conversion reaction is not affected by pressure since the number of moles of reactants and products are equal. At design conditions, CO content at HTSC outlet is reduced to 2.61 vol%.

11.4.2. Low-Temperature Shift Converter

The product gas from HTSC is routed to a boiler feed water pre-heater. The gas temperature is reduced to 230 °C (446 °F). Most of the CO is converted to CO_2 leaving the CO content less than 0.2 vol%. The catalyst is CuO/ZnO which is very expensive. It must be protected from sulphur and both high and low temperatures. Any condensation in the presence of carbon oxides damages this catalyst. The catalyst temperature should not exceed 288 °C (550 °F).

11.4.3. Carbon Dioxide Removal

The gases from the shift converter contain 16–20% CO_2, which is removed by selective absorption in an amine or carbonate solution. Amine absorption is an effective technique to remove CO_2; however, this technique has notable disadvantages. First, once the amine solution is saturated, the process to reactivate the solution (i.e., remove the bound CO_2 from the amine groups in the solution) for reuse requires a high amount of energy. Second, this process has a tendency to corrode equipment. Third, over a short period of time, the amine solution loses viability through amine degradation and loss.

11.4.3.1. Amine Treating

The amine absorber system is designed for the removal of carbon dioxide from the product gas. The system is highly efficient and results in a single operation requiring less equipment than other multiple absorbent systems. The carbon dioxide removal system consists principally of an absorber, regenerator and heat exchangers. CO_2 in the incoming gas is removed by scrubbing in an aqueous amine solution. Rich amine solution is regenerated by reboiling. The heat for reboiling is supplied by the process gas exiting the LTSC.

The amine solution removes CO_2 by chemical absorption; that is CO_2 bonds with the amine. Monoethanolamine (MEA) is usually used. However, it has two drawbacks: first, it requires higher energy for desorption of CO_2, secondly, carbamates which are very corrosive, are formed (equation 11.10).

$$CO_2 + \underset{\text{Amine}}{3H_2NC_2H_4OH} \rightarrow \underset{\text{Carbamates}}{OHC_2H_4NCOO} + 2H_3NC_2H_4OH \qquad (11.10)$$

Methylethanolamine (MDEA) has replaced MEA in many units. The weaker bond created between the amine and CO_2, without any carbamates being formed, makes the regeneration less energy-intensive and the amine solution less corrosive.

After cooling, the synthesis gas from LTSC flows to the bottom of the CO_2 absorber. The CO_2 content of the process gas is removed by scrubbing with 15–30% aqueous amine solution.

Rich amine solution from the bottom of the absorber at 65 °C (149 °F) is heated to 100 °C (212 °F) in amine exchangers. Then it is flashed into the top of the amine regenerator where CO_2 is stripped from the solution. The overhead stream (CO_2 + water vapour) from the regenerator flows to the condenser. It is cooled and most water vapour present is condensed. The CO_2 vapour stream is vented to the atmosphere. The desorption efficiency of the regeneration can be measured by the residual CO_2 loading of the lean solution. A simplified process flow diagram is shown in Figure 11.3. Operating variables for the absorption section are absorption temperature, flow rate and concentration of lean amine solution. Amine regeneration is affected by heat input in the reboiler, pressure and reflux.

11.4.3.2. Methanation

The purpose of the methanator is to convert the residual CO and CO_2 to methane according to the following reactions:

$$CO + 3H_2 \leftrightarrows CH_4 + H_2 \qquad (11.11)$$

$$CO_2 + 4H_2 \leftrightarrows CH_4 + 2H_2 \qquad (11.12)$$

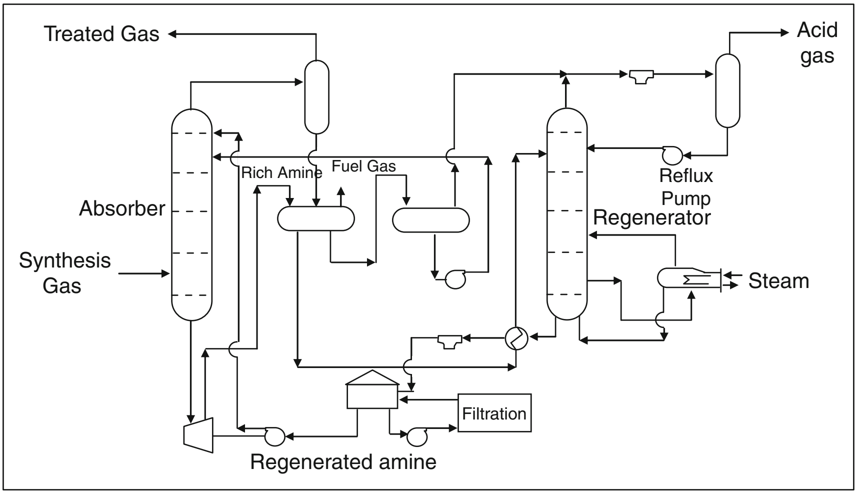


Figure 11.3 Amine treating process

Both reactions are exothermic. Methanation is carried out in a fixed-bed catalytic reactor at temperatures between 300 and 340 °C (572 and 644 °F) over a nickel catalyst. At these temperatures, conversion is almost complete with residual CO and CO_2 less than 10 ppm. The temperature rise in the catalytic bed is in the order of 30 °C (86 °F) for a CO content of 0.3% and CO_2 content of 0.1% in the inlet.

11.4.3.3. Pressure Swing Adsorption (PSA)

The reformed gas from the shift converter which contains 65–70 vol% hydrogen can be purified by adsorption instead of amine treatment and methanation. The process produces a higher purity hydrogen stream (99.9%).

PSA is a cyclic process involving the adsorption of impurities (CO, CO_2, CH_4 and N_2) from a hydrogen-rich gas stream at high pressure on a solid adsorbent such as a molecular sieve. The operation is carried out at room temperature and at the reformed gas pressure of 20–25 bar (294–368 psia). Several adsorption vessels (adsorbers) are employed as shown in Figure 11.4. The feed gas is switched from one adsorption vessel to another. While adsorption takes place in one vessel, the adsorbent in another vessel is being regenerated. A complete pressure swing cycle for each adsorber goes like this:

- Adsorption takes place in a fresh adsorber producing high purity gas. The impurities are adsorbed onto the internal surfaces of the adsorbent bed. When this adsorber reaches its adsorption capacity and no more impurities can be removed, it is taken off-line, and the feed is switched to another fresh adsorber.
- To recover the hydrogen trapped in the adsorbent void spaces in the adsorber, the adsorber is depressurised from the product side in the

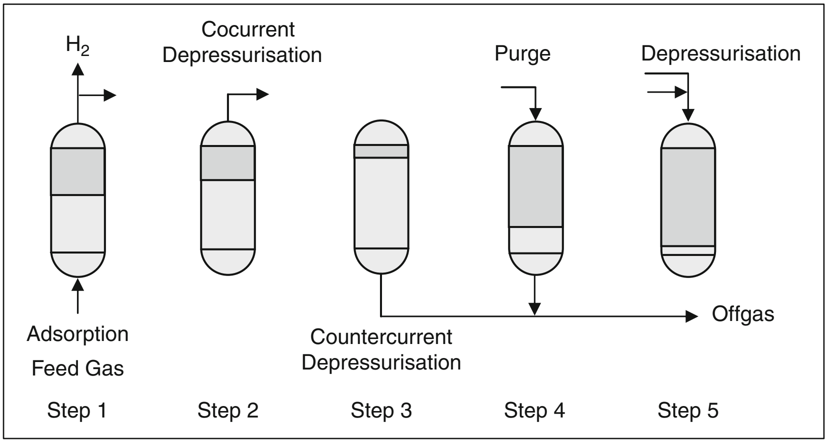


Figure 11.4 Pressure swing adsorption cycle (Stocker and Whysall, 1998)

same direction as the feed flow direction (cocurrent), and high-purity hydrogen is withdrawn. The hydrogen is used internally in the system to repressurise and purge other adsorbers.
- The bed is then partly regenerated by depressurising in a counter-current flow of gas from other beds, and the desorbed impurities are rejected to the PSA off-gas.
- The adsorbent is then purged with high-purity hydrogen (taken from another adsorber on cocurrent depressurisation) at constant off-gas pressure to further regenerate the bed.
- The adsorber is then repressurised with hydrogen prior to being returned to the feed step. The hydrogen for repressurisation is provided from the cocurrent depressurisation and with a slipstream from the hydrogen product. When the adsorber has reached the adsorption pressure, the cycle has been completed, and the adsorber is ready for the next adsorption step.

In addition to hydrogen production, PSA technology is used for purifying hydrogen streams from other units in the refinery, in petrochemical units, the steel industry and hydrogen for fuel cells. The advantages of the PSA process are:

- High purity of hydrogen: 99.9%. Conventional units with amine treating and methanation seldom achieve purity higher than 98%.
- Purity in conventional units depends on the quantity of inerts in the feed. The PSA process yields over 99.9% purity regardless of feed quality.
- The conventional process requires severe steam reforming operating conditions in the reformer furnace to get over 97% H_2 purity. The PSA process allows less severe operating conditions and still achieves high purity. However, this results in 3–8% unreacted methane in the purge stream.
- Purity can be increased on request.
- High efficiency of hydrogen recovery: up to 90%.
- PSA technology is more reliable and requires less capital cost.
- Operating costs in the PSA process are lower due to lower energy expenditures. The PSA purge is used as furnace fuel. Considerable steam is produced and can be exported to other units in the refinery.

11.5. NEW DEVELOPMENTS IN STEAM REFORMING

As the demand for hydrogen increases, and as energy costs increase, hydrogen manufacture by steam reforming is undergoing continuous improvements. Some of these recent developments are highlighted below (Rostrup-Nielsen, 2005):

- Development work is focused on new steam reforming catalysts with higher activity and lower pressure drops. The catalyst will also be less resistant to heat transfer, resulting in more heat to the reaction at a lower tube skin temperature and a closer approach to equilibrium conversion.
- New shift conversion catalysts operating at lower steam to carbon ratios and lower temperatures are being developed.
- In recent years, the energy efficiency of the process has improved significantly. The operating cost (feed and fuel – steam export) amounts to two-thirds of the hydrogen production cost. Old hydrogen plants operate at reforming temperatures well below 900 °C (1652 °F) and high steam to carbon ratio. These plants have poor energy efficiency as large quantities of steam have to be condensed. In addition, their investment costs are high as they require large flows. Modern plants are designed with reforming temperatures above 900 °C (1652 °F) and steam to carbon ratios below 2.5. The new developments include utilizing the more energy-efficient side-fired reforming furnace and using medium temperature shift catalyst.
- New improved tube materials with a design skin temperature up to 1050 °C (1922 °F) are utilized in reforming furnaces. New reformer designs with smaller tube diameters have a smaller size but twice the heat flux of older designs.

QUESTIONS AND PROBLEMS

11.1. For a reformer feed of methane and steam at a ratio of 3.5 at 20 bar, study the effect of the reaction temperature on the hydrogen purity on dry basis in the range 500–900 °C.

11.2. Calculate the synthesis gas composition in the reformer furnace for natural gas feed. The composition of the feed is: 97 mol% CH4 and 3 mol% CO_2. The steam to carbon ratio is 2.5. Pressure is 20 bar. The outlet temperature of the reforming synthesis gas is 850 °C.

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CHAPTER TWELVE

CLEAN FUELS

12.1. INTRODUCTION

Environmental awareness had been continuously increasing in many places in the second half of the last century, whether governmental wise or public wise. Environment Protection Agencies (EPAs) worldwide set regulations to forbid or control the pollution of the environment. Petroleum fuels are considered one of the main pollution problems. Clean fuels are free of impurities (sulphur and benzene) but sometimes work is needed to improve their properties (e.g. octane number for gasoline, cetane number for diesel and freezing point for jet fuels) if possible. The main ways of producing clean fuels are:

- Deep desulphurization of fossil fuels (produced from crude oil)
- Natural gas and gasification of coal
- Biofuel from available biological sources like wood, vegetable oil and seeds
- Alkylation

12.2. SPECIFICATIONS OF CLEAN FUELS

Clean fuels are fuels that contain very few of components that may harm the environment, like sulphur, nitrogen, and organometallic compounds. Benzene can also be included along with polycyclic aromatic hydrocarbons (PAH). Tables 12.1 and 12.2 list gasoline and diesel specifications, respectively (Chauhan, 2002). In addition, Tables 12.3 and 12.4 list ASEAN gasoline and diesel specifications, respectively (Chauhan, 2002).

The increase in octane, required as a result of lead phase out, has involved refineries investing in a wide range of octane boosting processes, including isomerization, reforming, alkylation, MTBE and other oxygenated compounds.

Fundamentals of Petroleum Refining
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Table 12.1 Key specifications for gasoline

Specification	Euro 2000	Euro 2005	USA 2005	Canada 2005
Sulphur max. (wppm)	150	50	80	30
Benzene max. (vol%)	1	1	1	<1
Aromatics max. (vol%)	42	35	–	–
Olefins max. (vol%)	18	–	–	–
Density (kg/m^3)	715	715	739	730

Table 12.2 Key specifications for diesel

Specification	Euro 2000	Euro 2005	USA 2005	Canada 2005
Sulphur max (wppm)	50	50	15	50
Density (kg/m^3)	820–845	820–845	840	
Cetane number	>51	>51	>51	>51
*PAH (wt%)	<11		11	
T95 °C	<360			

*PAH is poly cyclic aromatic hydrocarbon

Table 12.3 Domestic gasoline specifications in the ASEAN region

Specification	Malaysia	Thailand	Singapore	Indonesia	Philippines	Vietnam
RON	93/97	92/97	97	94	93	92
Sulphur max. (wt%)	0.1	0.1		0.2		0.05
Benzene max. (vol%)	–	3.5	–	–	6	5
Aromatics max. (vol%)	–	50	–	–	45	–
Olefins max. (vol%)	10	–	–	–	–	–

Table 12.4 Diesel quality specifications in the ASEAN region

Specification	Malaysia	Thailand	Singapore	Indonesia	Philippines	Vietnam
Sulphur max. (wt%)	0.05	0.05	0.5	0.5	0.5	0.3
Density (kg/m^3)	–	820–890	860 max.	820–870		860 max.
Cetane number	50	–	–	45		–
Aromatics (wt%)	–	–	–	–		–
PAH (wt%)	–	–	–	–		–
T90 °C	370	338	370	–		370
T95 °C	–	–	–	–		–

12.3. Production of Clean Fuels from Crude Oil

In the last few decades it was found that even those fractions that cannot be used can be treated to remove impurities and then utilized. The goal of producing clean or even ultra-clean fuels can be achieved in many ways from many sources like natural gas, biological fuels and alkylation. The most important and common concept in the production of clean fuels is deep desulphurization for producing clean and ultra-clean gasoline, diesel and jet fuel.

12.3.1. Deep Desulphurization

Deep desulphurization means that the sulphur content should be lowered as much as possible (e.g. 30 ppm for gasoline and 15 ppm for diesel). The approaches of deep desulphurization can be divided into two major categories: deep hydrodesulphurization (DHDS) and deep non-hydrodesulphurization (DNHDS). Figure 12.1 shows a flowchart of different desulphurization technologies. The major problem in deep desulphurization is how to remove the sulphur to approach the clean fuel level without increasing the aromatic content and losing the olefins which will result in the loss of octane number in the case of gasoline and the loss of cetane number in the case of diesel. These two major problems usually occur during the production of clean gasoline, diesel and jet fuels using the regular DHDS process.

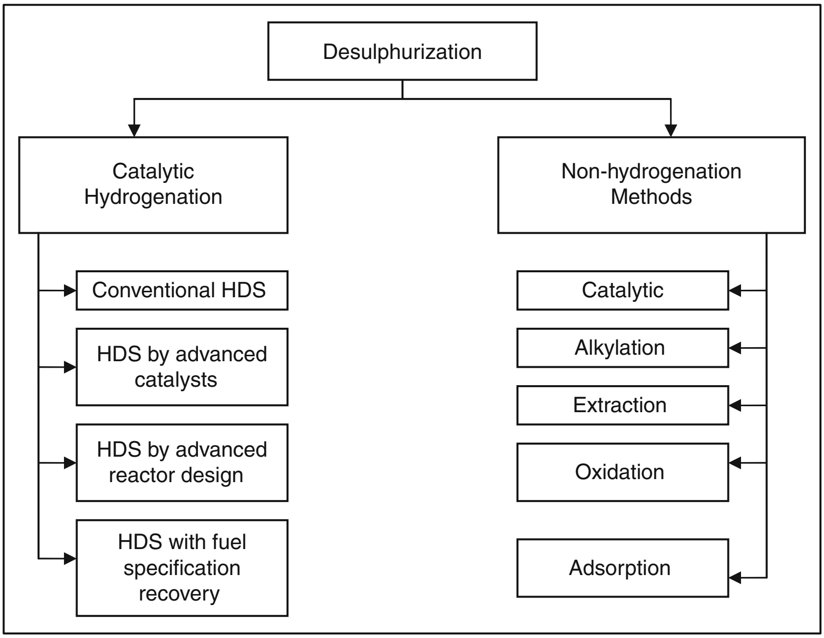


Figure 12.1 Desulphurization technologies classified by nature of a key process to remove sulphur

In light fuel fractions such as naphtha and kerosene, the removal of mercaptans and sulphides, as well as light benzothiophenes, can be carried out by hydrogenation. However, for heavier fractions such as gas oil, the removal of dibenzothiophenes is the key for efficient desulphurization. Dibenzothiophenes decrease in reactivity and increase in desulphurization hardness (refractory sulphur compounds) as their molecular weight increase. This behaviour is presented in Table 12.5.

The DHDS process for producing ultra-clean fuels requires severe operating conditions (high temperature and pressure) and low space velocity which will increase the fixed capital investment for the process due to the increase of equipment size and the high operating cost.

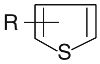
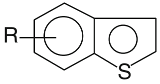
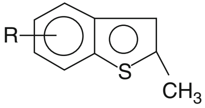
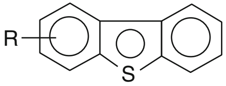
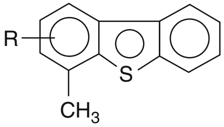
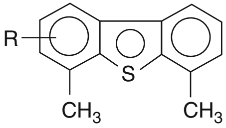
Example E12.1

100,000 BPD crude oil with 2 wt% sulphur is fed into a distillation column. The crude TBP and API as a function of liquid volume (LV%) are as follows:

$$\mathrm{TBP}(^\circ\mathrm{R}) = \left\{\left(2\ln\left(\frac{100}{100-\mathrm{LV\%}}\right)\right)^{2.5}+1\right\}490 \qquad \text{(E12.1.1)}$$

$$\mathrm{API} = -0.0004\,\mathrm{LV\%}^3 + 0.05\,\mathrm{LV\%}^2 - 2.4\,\mathrm{LV\%} + 72 \qquad \text{(E12.1.2)}$$

Table 12.5 Reactivity of various organic sulphur compounds in HDS versus their ring sizes and positions of alkyl substitutions on the ring

Compound name	Structural formula	Fuel range
Sulphide	R–SH	Gasoline
Disulfide	R–S–S–R	Gasoline
Thiophene		Gasoline
Benzothiophene		Gasoline
Methylbenzothiophene		Gasoline
Dibenzothiophene		Gasoline
Methyldibenzothiophene		Gasoline and jet fuel
DiMethyldibenzothiophene (DMDBT)		Jet fuel and diesel

Decrease of reactivity and increase of desulfurization hardness

The produced VGO (850–1050 °F) cut is fed to a hydrotreater unit to remove 90% of the sulphur. The clean VGO is then introduced to the FCC unit at 70% conversion to produce gasoline. More information is listed and shown in Figure E12.1.1. Calculate the amount of clean gasoline.

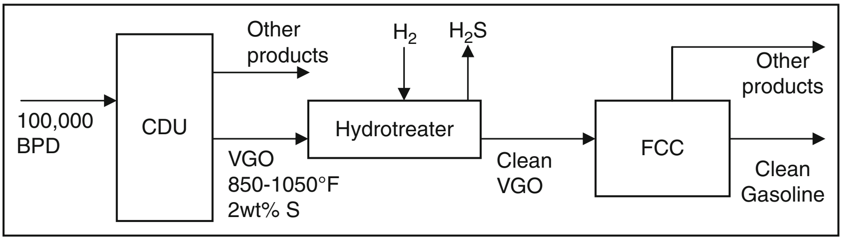


Figure E12.1.1 Process flowchart

Solution:

For VGO (850–1050 °F):

Substituting in equation (E12.1.1), we obtain LV% at IBP and EBP

Cut volume = 48.849–45.9 = 2.949%

API = 28 at mid LV% substituted in equation (E12.1.2)

Volume of VGO = 2949 BPD

Amount of VGO = 38,190 lb/h

Hydrotreating unit:

At 90% sulphur removal (severity) and using equation (7.26)

Required H_2 = 110.2(2) + 10.2 (90) – 659 = 480.6 SCFB

From equation (7.27)

$$\Delta API_p = 0.00297(SCFB\ H_2) - 0.11205\ API_f + 5.54 = 3.83188$$

$$API_p = 28 - 3.83188 = 24.168$$

Amount of sulphur in VGO = 0.02 (38,190) = 763.8 lb/h

Clean VGO = 38,190 – 0.9 (763.8) = 37,503 lb/h = 2828 BPD

FCC unit:

At 70% conversion and using the FCC correlations in Table 8.4

FCC gasoline vol% = 0.7754(70) − 0.778 = 57.377%

FCC gasoline API = −0.19028 (70) + 0.02772 (57.377) + 64.08 = 51.4

Gasoline amount = 0.57377 (2828) = 1622.6 BPD = 18,320 lb/h

12.3.1.1. Deep Hydrodesulphurization (DHDS)

Conventional HDS Hydrodesulphurization means using the regular hydrotreating process for the purpose of sulphur removal, as was discussed in detail in Chapter 7. The same regular hydrotreating process can also be used to achieve the goal of producing clean and ultra-clean fuels. In this case, the treated fuel will lose its olefin content due to the saturation that usually happens in the HDS reactor.

Selective DHDS means converting organic sulphur to H_2S by selective HDS while preserving olefins. The concept of this approach is mainly about redesigning the catalyst to be able to remove sulphur and not saturate the olefins. This can be done by eliminating the active sites that saturate the olefins from the catalyst surface. The final result of this approach is that the organic sulphur is converted to hydrogen sulphide, but the olefinic species are largely preserved for preventing octane loss in the case of gasoline. This approach uses both the concept of advanced catalysis and the new reactor design.

Example E12.2

100 lb/h stream contains 30 wt% C_5H_{10}, 15 wt% C_6H_6, 50 wt% C_8H_{18} and 5 wt% thiophene. This stream is fed to the HDS unit to remove 100% of the sulphur. The following reactions are assumed to take place:

$$C_4H_4S + 4\,H_2 \rightarrow C_4H_{10} + H_2S, \quad 100\%\ \text{conversion} \tag{E12.2.1}$$

$$C_5H_{10} + H_2 \rightarrow C_5H_{12}, \quad 70\%\ \text{conversion} \tag{E12.2.2}$$

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}, \quad 80\%\ \text{conversion} \tag{E12.2.3}$$

$$C_8H_{18} \rightarrow C_4H_8 + C_4H_{10}, \quad 80\%\ \text{conversion} \tag{E12.2.4}$$

Calculate the HDS unit production and the required hydrogen.

Solution:

It can be observed from the above reactions that reaction (E12.2.1) is desired due to the need of removing sulphur. But reaction (E12.2.2) is undesired because the olefin is converted to paraffin which will affect the octane yield. Reaction (E12.2.3) is desired because benzene is a carcinogenic compound and needs to be converted. The last reaction (E12.2.4) is the desired paraffin reaction into olefin.

Reaction (E12.2.1):
5 lb/h $C_4H_4S/84 = 0.0595$ lbmol/h
Needs 0.2381 lbmol/h = 0.4762 lb/h H_2
Produces 0.0595 lbmol/h $C_4H_{10} = 3.451$ lb/h
0.0595 lbmol/h $H_2S = 2.023$ lb/h
Reaction (E12.2.2):
30 lb/h $C_5H_{10}/70 = 0.428257$ lbmol/h
Reacted $C_5H_{10} = 0.428257\ (0.7) = 0.3$ lbmol/h
Exit $C_5H_{10} = 9$ lb/h
Needs 0.3 lbmol/h = 0.6 lb/h H_2
Produces 0.3 lbmol/h $C_5H_{12} = 21.6$ lb/h

Reaction (E12.2.3):
15 lb/h $C_6H_6/78 = 0.1923$ lbmol/h
Reacted $C_6H_6 = 0.1923\ (0.8) = 0.15385$ lbmol/h
Exit $C_6H_6 = 3$ lb/h
Needs = 0.9231 lb/h H_2
Produces 0.15385 lbmol/h $C_6H_{12} = 12.92$ lb/h
Reaction (E12.2.4):
50 lb/h $C_8H_{18}/114 = 0.4386$ lbmol/h
Reacted $C_8H_{18} = 0.4386(0.8) = 0.351$ lbmol/h
Exit $C_8H_{18} = 10$ lb/h
Produces 0.351 lbmol/h $C_4H_8 = 19.656$ lb/h
0.351 lbmol/h $C_4H_{10} = 20.358$ lb/h
Total hydrogen required = 1.9993 lb/h = 378.86 SCF

12.3.1.2. Deep Non-Hydrodesulphurization (DNHDS)

In 2005, the maximum sulphur limit in gasoline and diesel fuels was 50 ppm. This limit will be lowered to 10 ppm by the year 2010. Refineries have used the DHDS processes to meet these limitations but with huge capital investments. Researchers all over the world are suggesting a new approach to desulphurization that does not require a large capital investment. This approach is the DNHDS.

The DNHDS processes involve the selective adsorption of sulphur compounds by selective interaction in the presence of aromatic hydrocarbons under ambient or mild conditions without hydrogen. DNHDS may include oxidizing sulphur compounds by liquid-phase oxidation reactions, followed by the separation of the oxidized sulphur compounds. Bio-desulphurization can also be used to attack sulphur atoms by using bacteria via microbial desulphurization. More methods for desulphurization are either by extraction with new ionic liquids or by membrane separation technology that is integrated into a clean fuel strategy at low capital cost relative to hydrotreating.

Selective Adsorption for Sulphur Removal Selective adsorption for sulphur removal (SASR) is a new approach for DNHDS. The idea is still being studied in laboratories, but the results of the experiments show the approach that could replace the current HDS units in the next few years. The main idea of this approach is to selectively separate the sulphur compounds (Thiophens, benzothiophens, and di-benzothiophens) from the fuel using an appropriate adsorbent agent. As a result of this separation, only 1% by mass of the fuel is adsorbed by the adsorbent agent.

The sulphur compounds in fuels are first adsorbed and the hydrocarbon fuel with ultra-low-sulphur content is obtained. The sulphur compounds adsorbed on the surface of the adsorbent are recovered by solvent elution. The concentrated sulphur fraction is then sent to a small HDS reactor for

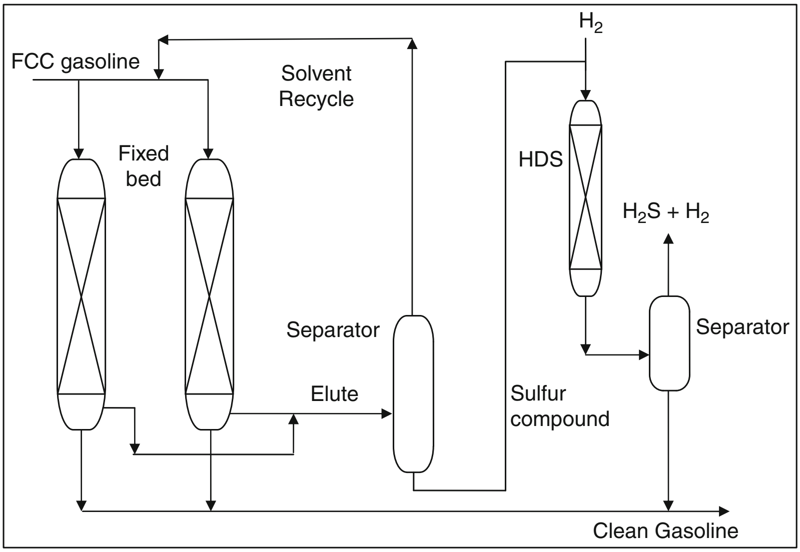
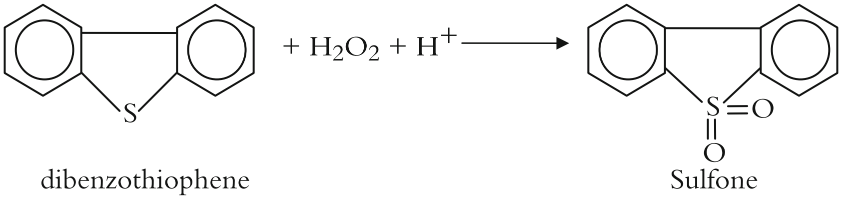


Figure 12.2 Selective adsorption for sulphur removal's (SASR) process flow diagram (Song and Ma, 2002)

hydrodesulphurization. The hydrodesulphurized product is blended with the hydrocarbon fraction from the adsorber (Song and Ma, 2002). Figure 12.2 is a proposed flow diagram of the process.

The main advantage of SASR adsorption process is that it is operated at ambient temperature and pressure. The rest of the residual sulphur is removed by HDS reaction at mild conditions.

Oxidation and Extraction for Desulphurization Oxidation of a sulphur atom in liquid phase with hydrogen peroxide followed by extraction of a oxidized species can lead to the desulphurization of diesel fuels. The oxidizing agents that can be used include *t*-butyl, peroxy organic acids, inorganic peroxy acids, and peroxy salts. Hydrogen peroxide in the presence or absence of catalysts under ambient conditions has been used (Hamad, 2008). A typical oxidation reaction is shown in equation (12.1). The resultant sulphur is extracted by suitable solvent such as N-methyl pyrrilidone (NMP).



(12.1)

It is important to select the proper solvent for separation of the desirable aromatic/olefinic compounds from the fuel or extracting less than a desired amount of the sulphur compounds from the fuel. In either case, the consequences can be costly. The advantages of the process are maximum sulphur removal and minimum impact on the fuel quality.

Bio-desulphurization Bio-desulphurization is a process that removes sulphur from fossil fuels using a series of enzyme-catalyzed reactions. Biocatalytic sulphur removal from fuels has applicability for producing low sulphur gasoline and diesel fuels. Certain microbial biocatalysts have been identified that can bio-transform sulphur compounds found in fuels, including ones that selectively remove sulphur from dibenzothiophene. The distillate stream is first mixed with an aqueous media containing the bacteria, caustic soda and nutrients for the bacteria. Enzymes in the bacteria first oxidize the sulphur atoms and then cleave some of the sulphur–carbon bonds. The sulphur leaves the process in the form of hydroxyphenyl benzene sulphonate which can be used commercially as a feedstock to produce surfactants.

Extraction with Ionic Solvent Ionic solvent can be used instead of organic solvent to extract sulphur compounds. The ionic solvent is prepared using a mixture of CuCl-based ionic liquid exhibits remarkable desulphurization ability in the desulphurization of gasoline when used as an extraction absorbent. The effectiveness of sulphur removal may be attributed to the complexation of a Cu ion with thiophene.

Ionic liquid systems of 1-butyl-3-methylimidazolium tetrachloroaluminate ($BMImAlCl_4$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($BMImBF_4$) have been investigated for the desulphurization of motor fuel. Excellent results have been obtained.

Membrane Separation One of the important membrane separation processes is the S-brane process. It is used as a complementary process to achieve low sulphur concentration complying with environmental regulations.

The S-brane process can be used to treat hydrotreated FCC gasoline. The membrane is capable to separate a feed of 300 ppm (as an example) and produce two streams. A clean gasoline, (less than 30 ppm sulphur) which is called retentate, contains 70 vol% of the feed and sent to the gasoline pool. The other concentrated sulphur compounds gasoline stream is called permeate and contains 30 vol% of the feed. The permeate stream is sent to a conventional hydrodesulphurization units. The hydrotreated gasoline is then sent to the gasoline pool. A schematic diagram of the process is shown in Figure 12.3.

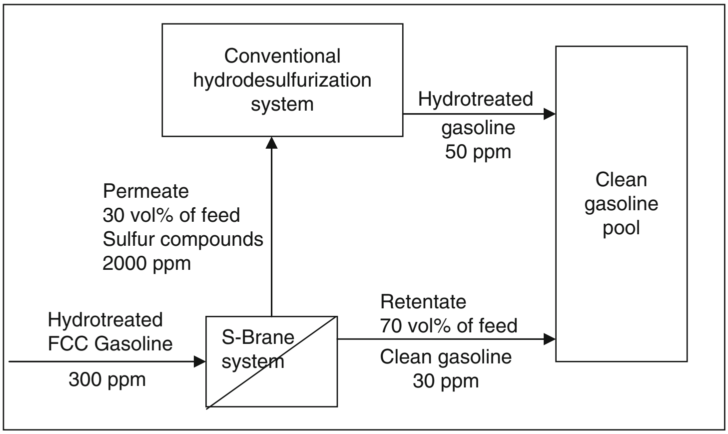


Figure 12.3 S-Brane place in refinery (Zhao and Krishnaiah, 2004)

The membrane is made of polymeric material which is selective for sulphur compound present in gasoline. The S-brane is operated as pervaporation mode membrane. A vacuum of about 0.5 to 0.1 bar (0.75-1.5 psia) is applied on the permeate side. Sulphur compounds flow through membrane to the permeate side while clean gasoline flow in the retentate side and then to the gasoline pool.

12.4. PRODUCTION OF CLEAN FUELS FROM NATURAL GAS AND COAL

Natural gas (NG) is a major source of clean fuels. It can be used directly as a gaseous clean fuel or processed to produce liquid clean fuel with low aromatic and zero sulphur content. The technology that is used to convert natural gas into liquid hydrocarbon fuels is called gas-to-liquid technology (GTL). The conversion of natural gas to hydrocarbons is currently one of the most promising topics in the energy industry.

Coal or heavy residues can be used on sites where these are available at low costs. Coal and natural gas can be converted into synthesis gas, a mixture of predominantly CO and H_2, by either partial oxidation or steam reforming processes. Possible reactions of synthesis gas are shown in Figure 12.4.

Fischer and Tropsch (FT) process is used to convert synthesis gas to aliphatic hydrocarbons. The major reactions in FT process is carbon monoxide hydrogenation over metal catalyst (iron, cobalt or nickel) at 180-250 °C (356–482 °F) and atmospheric pressure. Table 12.6 shows the main reactions in FT process.

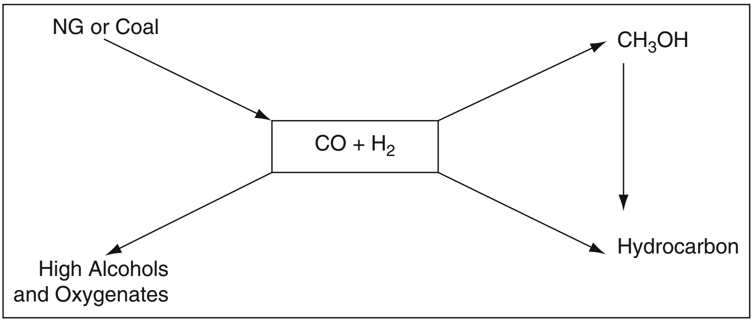


Figure 12.4 Possible reactions from synthesis gas (Kroshwitz and Howe-Grant, 1996)

Table 12.6 Reactions in the Fischer–Tropsch process (De swart, 1996)

Main reactions	
Paraffins	$(2n+1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O$
Olefins	$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$
Water gas shift reaction	$CO + H_2O \rightleftarrows CO_2 + H_2$
Side reactions	
Alcohols	$2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n-1)H_2O$
Boudouard reaction	$2CO \rightarrow C + CO_2$
Catalyst modifications	
Catalyst oxidation/reduction	a. $M_xO_y + yH_2 \rightleftarrows yH_2O + xM$
	b. $M_xO_y + yCO \rightleftarrows yCO_2 + xM$
Bulk carbide formation	$yC + xM \rightleftarrows M_xC_y$

The reactions of the FT synthesis on iron catalysts can be simplified as a combination of the FT reaction and the water gas shift (WGS) reaction:

$$\begin{gathered}(\mathrm{FT})\ \mathrm{CO} + (1 + m/2n)\mathrm{H_2} \longrightarrow 1/n\mathrm{C}_n\mathrm{H}_m + \mathrm{H_2O}, \\ -\Delta H = 165\ \mathrm{kJ/mol}\end{gathered} \tag{12.2}$$

$$\begin{gathered}(\mathrm{WGS})\ \mathrm{CO} + \mathrm{H_2O} \rightleftarrows \mathrm{CO_2} + \mathrm{H_2}, \\ -\Delta H = 41.3\ \mathrm{kJ/mol}\end{gathered} \tag{12.3}$$

where (n) is the average carbon number and (m) is the average number of hydrogen atoms of the hydrocarbon products. The WGS activity can be high over potassium-promoted iron catalysts and is negligible over cobalt or ruthenium catalysts.

As shown in Figure 12.5, the whole FT process consists of three stages: (1) synthesis gas production, (2) Fischer–Tropsch's synthesis, and (3) product upgrading.

Example E12.3

A feed rate of 100 lb/h is introduced to the FT process with $H_2/CO = 2.0$

Calculate the amount of hydrocarbon produced in the FT reaction (12.2). Assume 95% conversion and n equals 4.

Solution:

Given that $H_2/CO = 2.0$ then
$(1 + m/2n) = 2.0$ this gives that $2n = m$
If $n = 4$ then $m = 8$
The produced hydrocarbon is C_4H_8
Basis 1 lbmol CO = 28 lb fed to the FT unit
Then 2 lbmol H_2 = 4 lb
Then CO wt% = 28/(32) = 87.5 wt%
Then H_2 wt% = 4/(32) = 12.5 wt%
95% conversion
0.95 (87.5 lb/h CO)/(12 + 16) = 2.96875 lb mol CO reacted
This will produce
0.25 (2.96875) = 0.74218 lb mol C_4H_8 = 41.5625 lb/h C_4H_8

12.4.1. Synthesis Gas Production

Synthesis gas is a mixture of carbon monoxide and hydrogen with a ratio of 1:2. It can be obtained by steam reforming or by the (catalytic) partial oxidation of fossil fuels: coal, natural gas, refinery residues, biomass and off-gases.

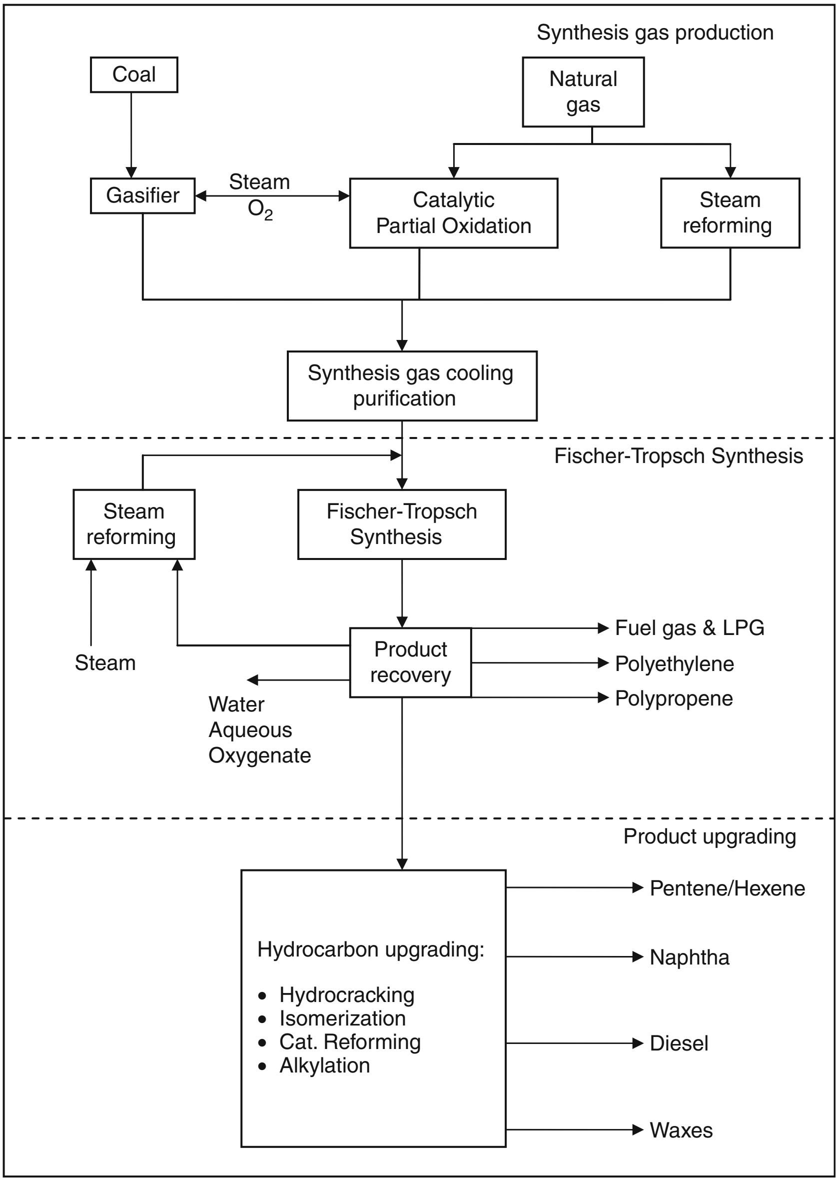


Figure 12.5 The three stages of the Fischer–Tropsch (FT) process

The common source of synthesis gas is natural gas by reforming with either steam or carbon dioxide or by partial oxidation as follows:

$$\text{Steam reforming} \quad CH_4 + H_2O \rightleftarrows CO + 3\,H_2 \tag{12.4}$$

$$CO_2 \text{ reforming} \quad CH_4 + CO_2 \rightleftarrows 2\,CO + 2\,H_2 \tag{12.5}$$

$$\text{Partial oxidation} \quad CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2\,H_2 \tag{12.6}$$

$$\text{Water gas shift reaction} \quad CO + H_2O \rightleftarrows CO_2 + H_2 \tag{12.7}$$

If synthesis gas with a H_2/CO ratio below 2 is used, this means that the composition of the synthesis gas is not stoichiometric for the Fischer–Tropsch reactions. In this case the water gas shift reaction is important to adjust the H_2/CO ratio to 2. Iron and cobalt catalysts are used in the production of synthesis gas from natural gas.

Iron catalysts, in comparison to cobalt, can directly convert low H_2/CO ratio synthesis gas without water gas shift reaction. Ceramic membranes might have significant role in adjusting H_2/CO ratio.

The Fischer–Tropsch synthesis section consists of the FT reactors, the recycle and compression of unconverted synthesis gas, the removal of hydrogen and carbon dioxide, the reforming of methane that is produced, and the separation of the FT products.

12.5. PRODUCTION OF CLEAN FUELS FROM BIOLOGICAL SOURCES (BIOFUELS)

The term biofuel was known for the first time in the nineteenth century. Back then, ethanol was the only biofuel known. Due to crude oil discoveries. The field of biofuel technology and research declined. During the twentieth century, other fuels, mainly gasoline and diesel, were derived from crude oil. The reason for the dominance of fossil fuels in this sector is the large and cheap supply of its main feedstock, crude oil. Gasoline and diesel are still the most common fuels used in vehicles, but the (experimental) application of biofuels has been expanding due to European and international environmental policies. Biofuels have been used as additives to improve the quality of fuels applied in road vehicles. The increasing application of biofuels in transport has also been stimulated by environmental goals to reduce carbon dioxide (CO_2) emissions that were set by national governments and international agreements, such as the Kyoto Protocol. As shown in Figure 12.6, biomass can produce different types of clean fuels that can be used directly by consumers.

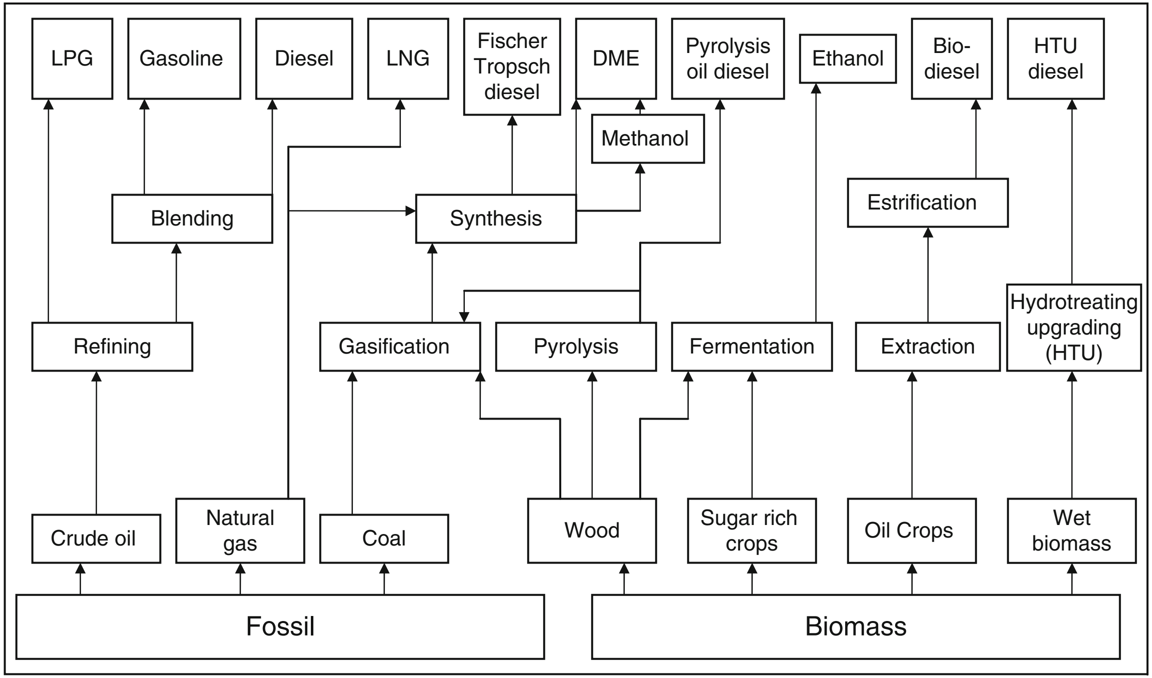
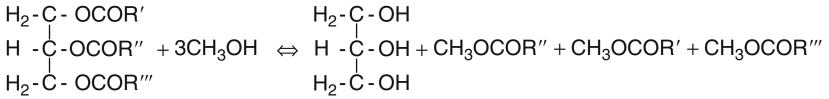


Figure 12.6 Different types of biofuels and fossil fuels

12.5.1. Bio-diesel

Vegetable oils are first produced by mechanical pressing or leaching oil seeds with a solvent such as hexane. The produced oil is highly viscous and has low cetane number (33–43). To improve its ignition quality, the vegetable oil is trans-esterified to change its structure from branched structure of triglycerides into smaller straight chain methyl esters which are similar to fossil diesel. In this case, the trans-esterification reaction is carried out in the presence of catalyst (typically a strong acid or base). The following reaction is the trans-esterification:



$$\begin{array}{lcl} H_2\text{-}C\text{-}OCOR' & & H_2\text{-}C\text{-}OH \\ \quad\ | & & \quad\ | \\ H\ \text{-}C\text{-}OCOR'' + 3CH_3OH & \Leftrightarrow & H\ \text{-}C\text{-}OH + CH_3OCOR'' + CH_3OCOR' + CH_3OCOR''' \\ \quad\ | & & \quad\ | \\ H_2\text{-}C\text{-}OCOR''' & & H_2\text{-}C\text{-}OH \end{array}$$

(12.8)

The produced methyl ester is called Rapeseed Methyl Ester (RME). The reaction is carried at 1 mol% of H_2SO_4, alcohol/oil molar ratio of 30 to 1.0 at 65 °C and 50 hours to reach complete conversion (Schuchardt et al., 1998).

Table 12.7 shows the comparison between bio-diesel RME, conventional diesel and dimethyl ether. The viscosity of RME is about twice the value of diesel fuel. Hence additive such as flow enhancers can be used to reduce viscosity.

Since RME has similar fuel properties compared to diesel, it can be blended with fossil diesel in any proportion for application in conventional diesel engines. However, if 100% RME is to be used, a number of relatively minor changes in the engines are required. Material incompatibility with some engine components should be taken into account because RME shows a high chemical aggressiveness towards metallic materials, rubber seals, coatings and elastomers. Although RME can be mixed with fossil diesel in any ratio, car manufacturers often recommend not applying mixtures in their engines with a proportion of RME higher than 5%. A reason for this is that the certification level for the engine with regard to NO_x emissions can be exceeded when a large proportion RME is used. Many diesel engine producers are working on an improved application of bio-diesel. Some car manufacturers have produced private cars especially for the use of pure RME. In another application of bio-diesel, a mixture with ethanol, known as esterol, has been developed for regular diesel engines.

Dimethylether (DME) has properties similar to LPG fuels. However, it has high cetane number (55) which makes it suitable to be used as a substitute for diesel. Inspecting Table 12.7, we find that diesel has 20 times the viscosity of DME which might cause engine leak. The boiling point of DME can be utilized as spray injected to engine cylinder. The high

Table 12.7 Fuel properties of bio-diesel (RME) compared to diesel and dimethyl ether (DME) (van Thuijl et al., 2003)

Fuel properties	Bio-diesel (RME)	Diesel	DME
Chemical formula	Methyl ester	$C_{12}H_{26}$	CH_3OCH_3
Molecular weight (kg/kmol)	296	170–200	46
Cetane number	54	50	55–60
Density (kg/l) at 15 °C	0.88	0.84	0.67
Lower calorific value (MJ/kg) at 15 °C	37.3	42.7	28.4
Lower calorific value (MJ/l) at 15 °C	32.8	35.7	18.8
Stoichiometric air/fuel ratio (kg air/kg fuel)	12.3	14.53	9
Oxygen content (wt%)	9.2–11.0	0–0.6	
Kinematic viscosity (mm^2/s) at 20 °C	7.4	4	4.443
Flash point (°C)	91–135	77	

oxygen content of DME ensures that it has high octane number (>55) which leads to good knocking properties. It can be produced from the direct dehydration of methanol (Semlsberger et al., 2006).

$$2CH_3OH \Leftrightarrow CH_3 - O - CH_3 + 2H_2O \quad \Delta H = 23.4\ \text{kJ/mole} \qquad (12.9)$$

12.5.2. Ethanol and Methanol

Ethanol has been used on a large scale as a transportation fuel, especially in Brazil. There, 60% of the produced ethanol is sold in a hydrated form (93 vol% ethanol and 7 vol% water), which completely replaces gasoline in vehicle engines. The remaining 40% ethanol is applied in water-free form in a mixture with gasoline up to 24%. The predominant technology for converting biomass to ethanol is fermentation followed by distillation (Figure 12.7). Fermentation is a biochemical conversion process in which the biomass is decomposed using micro-organisms (bacteria or enzymes). This technology can be used for various types of biomass feedstocks (e.g. food crops, which are traditional feedstocks, and woody biomass, which is currently gaining a lot of attention).

Like ethanol, methanol has also been used as a transportation fuel for quite a long time, especially in the USA. Methanol can be produced from

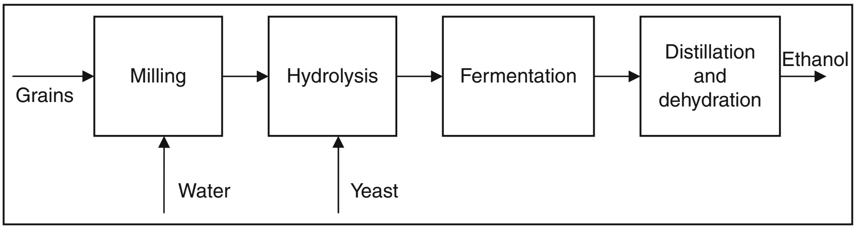


Figure 12.7 Converion process scheme for ethanol production from grain

Table 12.8 Fuel properties of ethanol, and methanol compared to gasoline (van Thuijl et al., 2003)

Fuel properties	Ethanol	Methanol	Gasoline
Chemical formula	C_2H_5OH	CH_3OH	C_8H_{15}
Molecular weight (kg/kmol)	46	32	111
Octane number (RON)	109	110	97
Octane number (MON)	92	92	86
Cetane number	11	5	8
Reid vapour pressure (kPa) at 15 °C	16.5	31.7	75
Density (kg/l) at 15 °C	0.8	0.79	0.75
Lower calorific value (MJ/kg) at 15 °C	26.4	19.8	41.3
Lower calorific value (MJ/l) at 15 °C	21.2	15.6	31
Stoichiometric air/fuel ratio (kg air/kg fuel)	9	6.5	14.7
Boiling temperature (°C)	78	65	30–190

synthesis gas, which results from the gasification of biomass. Table 12.8 compares ethanol, methanol and gasoline fuel properties.

12.5.3. Bio-Fuel from Flash Pyrolysis

Flash pyrolysis is the fast thermal decomposition of biomass in the absence of oxygen. The results of this pyrolysis are: gases, bio-fuels and char. Flash pyrolysis takes place at high temperatures between 700-1000 °C (1292-1832 °F). The residence time in the reactor is below 1 second. This process is run to produce mainly liquid biofuels where the produced vapours are cooled and condensed. In this process very high heating rates of the biomass is followed by very rapid cooling of the produced vapours. Figure 12.8 shows the steps of pyrolysis plant. The biomass is first dried and grinded, then it is fed to the reactor.

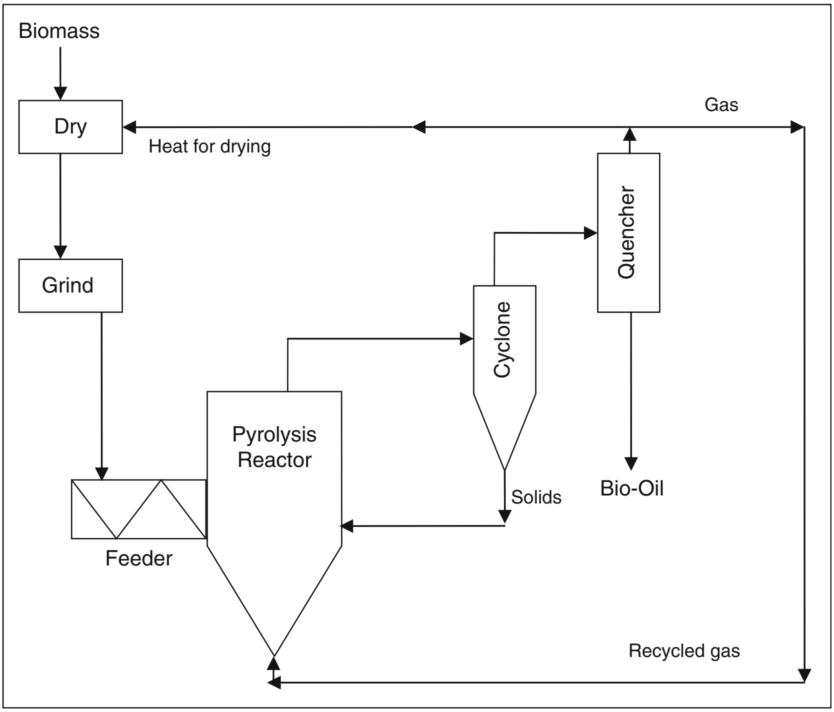


Figure 12.8 General process scheme flash pyrolysis

12.5.4. Bio-Fuel from Hydrothermal Upgrading (HTU)

The biomass in hydrothermal upgrading (HTU) is decomposed in water to produce a crude oil-like liquid called "bio-crude". Objectives of this process were to concentrate the energy of the biomass into an (automotive) fuel with a higher energy density. However, due to unfavourable economic conditions, the experiments were stopped.

12.5.5. Gasification Routes

Biomass can be converted by means of a gasification process. Any type of biomass can be used as a feedstock, including lignocellulosic such as cellulosic materials from agricultural crops (straw, molasses) grasses and trees from forest plantations. Wet biomass, like municipal solid waste and agricultural residues can be used but with a lower efficiency. Gasification of biomass results in a mixture of combustible gases. This is called synthesis gas. A broad range of liquid biofuels can be produced by synthesis from this gas, depending on the process conditions. The steps of this process are shown in Figure 12.9.

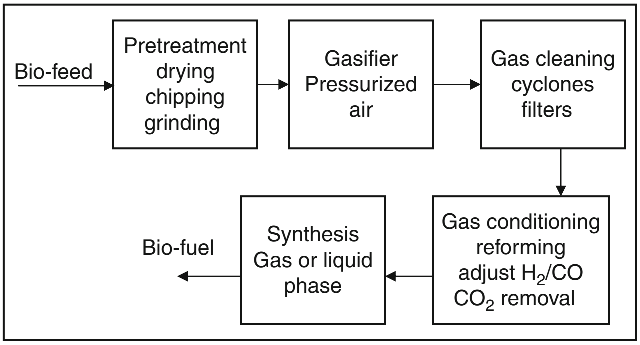


Figure 12.9 General conversion scheme biomass gasification and synthesis

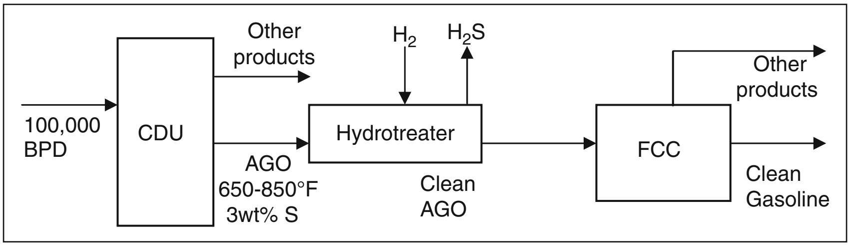
QUESTIONS AND PROBLEMS

12.1. 100,000 BPD crude oil with 3 wt% sulphur is fed to a distillation column. The crude TBP and API as a function of liquid volume (LV%) are as follows:

$$\mathrm{TBP}(^\circ\mathrm{R}) = \left\{\left(2\ln\left(\frac{100}{100-\mathrm{LV\%}}\right)\right)^{2.5} + 1\right\}490$$

$$\mathrm{API} = -0.0004\,(\mathrm{LV\%})^3 + 0.05\,(\mathrm{LV\%})^2 - 2.4\,\mathrm{LV\%} + 72$$

The produced VGO (650–850 °F) cut is fed to a hydrotreater unit to remove 100% of the sulphur. The clean VGO is then introduced to FCC unit at 72% conversion to produce gasoline. More information are listed and shown in the figure below. Calculate the amount of clean gasoline.



12.2. 100 lb/h stream contains 20 wt% C_5H_{10}, 20 wt% C_6H_6, 50 wt% C_8H_{18} and 10 wt% thiophene. This stream is fed to HDS to remove 100% of sulphur. The following reactions take place in the HDS unit:

$$C_4H_4S + 4\,H_2 \longrightarrow C_4H_{10} + H_2S, \quad 100\%\ \text{conversion}$$

$$C_5H_{10} + H_2 \longrightarrow C_5H_{12}, \quad 80\%\ \text{conversion}$$

$$C_6H_6 + 3H_2 \longrightarrow C_6H_{12}, \quad 85\% \text{ conversion}$$

$$C_8H_{18} \longrightarrow C_4H_8 + C_4H_{10}, \quad 85\% \text{ conversion}$$

Calculate the HDS unit production and the required hydrogen.

12.3. A feed rate of 100 lb/h is introduced to the FT process with $H_2/CO = 2.0$. Calculate the amount of hydrocarbon produced, assuming 100% conversion of reaction with $n = 8$.

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CHAPTER THIRTEEN

RESIDUE UPGRADING

13.1. INTRODUCTION

The demand for high value petroleum products such as middle distillate, gasoline and lube oil is increasing, while the demand for low value products such as fuel oil and residue-based products is decreasing. On the other hand, the worldwide trend in the crude oil supply indicate a continuous increase of heavy crude production. The increase in the yield of residue in distillation is accompanied with the increase in its sulphur content. Refineries around the world are facing economical and environmental problems. These environmental problems are discussed in details in Chapter 17. The production of clean fuels having zero sulphur levels through deep hydrodesulphurization is discussed in Chapter 12.

To solve the economical problem, additional distillates have to be produced by upgrading the residue. The upgrading step generates final residues, such as tar by visbreaking, coke by delayed coking and asphalt by deasphalting. The final residues can either be converted to usable products, Like hydrogen, steam, ammonia and chemicals, or used as they are.

The major problem with heavy oil fractions is the complexity of the feedstock and the analysis of its components. Apart from several other complex structures, asphaltene remains as one of the common, uncertain molecules in heavy oil. Asphaltene is thought to be the most complex. It has a high molecular weight, is polar and is a highly aromatic molecule present in petroleum. A typical structure of asphaltene is shown in Figure 13.1.

The need to convert the bottom of the barrel into cleaner and more valuable liquid products is continuously increasing. The residue represents a significant portion of a barrel of crude, and its disposal treatment is not yet up to the mark. It must be converted into more valuable products such as gasoline or diesel. The process economy of residue conversion is strongly affected by the amount of the low value by-products produced and the amount of hydrogen input requirements. There are two types of residue, depending on the source: atmospheric residue (AR > 343 °C (650 °F)) from the atmospheric distillation tower and vacuum residue (VR > 565 °C (1050 °F)) from the vacuum tower obtained at 25–100 mm Hg.

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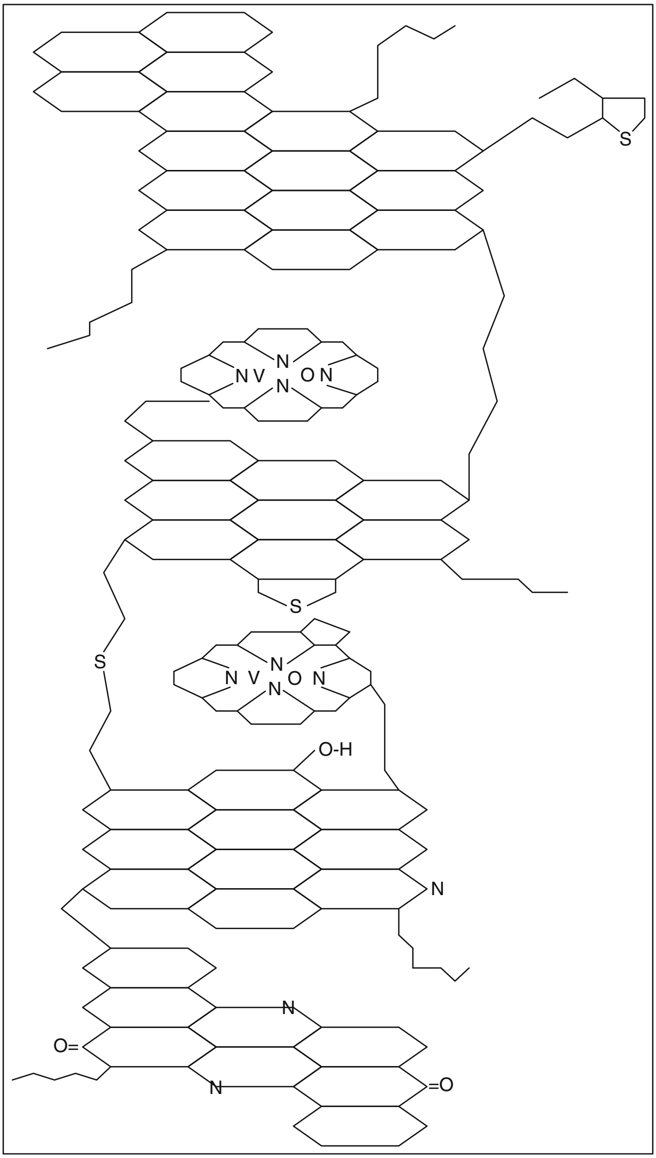


Figure 13.1 Hypothetical asphaltene molecule (Rana *et al.*, 2007)

13.2. UPGRADING OPTIONS

The options for refiners processing high sulphur residue will be a combination of upgrading schemes and by-product utilization. Residue upgrading options are listed in Table 13.1.

Table 13.1 Classification of residue upgrading processes (Rana *et al*., 2007)

Non-catalytic processes	Catalytic processes
Solvent deasphalting	Residue fluid catalytic cracking (RFCC)
Thermal	Hydroprocessing
Gasification	Fixed bed hydrotreating
Delayed coking	Fixed bed hydrocracking
Fluid coking	Slurry hydrocracking
Flexicoking	Ebullated bed hydrotreating
Visbreaking	Ebullated bed hydrocracking
	Aquaconversion

13.3. Non-catalytic Residue Upgrading Processes

13.3.1. Solvent Deasphalting

Solvent deasphalting (SDA) is a unique separation process in which the residue is separated by molecular weight (density) instead of by boiling point, producing a low contaminant deasphalted oil (DAO) that is rich in paraffins. It has the advantage of being a relatively low cost process that has flexibility to meet a wide range of DAO qualities. As with vacuum distillation, there are constraints with respect to how deep a SDA unit can upgrade the residue or how much DAO can be produced. These constraints are typically:

- The DAO quality specifications required by downstream conversion units, and
- The final high-sulphur residual fuel oil stability and quality.

The well-proven SDA process normally separates vacuum residue feedstock into relatively low metal/carbon DAO and a heavy pitch stream containing most of the contaminants. A solvent (typically C_3–C_7) is used and recovered from both product streams by supercritical recovery methods, thereby minimizing utilities consumption (Gillis, 1998).

During the SDA process, the feed is mixed with a light paraffinic solvent such as propane (propane-deasphalting), and the oil is solubilized in the solvent. The insoluble pitch will precipitate out of the mixed feedstock as asphaltene. The separation of the DAO phase and the pitch phase occurs in the extractor. The extractor is designed to efficiently separate the two phases

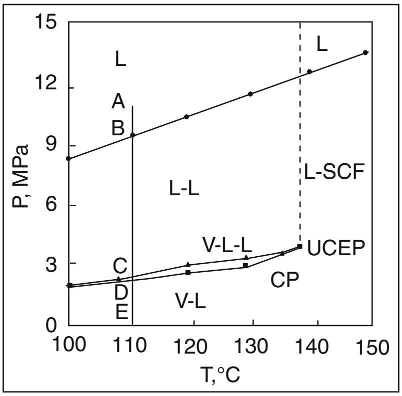


Figure 13.2 Fully developed phase diagram for residue in *iso*-butane (Zhao *et al.*, 2001)

and minimize the contaminant entrainment in the DAO phase. At a constant solvent composition and pressure, a lower extractor temperature increases the DAO yield and decreases the quality. Figure 13.2 shows a typical phase diagram of isobutane and residue. The Liquid–liquid (L-L) area is the preferable commercial conditions in which the solvent dissolves some of oil, and the result is two phases ready for separation. While an increase in solvent amount does not increase the DAO, it improves the degree of separation of individual components and results in the recovery of a better quality DAO. The solvent recovered under low pressure from the pitch and DAO strippers is condensed and combined with the solvent recovered under high pressure from the DAO separator, which is then recycled back to the initial stage. DAO is normally used as FCC or hydrocracker feedstock due to its low metal (Ni and V) contents. SDA technology can be applied in many ways, allowing the refiner to move towards zero fuel oil residue production over time in a phased manner.

Another well-known solvent deasphalting process is the ROSE process. The ROSE process is an energy efficient and cost-effective solvent deasphalting technology. Figure 13.3 is a simplified process flow diagram of this process (Nelson and Goodman, 1985). The feedstock is mixed with a portion of the solvent and fed to an asphaltene separator where additional solvent is contacted with the feed in a countercurrent mode at an elevated temperature and pressure. The heavy asphaltene fraction drops out of the solution and is withdrawn from the bottom. The solvent dissolved in the asphaltenes is separated, recovered and recycled.

Figure 13.4 shows the relationship between DAO yield and quality. Figure 13.5 shows how increasing the solvent to oil ratio increases the percent of deasphalting. In addition, decreasing the temperature increases the deasphalting process. Figure 13.6 shows the role of the ROSE process in the refinery.

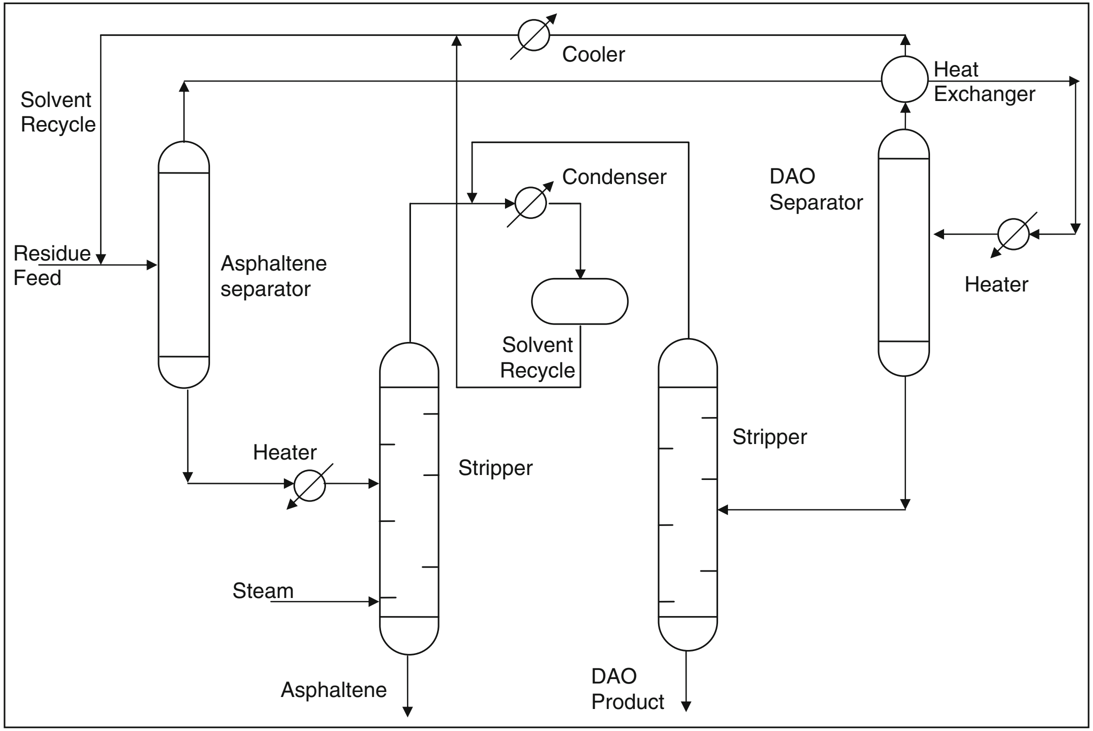


Figure 13.3 Schematic of the ROSE process

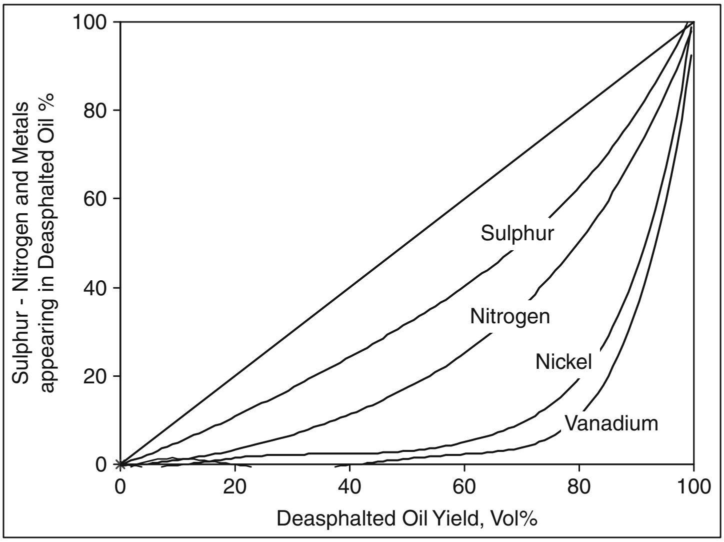


Figure 13.4 Deasphalted oil product yield-quality relationships (obtained when solvent deasphalting typical vacuum residues) (Gillis, 1998)

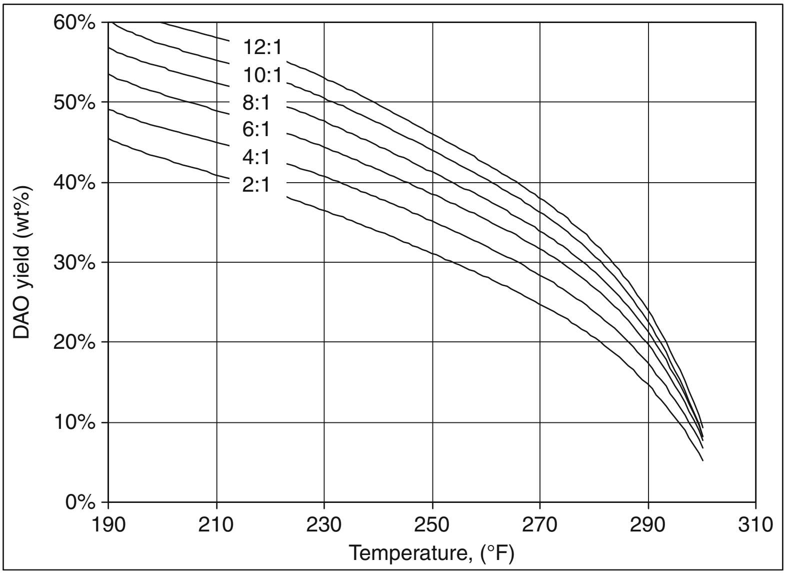


Figure 13.5 Effect of temperature on DAO yields at different solvent to oil ratios (Gillis, 1998)

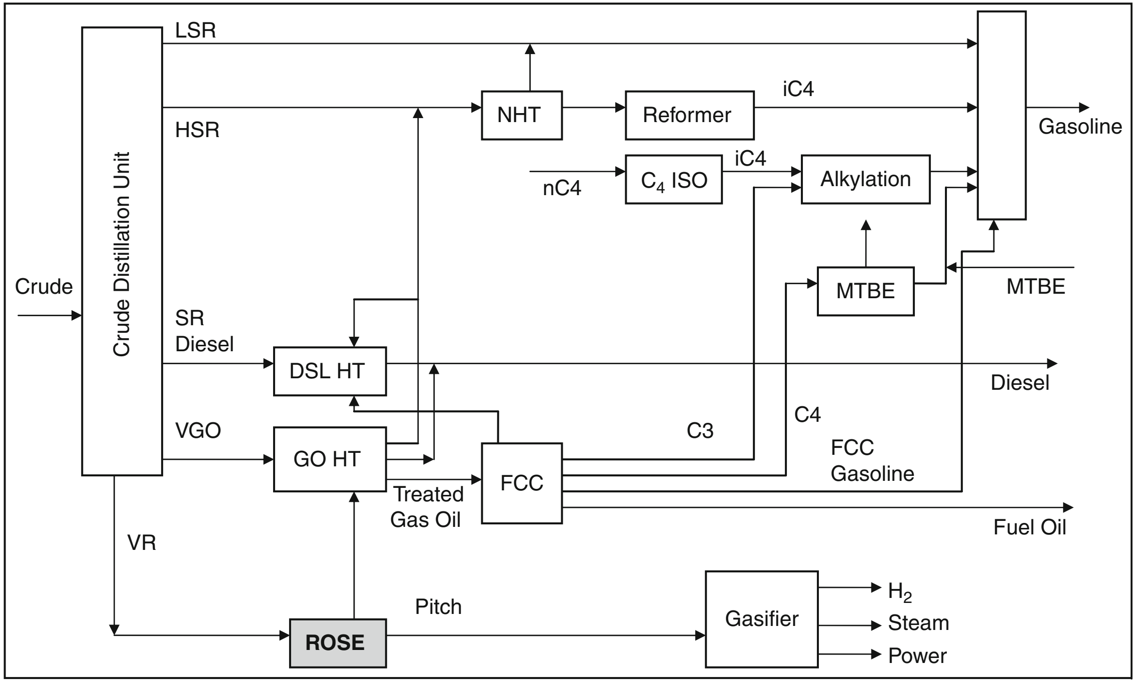


Figure 13.6 Refinery with solvent deasphalting, Rose-residue oil supercritical extraction unit

Example E13.1

100 lb/h residue was introduced to a deasphalting process which operates at 220 °F. The residue has the following properties: API = 6.6, *S* wt% = 4.8%. A solvent enters the process at a rate of 600 lb/h. The DAO produced has API = 19.8.

Calculate the yield of DAO and its sulphur content.

Solution:

Solvent to oil ratio = 600/100 = 6
At 220 °F and using Fig. 13.5, the DAO wt% = 45%
DAO amount = 0.45 (100) = 45 lb/h
DAO API = 19.8 gives SG = 0.935 and residue API = 9.9 gives SG = 1.0246

$$\text{vol\%}\quad \text{yield} = \frac{45/0.935}{100/1.0246} \times 100 = 49.3\%$$

From Figure 13.4 sulphur in the feed appearing in DAO = 30% at the calculated yield of 49.3%. Sulphur in DAO = (0.3) (0.048) (100) = 1.44 lb/h

13.3.1.1. Correlations for Solvent Deasphalting

The following correlations are generated from plant operation data compiled by (Maples, 1993). The correlation coefficients for the regression range between 0.996 and 0.999. Table 13.2 lists the deasphalted oil correlations.

Table 13.2 Deasphalted oil (DAO) correlations

$\text{DAO wt\% yield} = 117.15 - 4.7\,\text{API}_f$

$\text{DAO vol\%} = 0.9617(\text{DAO wt\%}) + 4.249$

$\text{CCR in DAO} = (0.000092\,(\text{DAO wt\%})^2 - 0.00023(\text{DAO wt\%}) + 0.006511)(\text{CCR in feed})$

$\text{S in DAO} = (\text{S in feed})\,\{0.0062(\text{DAO wt\%}) + 0.389505\}$

$\text{N in DAO} = (\text{N in feed})\,\{-0.000151(\text{DAO wt\%})^2 + 0.028797(\text{DAO wt\%}) - 0.566853\}$

$\text{Ni in DAO} = (\text{Ni in feed})\,\{0.000106(\text{DAO wt\%})^2 - 0.006838(\text{DAO wt\%}) + 0.142016\}$

$\text{V in DAO} = (\text{V in feed})\,\{0.000108(\text{DAO wt\%})^2 - 0.007727(\text{DAO wt\%}) + 0.156711\}$

$\text{Metals in DAO} = (\text{Metals in feed})\,\{0.000046(\text{DAO wt\%})^2 - 0.003861(\text{DAO wt\%}) + 0.087188\}$

Example E13.2

10,000 lb/h residue with the following properties:
API = 8.1, CCR = 17.4 wt%, *S* wt% = 2.7 wt%, *N* wt% = 0.5 wt%.
This is introduced to a deasphalting process.
Calculate the yield, CCR, sulphur and nitrogen contents of DAO.

Solution:

From Table 13.2

DAO wt% = 117.15 − 4.7 (8.1) = 79.08 wt%

DAO mass rate = 0.7908 (10,000) = 7908 lb/h

DAO vol% = 0.9617 DAO wt% + 4.249 = 80.3 vol%

$$\text{DAO CCR} = \{0.000092\ (79.08)^2 - 0.00023\ (79.08) + 0.006511\}\ (17.4) = 9.8\ \text{wt\%}$$

$$\text{S in DAO} = (2.7)\ \{0.0062\ (79.08) + 0.389505\} = 2.37\ \text{wt\%}$$

$$\text{N in DAO} = (0.5)\ \{-0.000151\ (79.08)^2 + 0.028797\ (79.08) - 0.566853\} = 0.383\ \text{wt\%}$$

13.3.2. Thermal Processes

13.3.2.1. Coking

Thermal conversion is an important process for residue conversion. Thermal cracking of residue is carried out at relatively moderate pressures and it is often called the coking process (refer to Chapter 6). The coking process tends to increase the H/C ratio of the products by the production of carbon (coke). The residue has a H/C ratio of about 0.5–1, which can be increased by either adding hydrogen or removing carbon.

13.3.2.2. Gasification

The gasification process involves the complete cracking of residue into gaseous products. The gasification of residue is carried out at high temperatures (greater than 1000 °C (1832 °F)), producing synthesis gas, carbon and ash as major products. The integrated gasification combined cycle (IGCC see Figure 13.7) is an alternative process for heavy residue conversion and an emerging technology for efficient power generation with minimum effect on the environment. It is used to produce power from vacuum residue and FCC slurry. A key benefit of IGCC is power generation with the lowest SO_x and NO_x. Air emissions from IGCC compared to the European standard for conventional power stations are presented in Table 13.3.

Gasification is a partial oxidation process in which carbonaceous solids react with oxygen, enriched air or air according to the overall reaction (Furimsky, 1999)

$$C_nH_m + n/2O_2 \rightarrow n\text{CO} + m/2\text{H}_2$$

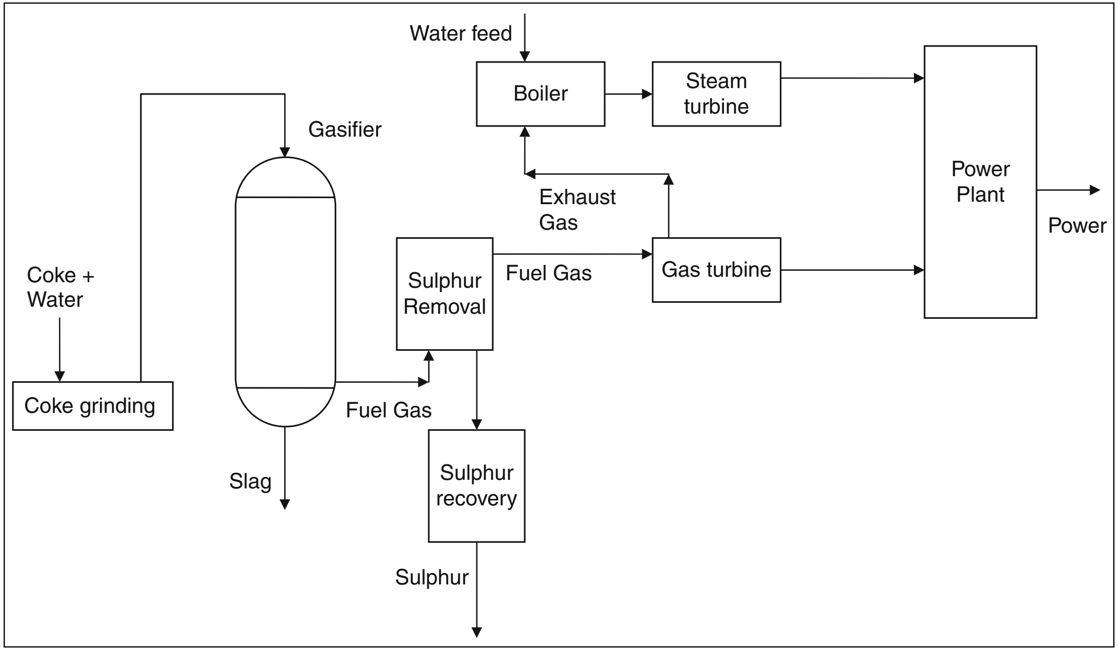


Figure 13.7 IGCC plant

Table 13.3 Sulphur and nitrogen compounds emissions (Phillips and Liu, 2002)

	Air emissions (mg/normal m^3)	
	Typical IGCC	European standard for conventional power station
SO_x	10	130
NO_x	30	150
Particulates	10	16

The following reactions are involved:

Gasification with O_2:

$$C + 1/2O_2 \rightarrow CO, \quad \Delta H = -123.1 \text{ kJ/mol} \tag{13.1}$$

Combustion with O_2:

$$C + O_2 \rightarrow CO_2, \quad \Delta H = -405.9 \text{ kJ/mol} \tag{13.2}$$

Gasification with CO_2:

$$C + CO_2 \rightarrow 2CO, \quad \Delta H = 159.7 \text{ kJ/mol} \tag{13.3}$$

Gasification with steam:

$$C + H_2O \rightarrow CO + H_2, \quad \Delta H = 118.9 \text{ kJ/mol} \tag{13.4}$$

Most of the O_2 fed to the gasifier is consumed in reactions (13.1) and (13.2). These reactions generate heat to increase temperatures at which chemical bonds are broken and gasification reactions (13.3) and (13.4) become favourable. If the gas is considered for a subsequent synthesis, the water-gas shift reaction is involved:

$$CO + H_2O \rightarrow H_2 + CO_2, \quad \Delta H = -40.9 \text{ kJ/mol} \tag{13.5}$$

A water-gas shift reaction becomes important for adjusting the H_2/CO ratio. Otherwise, the primary objective is to maximize the content of combustibles such as CO and H_2. CH_4 can also be formed at low gasification temperatures. Sulphur in the feed is mainly converted to H_2S, and a small amount of COS. Traces of S_2 and CS_2 can also be formed. Most of the nitrogen in the feed is converted to N_2. However, small amounts of HCN and NH_3 are also formed. HCl is the main Cl-containing product formed during gasification.

The role of the gasifier in a typical refinery is shown in Figure 13.8.

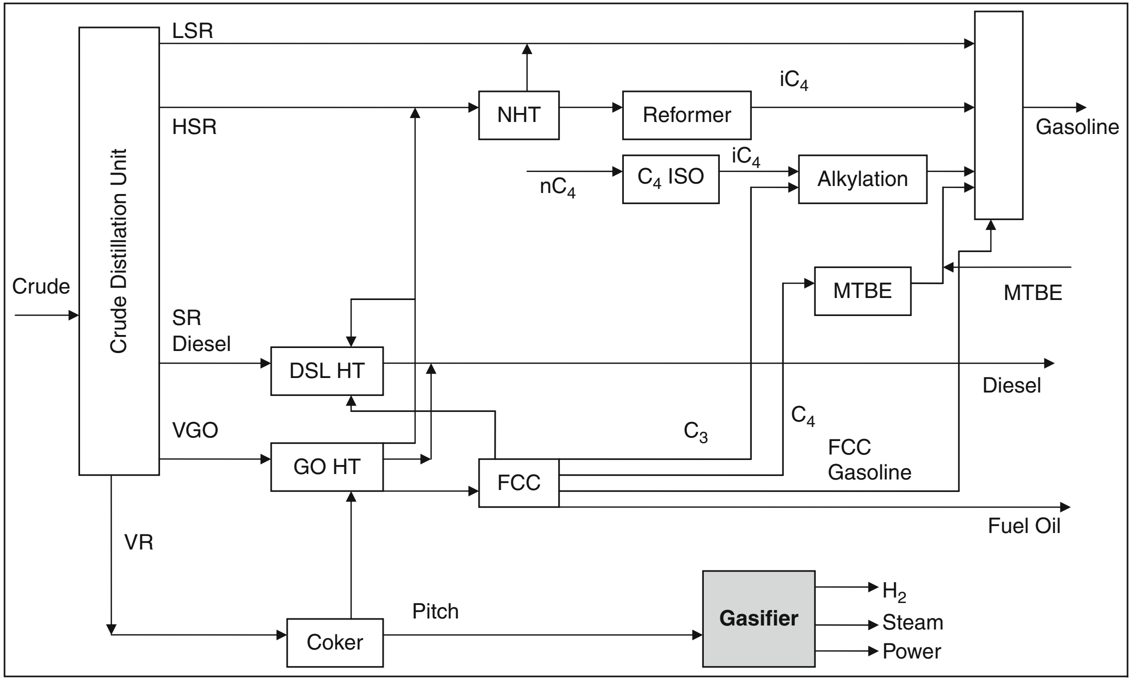


Figure 13.8 Refinery flowsheet with gasification (note that there is no final residue in the products)

Example E13.3

Fuel ($C_nH_mS_o$) at 800 °C is combusted in a gasifier at 1200 °C. Air is available at 200 °C. 10 kmol/h steam, available at 150 °C, is also introduced to the gasifier. The dry basis flue gas analysis is as follows: 12 mol% CO_2, 5 mol% CO, 2 mol% O_2, 80 mol% N_2 and 1 mol% SO_2. On the basis of 100 kmol/h of dry flue gas, find the chemical formula of the fuel burned $C_nH_mS_o$ and calculate the gasifier heat load.

Solution:

Basis 100 kmol/h dry gas
From S-balance moles of S in the fuel (o) = 1 kmol/h
From C-balance moles of C in the fuel (n) = 12 + 5 = 17 kmol/h
N_2 in = N_2 out = 80 kmol/h
O_2 in = 80/0.79 (0.21) = 21.265 kmol/h
O-balance:

O_2 for carbon burn = 12 + 2.5 = 14.5 kmol
O_2 remain for H burn = 21.265 − 14.5 − 2 = 4.765 kmol/h

H-balance:

$$2H + 0.5\ O_2 = H_2O$$
$$H = 4.765(2)/(0.5) = 19.06\ \text{kmol/h}$$

Then the chemical formula of the fuel is $C_nH_mS_o = C_{17}H_{19}S$. UNISIM can be used to find the heat capacity and other properties of this hypothetical compound needed for calculation of the burner heat load.

Heat capacity = 0.236 kJ/kmol °C
Heat of formation = 511,950 kJ/kmol
Molecular weight = 255.4 kg/kmol
Liquid density = 881.97 kg/m^3

$$\text{Heat load on the reactor} = q = \sum \Delta H_r + \sum n_{out} H_{out} - \sum n_{in} H_{in}$$

There are three reactions that take place

$$C + O_2 \rightarrow CO_2, \qquad \Delta H_r = -393.5 \times 10^3\ \text{kJ/kmol}$$
$$H + 0.25\ O_2 \rightarrow 0.5\ H_2O, \qquad \Delta H_r = -241.8 \times 10^3\ \text{kJ/kmol}$$
$$S + O_2 \rightarrow SO_2, \qquad \Delta H_r = -296.9 \times 10^3\ \text{kJ/kmol}$$
$$C + 0.5\ O_2 \rightarrow CO, \qquad \Delta H_r = -110.52\ \text{kJ/kmol}$$

$$\sum \Delta H_r = \Big(12(-393.5) + 19(-241.8) + (-296.9) + 5(-110.52)\Big) \times (1000) = -1.017 \times 10^7\ \text{kJ}$$

$Cp_{CO_2} = 0.03611$ kJ/mol, $Cp_{CO} = 0.02895$ kJ/mol, $Cp_{O_2} = 0.0291$ kJ/mol

$$Cp_{N_2} = 0.029\ \text{kJ/mol},\quad Cp_{SO_2} = 0.03891\ \text{kJ/mol},\quad Cp_{H_2O} = 0.03346\ \text{kJ/mol}$$

$$\sum n_{out}H_{out} = \sum n_{out}Cp(T_{out} - T_{ref}) = [12(0.03611) + 5(0.02895) + 2(0.0291) + 80(0.029) + 1(0.03891) + 19.06(0.03346)](1000)(1200 - 25) = 4.269 \times 10^6\ \text{kJ}$$

$$\sum n_{in}H_{in} = n_{steam}H_{steam} + \sum n_{in}Cp(T_{in} - T_{ref}) = 10(48,168) + 80(0.029)(1000)(200 - 25) + 21.265(1000)(0.0291)(200 - 25) + (17 + 19 + 1)(1000)(0.236) \times (800 - 25) = 6.76 \times 10^6\ \text{kJ}$$

$$q = -1.017 \times 10^7 + 4.269 \times 10^6 - 6.76 \times 10^6 = -1.3 \times 10^7\ \text{kJ}$$

13.4. CATALYTIC PROCESSES

Table 13.4 summarizes the catalytic hydroconversion processes.

13.4.1. Residue-fluidized Catalytic Cracking

Residue-fluidized catalytic cracking (RFCC) is essentially an evolution of the well-proven FCC process. To accommodate residue, licensors and catalyst suppliers have modified the traditional FCC technology in key areas, including:

- Catalyst design
- Feed injection
- Riser design
- Catalyst/oil product separation
- Regenerator design
- Overall reactor/regenerator design

The design of catalysts for residue cracking requires that both the zeolite and matrix components offer high stability, low coke, and good metal tolerance properties compared to the VGO operation.

Each major licensor has its own proprietary nozzle design for injecting feed into the base of the riser. Efficient mixing of feed with a catalyst is particularly important when residue is processed. Modern catalysts allow a substantial reduction in residence time in the riser, providing greater selectivity and control over required distillate product.

Table 13.4 Residue hydroconversion processes (Scheffer *et al*., 1998; Ancheyta and Speight, 2007)

Reactor type	Process	Licenser
Fixed bed	Continuous catalyst replacement (OCR)	Chevron Lumus Global (CLG)
	UFR, Up-flow reactor	Shell (Bunker flow)
	Hycon, Bunker type reactor	Axen (Swing reactor)
	Hyvahl, swing reactor concept	Shell
		IFP (Axen)
Ebullated bed	H-oil	Axen (HRI/IFP)
	T-star	Chevron
	LC-fining	ABB Lummus
		Amoco oil (BP)
Slurry system	Microcat-RC	ExxonMobil
	Veba combi-cracking	Veba
	Hydrocracking distillation hydrotreating (HDH)	Oel
	Cash, Chevron activated slurry hydroprocessing	Intevep
	EST, Eni slurry technology	Technologies
	CanMet Energy Research Laboratories, Canada	Eni
		Chevron
		Snamprogetti

Efficient catalyst regeneration is the key to FCC process performance. Two approaches are usually considered:

- Two-stage regeneration, allowing improved regenerator temperature control and combustion air distribution
- Catalyst cooling in which a portion of the catalyst is cooled externally to the regeneration, thereby preventing excessively high regenerator temperatures which could harm the catalyst

Figure 13.9 shows a simplified flowsheet of the RFCC process. RFCC consists of an absorber, debutaniser, depropaniser and propane-propylene-splitter. A three-cut gasoline splitter is used to produce light and heavy gasoline, with the bottom stream of the gasoline splitter alternatively sent to LCO or to HCO. Adip, caustic and Merox treatments, propylene drying, polishing units and sour water stripper are installed within the RFCC complex.

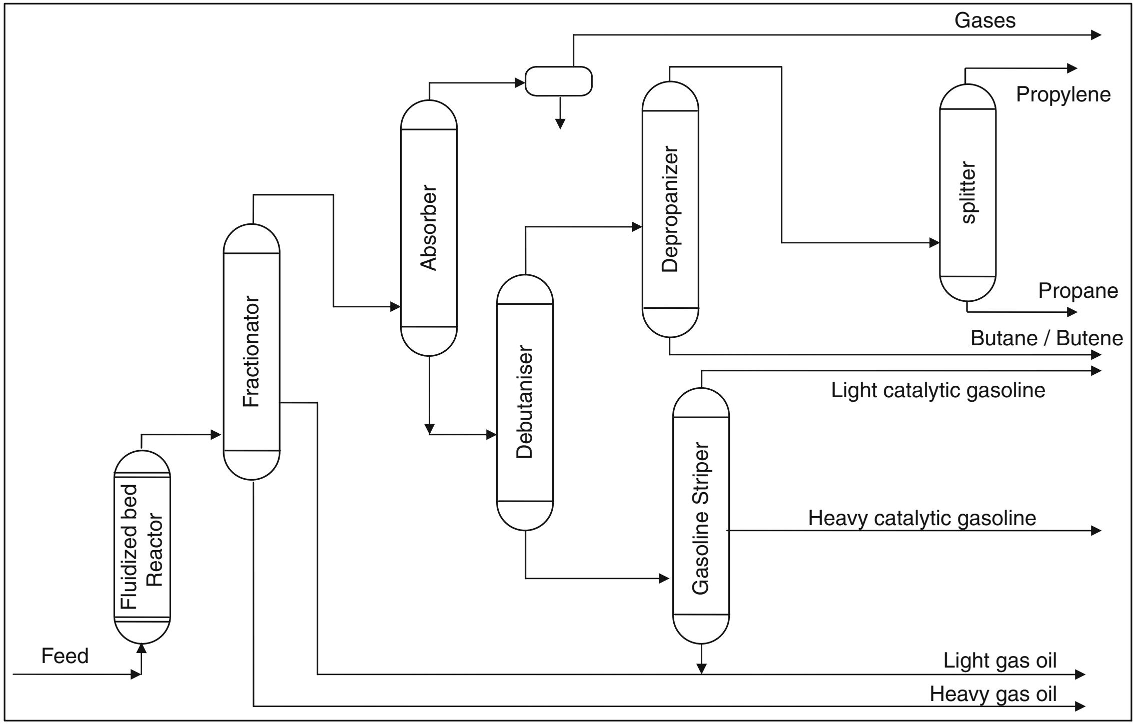
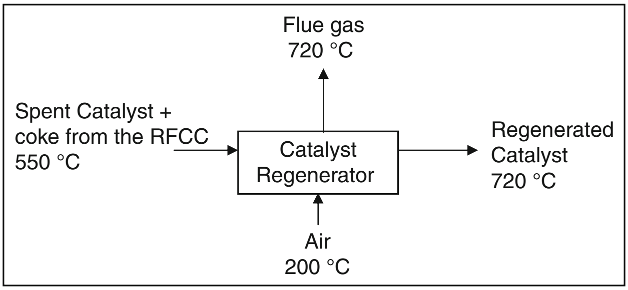


Figure 13.9 RFCC process flowsheet

Example E13.4

The capacity of a RFCC unit is 40,000 BPD, and the API of the feed oil is 22. The RFCC unit works at a conversion of 70%. The following operating data were obtained from a RFCC regeneration unit:



Composition of the regenerator flue gas (dry basis: excluding water fraction):

O_2	0.5 mol%
SO_2	0.2 mol%
CO	3 mol%
N_2	81.3 mol%
CO_2	15 mol%

(A) Calculate the amount (kmol/h) of the flue gas.
(B) Estimate the flow rate of the catalyst (ton/min).

Available information:

$$Cp_{O_2} = 34.777\ \text{kJ/kmol}^\circ\text{C}, \quad Cp_{H_2O} = 41.014\ \text{kJ/kmol}^\circ\text{C}$$

$$Cp_{SO_2} = 86.62\ \text{kJ/kmol}^\circ\text{C}$$

$$Cp_{CO} = 32.92\ \text{kJ/kmol}^\circ\text{C}, \quad Cp_{CO_2} = 54.4\ \text{kJ/kmol}^\circ\text{C},$$

$$Cp_{N_2} = 32.48\ \text{kJ/kmol}^\circ\text{C}$$

$$Cp_{air} = 29.88\ \text{kJ/kmol}^\circ\text{C}, \quad Cp_{catalyst} = 1.11\ \text{kJ/kg K},$$

$$Cp_{coke} = 21.1\ \text{kJ/kg K}, \quad T_{ref} = 15^\circ\text{C}$$

Coke heat of combustion $= 0.393 \times 10^6$ kJ/kmol
Sulphur heat of combustion $= 0.293 \times 10^6$ kJ/kmol
Hydrogen heat of combustion $= 0.237 \times 10^6$ kJ/kmol

Solution:

(A) Using Table 8.6

Coke wt% = 0.05356 (%conv) − 0.18598 (API_f) + 5.966975 = 5.6246 wt%

Feed amount = 40,000 (13.45) = 538,000 lb/h = 1,186,085 kg/h

Carbon in feed = 66,712.5 kg/h = 5,559.4 kmol/h

Flue gas analysis: 15 mol% CO_2 and 3 mol% CO

Carbon balance on the flue gas

$$5559.4 = 0.15\text{ flue} + 0.03\text{ flue}$$

Then, Flue gas flow rate = 30,885 kmol/h

$$\text{(B) } N_2 = 0.813(30,885.6) = 25,110\text{ kmol/h}$$

Air in = 25,110/0.79 = 31,785 kmol/h

O_2 in = 6,675 kmol/h

O_2 used in C burn = 0.15(30,885) + 0.03(30,885)/2 = 5096 kmol/h

O_2 used in S burn = 0.002(30,885) = 61.77 kmol/h

O_2 remain for H_2O = 6,675 − 5096 − 61.77 − 0.005(30,885) = 1,363 kmol/h

H_2O produced = 2(1,363) = 2726 kmol/h

$$\begin{aligned}\text{Flue gas heat} &= \sum m_i \mathrm{Cp}_i (T - T_{\mathrm{ref}})\\ &(720-15)[0.005(30,885)(34.777) + 4633(54.4) + 927(32.92)\\ &+ 61.777(86.62) + 25,110(32.48) + 2726(41.014)]\\ &= 866,361.350\text{ kJ/h}\end{aligned}$$

Energy balance around regenerator:

$$\text{Heat in} = \text{Heat out} = \text{Flue gas heat} + \mathrm{m_{cat}}(1.11)(720-15)$$

$$\begin{aligned}\text{Heat in} = {} & 31,785(29.88)(200-15) + m_{\mathrm{cat}}(1.11)(550-15) + 66,713(21.1)\\ & (550-15) + 2726(0.237\times10^6) + 5559(0.393\times10^6)\\ & +61.777(0.293\times10^6) = 3,850,548,172 + 593.85\ m_{\mathrm{cat}}\end{aligned}$$

$$3,850,548,172 + 593.85\ m_{\mathrm{cat}} = 886,361,350 + m_{\mathrm{cat}}(1.11)(720-15),$$
$$m_{\mathrm{cat}} = 296.7\text{ ton/min}$$

13.4.2. Hydroprocessing

Hydroprocessing (refer to Chapter 7) consumes a substantial amount of hydrogen and is relatively high in investment and operating costs compared with thermal processes. However, it has a high product selectivity of light products. In addition, hydroprocessing offers better selectivity of liquid yield (85% and higher) than any other process discussed above. The residue HDT improves the quality of liquid products, and residue HCR is the most rigorous form of residue hydroprocessing. Various HDT processes (e.g.,

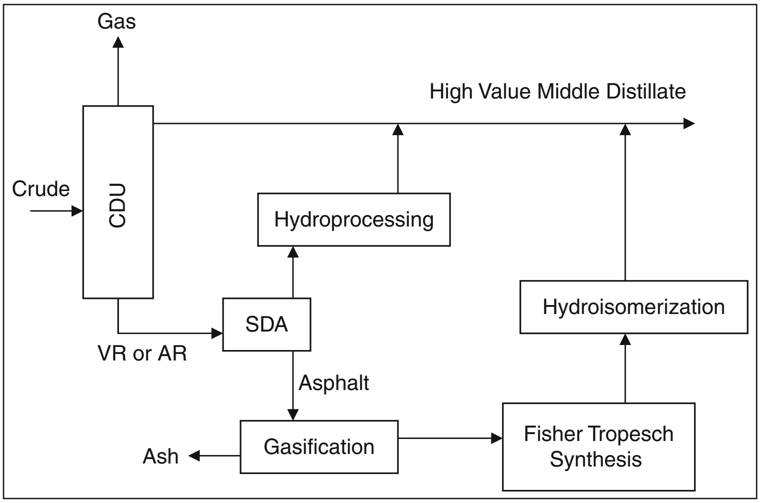


Figure 13.10 Combination of residue upgrading processes including hydroprocessing

HDS, HDN, HDM and HCR) developed over the years now provide the necessary toolbox, at the disposal of industry, to achieve its objectives. Furthermore, the technology continues to improve and diversify considerably. Therefore, not only the better product selectivity is one characteristic of hydroprocessing, but we can also obtain cleaner fuel specifications. However, the race to high activity per volume unit for a long run is still a matter of catalyst formulation and some process parameter optimizations. Figure 13.10 shows typical residue upgrading processes, including hydroprocessing.

Example E13.5

1000 kg/h VR, with the following properties: CCR = 10 wt%, Nickel concentration is 150 wppm, Vanadium concentration is 400 wppm and 5 wt% coke, is introduced to a hydrotreating (HDT) process. 10 kg of catalyst with a surface area of 140 m^2/g and a void volume of 0.8 cm^3/g are used. Knowing that the vanadium component's density is 4700 kg/m^3, the nickel component's density is 5500 kg/m^3 and the carbon density is 1900 kg/m^3, calculate the maximum contaminant removal efficiency.

Solution:

Volume occupied by coke $= 0.05\ (1000)/1900 = 0.0263\ m^3/h$
Volume occupied by nickel $= (150/1 \times 10^6)\ (1000)/5500 = 2.727 \times 10^{-5}\ m^3/h$
Volume occupied by vanadium $= (400/1 \times 10^6)\ (1000)/4700 = 8.5 \times 10^{-5}\ m^3/h$
Total volume $= 0.02643\ m^3/h$
Available void volume $= 0.8\ cm^3/g\ (10{,}000\ g)\ (1\ m^3/1 \times 10^6\ cm^3) = 0.008\ m^3/h$
% removal $= (0.008/0.02643) = 30\%$

Table 13.5 Properties of typical residue (Morel and Peries, 2001)

Property	Type of residue Atmospheric Arabian	Vacuum Kuwait	Vacuum Safaniya
Yield on crude (%wt)	48	22.5	34
SG	0.988	1.031	1.035
Viscosity at 100 °C (mm^2/s)	95	4,010	3,900
Sulphur (wt%)	3.95	5.51	5.28
Nitrogen (wt%)	0.29	0.36	0.46
Conradson carbon (wt%)	13.8	21.8	23
C_7 asphaltene (wt%)	5.7	9.0	11.5
Ni + V (ppm)	104	169	203

Petroleum residues include a wide range of heavy cuts that typically have boiling points above 345 °C (650 °F). These include atmospheric residue (AR), vacuum residue (VR), heavy gas oil (HGO) and vacuum gas oil (VGO). Heavy oils can make up to 40% residue. These residues usually contain high metal content (Ni, V, Fe, Cu, Na), asphaltenes and resin. Metal deposition and coke formation contribute to rapid deactivation of the catalysts. Typical residue and their properties are given in Table 13.5.

A variety of hydroprocessing schemes are being used depending on feed properties, composition, catalyst properties and target product specifications. These can be generally classified as: fixed bed, moving bed, ebullated bed and slurry phase processes. A comparison of the performance of these processes is given in Figure 13.11 (Ancheyta and Speight, 2007).

13.4.2.1. Fixed Bed Process

Fixed bed processes are the most widely used in 80% of current residue hydroconversion processes. The process details are similar to those described for the ARDS process in Chapter 7.

13.4.2.2. Moving Bed Process

In the moving bed processes, fresh or regenerated catalyst is added to the top of the reactor co-currently with the feed (Hycon shell process). A flow diagram of the Hycon process is shown in Figure 13.12. More recently, a moving bed process was developed by adding the catalyst at the top and

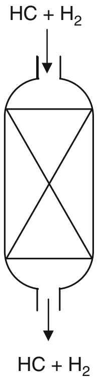
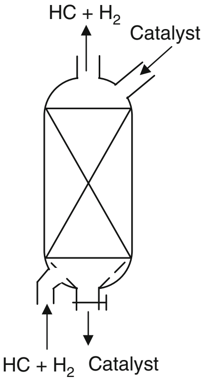
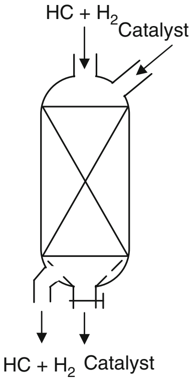
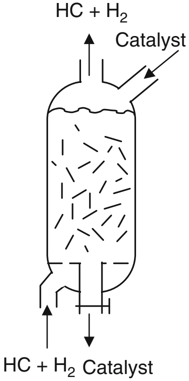
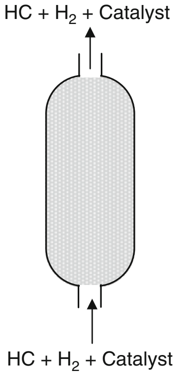
Reactor Configuration					
Process	Fixed bed (trickle bed)	Moving bed (counter current)	Moving bed (cocurrent)	Ebullated bed (three phase fluidizing)	Slurry bed
Licensor	RCD VRDS (Chevron) Hyvahl (IFP)	Hycon (Shell)	OCR (Chevron)	H-oil (Texaco) KLC-Fining (Amco)	CANMET Veba Combicracking Aurabam (UOP)
Catalyst vol%	60	60	60	40	1
Catalyst size, mm	1.5 x 3	1.5 x 3	1.5 x 3	0.8 x 3	0.002
Particles, cm^3	120	120	120	250	2.4 x10^9

Figure 13.11 Comparison of reactor technologies

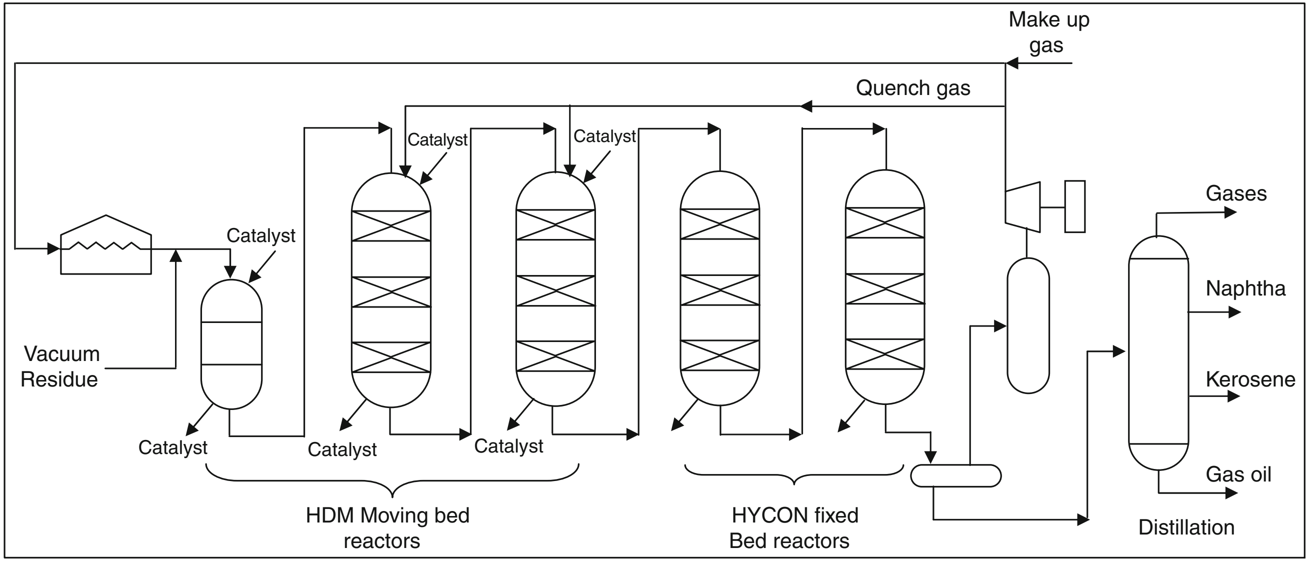


Figure 13.12 Hycon process flow scheme (Scheffer *et al.*, 1997)

the feed at the bottom (OCR Cheveron process). In both cases, the spent catalyst is withdrawn from the bottom and regenerated outside the process. The main advantage of the moving bed processes is that they can treat feeds with high metal contents for a long operation.

13.4.2.3. Ebullated Bed Process

The ebullated (expanded) bed, such as H-oil is a well-established technology. The H-oil process is based on the unique design of the reactor as shown in Figure 13.13. This rector has several advantages over the fixed bed reactor as follows:

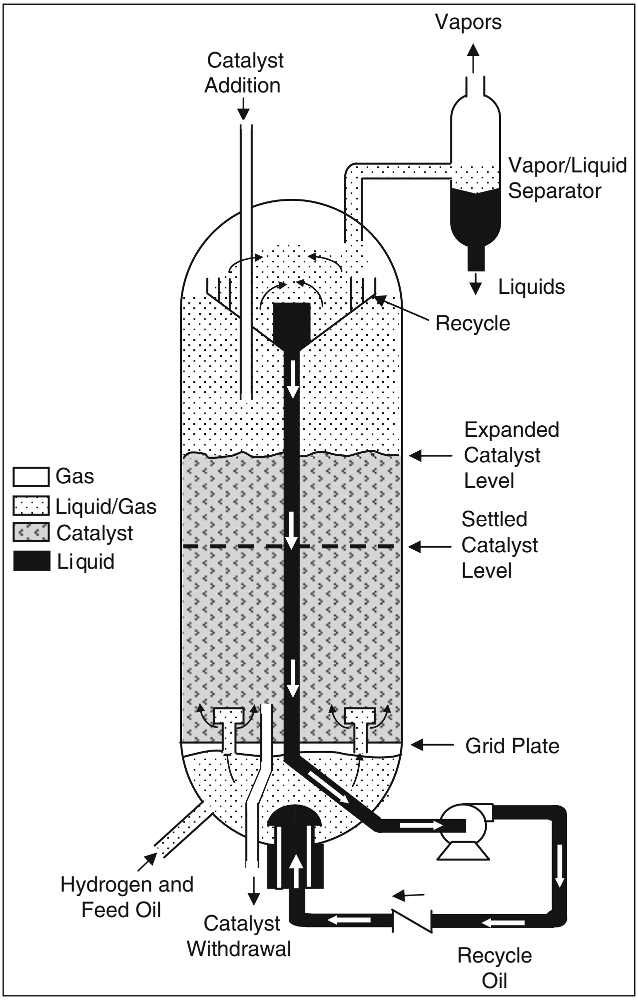


Figure 13.13 Ebullated bed reactor (Rana *et al.*, 2007)

- Due to the loose structure of flow inside the reactor, the solids do not plug the flow.
- Good mixing results in uniform temperatures.
- Catalysts are added and withdrawn continuously, allowing for a long period of operation.

Ebullated bed operability is more difficult than fixed bed because the catalyst renewal operation is carried out at high pressure and temperatures. A flow scheme of H-oil with two reactors is given in Figure 13.14. The reactor operation is compared with other options in Table 13.6. A comparison of the process and operating conditions is also compared with other processes in the same table.

13.4.2.4. Slurry Bed Process

Slurry bed processes are designed to handle residue with high dirt content, high asphalt or even high wastes. Very fine particles of catalyst in the slurry reactor will insure low pressure drop and a high conversion of 90%. A fixed bed reactor is used after the slurry reactor to insure refining of the produced light fraction. Operation of a slurry reactor is difficult. The catalyst tends to accumulate in the reactor, leading to the plugging of down-stream equipment.

13.4.3. Aquaconversion

The main strategy in the aquaconversion process as an option for heavy, extra-heavy crude, with properties listed in Table 13.7, is to use a conversion process severity that is just sufficient to transform heavy crudes into gasoline and diesel.

The aquaconversion process is based on the hydrogen transfer catalyst from water to the feedstock. The typical visbreaking technology is limited by low conversion to control the stability of the product. The hydrogen incorporation is high enough to saturate the free radicals formed in the process. Thus, a higher conversion levels can be achieved. Typical aquaconversion reactions (Marzin *et al.*, 1998) are shown in Figure 13.15. The process produces high API and low viscosity products.

Aquaconversion technology does not produce coke and requires hydrogen at high pressures. Aquaconversion can be carried out in the field to reduce handling problems.

Table 13.8 shows the level of upgrading that is obtained with aquaconversion technology. Figure 13.16 shows the scheme of the aquaconversion process.

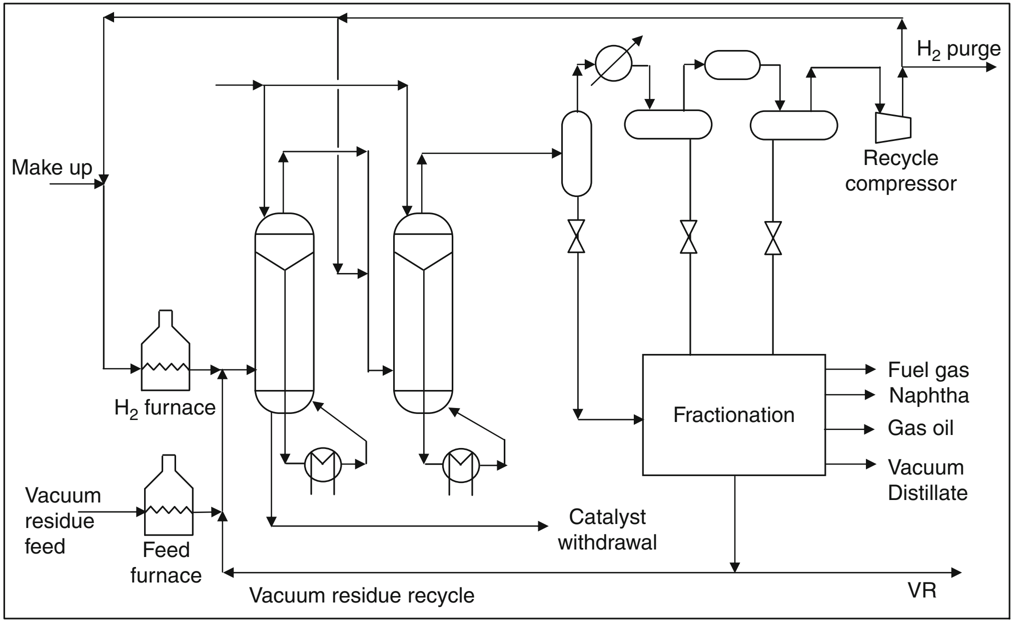


Figure 13.14 Flow scheme of H-oil process with two reactors (Morel and Peries, 2001)

Table 13.6 Comparison of performance of residue upgrading processes (Morel and Peries, 2001)

	Fixed bed	Moving bed	Ebullated bed	Slurry bed
Maximum (Ni + V) content in feed (wppm)	120–400	500–700	>700	>700
Tolerance for impurities	Low	Low	Average	High
Maximum conversion of 550 °C (wt%)	60–70	60–70	80	90
Distillate quality	Good	Good	Good	Poor
Fuel oil stability	Yes	Yes	Borderline	No
Unit operability	Good	Difficult	Difficult	Difficult
Operating pressure, bar (psig)	140 (2100)	200 (3000)	100–200 (1500–3000)	135–205 (2000–3000)
Operating temperature, °C (°F)	400–450 (750–800)	400–450 (750–800)	420–450 (790–800)	450–480 (840–895)
Feed characterization	Low solids	High metals	High metals High solids	High asphaltenes

Table 13.7 Example of heavy and extra-heavy crude (Pereira *et al.*, 2005)

	Heavy crude	Extra-heavy crude
API gravity	22.9	8.5
Sulphur (wt%)	1.13	3.96
Nitrogen (wt%)	0.22	0.73
C_7 Asphaltene (wt%)	2.0	10.2
Conradson carbon (wt%)	4.76	15.8
Vanadium (ppm)	49	488
Nickel (ppm)	11	105
Viscosity (cSt)		
50 °C	7.4	14,257
60 °C	5.9	5533
Pour point (°C)	<-51	27
TAN (mg KOH/g)	0.36	2.27
Yields (vol%)		
350 °C+	52	88
520 °C+	21	56

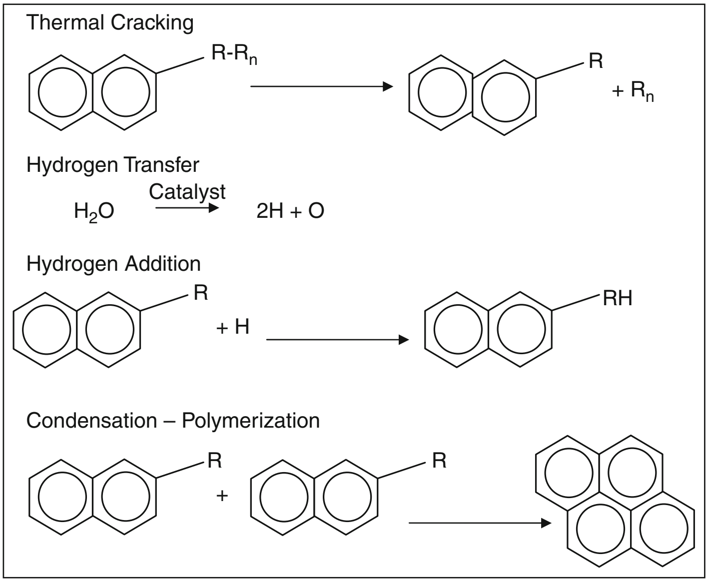


Figure 13.15 Reactions in aquaconversion reactor

Table 13.8 Aquaconversion process performance (Pereira *et al*., 2005)

Feedstock	Extra-heavy crude	Aquaconversion product
API gravity	8.5	14.0
Sulphur (wt%)	3.96	3.3
Nitrogen (wt%)	0.73	0.55
C_7 Asphaltene (wt%)	10.2	8.3
Conradson carbon (wt%)	15.8	13.6
Viscosity (cSt)		
50 °C	14,257	60
60 °C	5533	–
100 °C	–	8
Total acid number (TAN) (mg KOH/g)	2.27	0.3
Yields (vol%)		
350 °C+	88	
520 °C+	56	

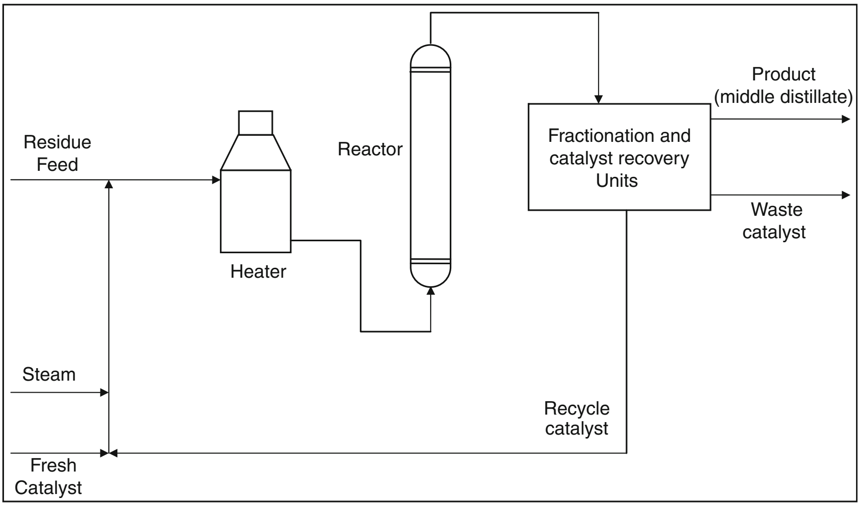


Figure 13.16 Simplified process scheme for aquaconversion residue upgrading unit

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Example E13.6

The following reaction occurs in the aquaconversion process:

$$C + 2\,H_2O \rightarrow 2H_2 + CO_2$$

The bitumen feed (API = 9) has the following elemental analysis:

84.3% C, 10.3% H and 5.37% S

The maximum allowable density is 990 kg/m^3 and can be correlated with elemental residue contents as follows:

$$\rho = 1033 - 13.69 \text{ H wt\%} + 13.85 \text{ S wt\%}$$

How much carbon per bbl feed must react in order to meet the maximum allowable density?

Solution:
Basis 1 bbl feed = 160 kg

$$\text{C} = 0.843(160) = 134.88 \text{ kg} = 11.24 \text{ kmol}$$

Assume reaction conversion x kg C
This will produce = $(x/12)(2)(2) = 0.33x$ kg hydrogen
H_2 in = 0.103(160) = 16.48 kg
H_2 out = $16.48 + 0.33x$

$$\text{wt\% } H_2 = \frac{H_2 \text{ out}}{\text{mass of upgraded oil}} = \frac{16.48 + 0.33x}{160 - x - 0.33x}$$

$$\text{wt\% S} = \frac{0.0537(160)}{160 - x - 0.33x}$$

$$\rho = 990 = 1033 - 13.68\left[\frac{16.48 + 0.33x}{160 - x - 0.33x}\right] + 13.85\left[\frac{0.0537(160)}{160 - x - 0.33x}\right]$$

Solving for conversion x = 8.94 kg C per bbl feed

QUESTIONS AND PROBLEMS

13.1. 100 kg/h residue is introduced to a deasphalting process, which operates at 240 °F. The residue has the following properties: API = 8, S wt% = 6%. A solvent at a rate of 1200 kg/h is used. The DAO produced has API = 21. Calculate the yield of DAO and its sulphur content.

13.2. 10,000 lb/h residue has the following properties: API = 10, CCR = 15 wt%, S wt% = 4.7 wt%, N wt% = 0.7 wt%. The above feed is introduced to a deasphalting process. Calculate the yield of DAO, its CCR, and its sulphur and nitrogen contents.

13.3. Fuel which has the general formula $C_nH_mS_p$ is burned in a gasifier. The dry basis flue gas analysis is as follows: O_2 0.5 vol%, SO_2 0.2 vol%, CO 3 vol%, N_2 81.3 vol%, CO_2 15 vol%. Find the chemical formula of the fuel burned.

13.4. The following reaction occurs in aquaconversion process:

$$C + 2H_2O \rightarrow 2H_2 + CO_2$$

The bitumen feed (API = 11) has the following elemental analysis:

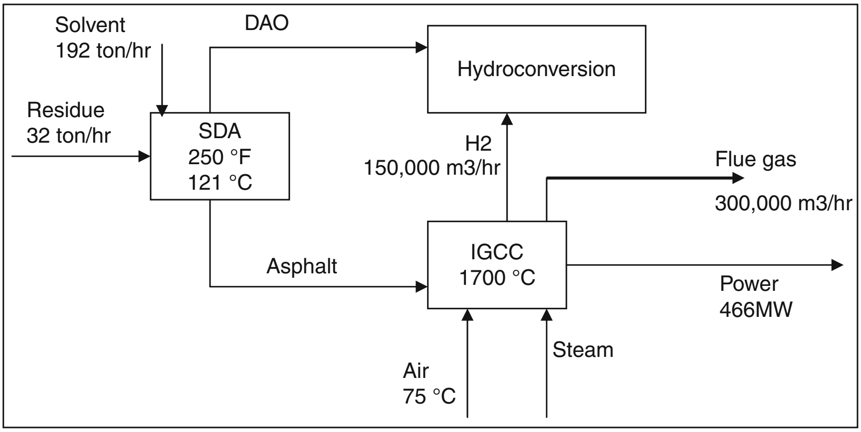
$$80\%\ \mathrm{C},\ 14\%\ \mathrm{H}\ \text{and}\ 6\%\ \mathrm{S}$$

The maximum allowable density is 1000 lb/ft^3 and can be correlated with an elemental residue content as follows:

$$\rho = 1033 - 13.69\ \mathrm{H\ wt\%} + 13.85\ \mathrm{S\ wt\%}$$

Determine whether the produced hydrogen is enough to remove the sulphur in the feed

13.5. The following flowsheet shows the role of the IGCC process in the refinery. The residue flow rate is 32 ton/h with API 6. Air is used at a rate of 10,000 kmol/h. Steam enters at gauge pressure of 2 bar. Hydrogen is produced at a rate of 150,000 m^3/h. Flue gas flow rate is 300,000 m^3/h with the following analysis: NO_2 50 mg/m^3, SO_2 10 mg/m^3 CO 30 mg/m^3 particulates 10 mg/m^3. Calculate the amount of steam that enters the IGCC unit.



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CHAPTER FOURTEEN

SAFETY IN PETROLEUM REFINERIES

14.1. INTRODUCTION

Safety is of extreme importance in all petroleum refineries. Every employee is involved in developing the regulations and procedures for work safety. In this way, anyone who works in the refinery is part of the safety system and will always be sure to work safely and help others work safely.

All routine jobs in the refinery should conform to high safety standards. No work can be carried out without a permit. This is in order to ensure that personnel always know where work is being done and, therefore, they can prevent jobs from overlapping. Whenever workers are in the refinery site, they have to wear safety clothing known as personal protective equipment (PPE).

14.2. HAZARDS IN REFINERY UNITS

14.2.1. Crude Oil Pre-treatment

Hydrogen sulphide, hydrogen chloride and salts in the desalter are the main causes of corrosion in the unit. Corrosion is the source of leakage of oil and evaporated hydrocarbons. Low boiling point hydrocarbon leaks can possibly lead to fires and explosions in the unit. Scheduled maintenance is required to prevent salt fouling and corrosion.

14.2.2. Crude Oil Distillation

Low boiling point hydrocarbons may leak from improper connections between furnace, heat exchangers and distillation column. When the hydrocarbon leaks find any source of ignition, a fire and/or an explosion may occur. Thermal cracking is the source of coke formation which may block lines and connections leading to over-pressurising and sometimes unit failure and consequent shut down. Coke formation can be prevented by controlling the temperature and pressure. Relief valves should be provided and regularly inspected for over-pressure.

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Sour crude distillation, especially at a high temperature of 232 °C (450 °F), causes severe corrosion. Anti-corrosive chemicals and sufficient wash water are injected to avoid corrosion.

14.2.3. Catalytic Reforming

Catalyst handling and loading should be based on standard operating procedure so as not to crush the catalyst leading to fine particulates that may either escape into the atmosphere or be deposited in the reformer lines and connections. Hydrogen chloride and ammonium chloride may form in the unit pre-heater which can lead to fouling and corrosion. Scheduled maintenance is required to prevent corrosion and ensure the temperature is controlled to avoid hot spots in the reactor.

14.2.4. Thermal Cracking

When sour crude is processed in the delayed coking unit, procedures must be carried out carefully to prevent corrosion, since the unit is working at high temperatures between 232 and 482 °C (450 ° and 900 °F). Above 482 °C (900 °F) steam is injected to prevent coke formation in the lines. Scheduled maintenance is required to ensure that the temperature control units are working properly. Hydrogen sulphide corrosion may occur in the furnace, coking drums and reactors. Water jets used for coke removal from the coke drum should be drained properly and completely to avoid explosion when fresh coke forms again during operation.

14.2.5. Hydrotreating and Hydrocracking

Catalyst handling and loading must be carried out with care so that fine particles from crushed catalyst are not produced. Fine particulates may result in a dust explosion. Since hydrogen sulphide is present regular maintenance is required to avoid corrosion. A high operating temperature leads to coke formation on the catalyst; therefore, care should be taken during the catalyst regeneration process to avoid fire and explosion.

14.2.6. Fluid Catalytic Cracking

Catalyst handling and loading should be based on the standard operating procedure to prevent catalyst dust explosion. Oil coating the spent catalyst should be stripped out in the stripper section of the reactor before sending it to the regenerator. If not removed, the presence of this oil will cause explosion during contact with air in the regenerator. Hydrocyclones must be carefully operated, otherwise catalyst fines will be carried out over to the distillation column. These fines will be concentrated in the decant oil.

14.2.7. Alkylation

In the alkylation unit, two systems are used, either sulphuric acid or hydrofluoric acid, which are both considered hazardous chemicals. Material handling with extreme care is required especially the hydrofluoric acid during cleaning processes in which water is used. Improper contact of the acid with water may lead to an explosion. A concentrated acid is used with small amounts of water to avoid corrosion. Acid effluent must be neutralised before it is sent to the sewers.

14.2.8. Hydrogen Production

Scheduled maintenance is required to prevent corrosion and ensure that temperature and pressure are controlled. This must be done in order to avoid hot spots in the reactor. Low boiling point hydrocarbons released from a leak may lead to a fire and/or an explosion. Inspections for piping and connections should be done regularly to assure hydrogen production quality.

14.3. SAFETY PROGRAMS AND REGULATIONS

Regulatory agencies such as the Occupational Safety and Health Administration (OSHA) (OSHA, 2004) and the Chemical Safety and Hazard Investigation Board (CSIB) in the United States set safety regulations and accident investigation procedures to ensure work safety in industrial environments. Refining processes have special safety requirements due to the handling of crude oil and flammable hydrocarbons. Recently, every refinery began making its own safety programs based on its processing scheme, environmental regulations and manpower.

14.4. ACCIDENTS AND LOSS PREVENTION MEASURES

All accidents and near misses, which are unplanned events that do not result in injury, should be reported. Statistical analyses based on the reported accident data improve regulations and procedures to save lives and property by reducing and eliminating accidents in industry. The benchmarking indicators for accident reporting (Ball, 1991) are: lost time accident (LTA) rate, recordable accident rate, LTA severity rate and days lost per LTA.

Accident frequency rates are calculated on the basis of number of accidents per 100,000 working hours. The typical LTA rate is 0.3. An LTA value of 0.3 means 0.3 injuries per 100,000 h. The average time at work in refineries is 2000 h per year (50 work weeks/year × 40 h/week).

For example, if a refinery has 1000 employees, the working hours will be 2 million (1000 employee × 2000 h), and with a LTA rate of 0.3, this gives 6 accidents per year in this refinery based on OSHA's LTA.

OSHA's incidence rate (2004) is based on the number of incidents per 100 workers years (2000 h/year). Therefore, OSHA incidence rate is based on 200,000 h of all workers exposed to hazards, either based on injuries (equation 14.1) or based on lost workdays (equation 14.2):

$$\begin{pmatrix}\text{OSHA incidence rate}\\ \text{based on injuries}\end{pmatrix} = \frac{\text{number of injuries} \times 200000}{\text{total hours worked by all employees}} \tag{14.1}$$

$$\begin{pmatrix}\text{OSHA incidence rate}\\ \text{based on lost workdays}\end{pmatrix} = \frac{\text{number of lost workdays} \times 200000}{\text{total hours worked by all employees}} \tag{14.2}$$

The OSHA incidence rate provides information on all types of work related accidents.

Example E14.1

A refinery has 1500 full-time employees. In a particular year, this plant had 28 reportable lost-time injuries that resulted in 175 lost workdays. Compute the OSHA incidence rate based on injuries and lost workdays.

Solution:

Since total working hours for all employees is 1500 × 2000,

$$\begin{pmatrix}\text{OSHA incidence rate}\\ \text{based on injuries}\end{pmatrix} = \frac{28 \times 200000}{1500 \times 2000} = 1.87$$

$$\begin{pmatrix}\text{OSHA incidence rate}\\ \text{based lost workdays}\end{pmatrix} = \frac{175 \times 200000}{1500 \times 2000} = 11.67$$

14.5. RISK MANAGEMENT AND RISK ASSESSMENT

High risk is addressed in refineries because of the handling of hazardous and flammable materials such as hydrocarbons and processing chemicals. Risk assists in terms of frequency of occurrence and consequences as follows (Maher and Sharp, 1996):

$$\text{Risk} = (\text{Frequency})(\text{Consequence}) \tag{14.3}$$

Accident probability and worst case scenarios are typical key issues in calculating the risk. Process failure is based on equipment failure probabilities.

Table 14.1 Failure rate data for commonly used process components (Crowl and Louvar, 2002; Lees, 1986)

Instrument	Failures/ year	Instrument	Failures/ year
Controller	0.29	Level measurement (solids)	6.86
Control valve	0.60	Pressure Switch	0.14
Flow measurement (fluids)	1.14	pH-meter	5.88
Flow measurement (solids)	3.75	Pressure relief valve	0.022
Flow switch	1.12	Pressure switch	0.14
Gas-liquid chromatograph	30.6	Solenoid valve	0.42
Hand valve	0.13	Stirrer motor	0.044
Indicator lamp (alarm)	0.044	Strip chart recorder	0.22
Level measurement (liquids)	1.70	Thermocouple measurement	0.52
Valve positioned	0.44	Thermometer measurement	0.027

The probability of a failure in a process depends on the time of usage and the demand on a control unit, the maintenance time period, and device specifications. Table 14.1 lists failure rates for some selected process components. The probability P that the component will fail during the time interval (t), knowing the average failure rate (μ) is

$$P = 1 - e^{-\mu t} \tag{14.4}$$

Process components interact in two way; first, process failure can occur when components fail in parallel, which means that all components in parallel must fail together to lead to process failure. The gate is an AND in the parallel components. Second, process failure occurs when some components fail. The gate here is OR. For the first type the failure rate is

$$P_{\text{process}} = \prod P_i = P_1 \times P_2 \times P_3 \ldots \tag{14.5}$$

For the second type, the formula is

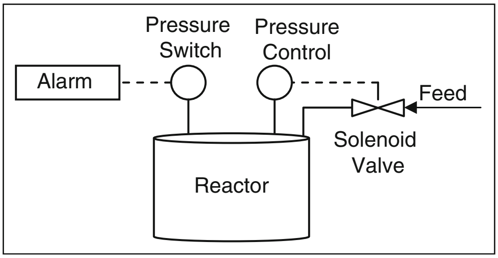
$$P_{\text{process}} = \sum P_i \tag{14.6}$$

The total reliability R of a process is the probability that components in a process will not fail and can be calculated as

$$R = 1 - P = \mathrm{e}^{-\mu t} \tag{14.7}$$

Example E14.2

In the reformer unit, a reactor works at high pressure and temperature. The reactor contains two control units (see the attached figure). The first unit consists of a high pressure alarm to alert the operator in case of any emergency increase in pressure and a pressure relief switch. The second control unit consists of pressure controller connected to a solenoid valve to close the feed supply to the reactor. Estimate the probabilities of process failure due to high pressure.



Solution:

Failure rate for each component is selected from Table 14.1. The probability P is then calculated using equation (14.4). An increase in pressure occurs when both (AND) the alarm and the shut down system fails in supplying feed. Failure in the alarm unit is in a series (OR) with a pressure switch and assuming t = 1 year. Therefore,

$$P_{\text{alarm}} = (1 - e^{-0.14}) + (1 - e^{-0.044}) = 0.1736$$
$$P_{\text{shutdown}} = (1 - e^{-0.29}) + (1 - e^{-0.42}) = 0.5946$$

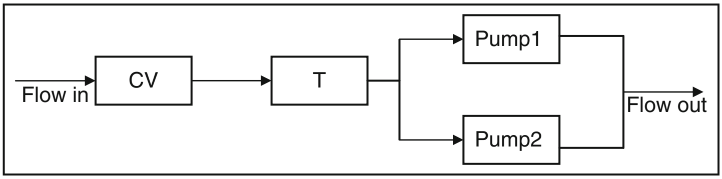
The probability of process failure is

$$P_{\text{process}} = (P_{\text{alarm}})(P_{\text{shutdown}}) = (0.1736)(0.5946) = 0.103/\text{year}$$

This means that failure may occur once every 9.7 years (1/0.103 = 9.7).

Example E14.3

Consider a control valve (CV), a tank (T) and two pumps (Pump1 and Pump2) in the following configuration.



Assume that Pump2 is a full capacity spare for Pump1. Pump2 is only needed when Pump1 fails and cannot perform its function. Determine the reliability within the system.

Data: the failure rate of Pump1 and Pump2 are 0.91 and 0.81, respectively. Tank failure rate is 0.99 and control valve failure rate is 0.9.

Solution:

From the flow diagram Pump1 and Pump2 are in parallel (AND) and other components are in series (OR):

The reliability rate for pump 2 per year is:

$$R = e^{-\mu t} = \exp(-0.81) = 0.4448$$

Other reliability rates can be calculated similarly.

The reliability of the system is

$$R = R_{CV} + R_T + (R_{Pump1} \times R_{Pump2})$$

$$R = 0.4065 + 0.3715 + (0.4448 \times 0.4025) = 0.95$$

This means that the system is reliable and safe 95% of the operating time during the one year period.

14.6. FIRE AND EXPLOSIONS

Accidental vapour cloud explosion hazards are of great concern to the refining and chemical processing industry, and a number of catastrophic explosion accidents have had significant consequences in terms of death, injury, property damage, loss of profit, and environmental impact.

Fuel-air explosives (FAE) disperse a cloud of fuel which is ignited by a source to produce an explosion. The main destructive force of FAE is high over-pressure. For fuel vapour cloud explosion, there is a minimum ratio of fuel vapour to air below which ignition will not occur. Also there is a maximum ratio of fuel vapour to air, at which ignition will not occur. These limits are the lower (LEL) and upper explosive limits (UEL). For gasoline vapour, the typical explosive range is from 1.3 to 6.0 mol% vapour to air, and for methane, this range is 5–15 mol%. Flammability limits are related to explosive limits since most explosions are followed by fire. The mass and type of material released contribute to the potential damage from a vapour cloud explosion.

Example E14.4

A mixture of propane in air containing 4.03 mol% C_3H_8 is the feed to a combustion furnace. If there is a problem in the furnace, a stream of pure air (dilution air) is added to the fuel mixture prior to the furnace inlet to make sure that ignition is impossible. If propane flows at a rate of 150 mol/s in the original fuel gas mixture, what is the minimum molar flow rate of the dilution air needed?

The LFL of propane in air is 2.05 mol% C_3H_8 and the UFL is 11.4 mol%

Solution:

Suppose that n_1 is the fuel gas flow rate
Propane feed rate: $0.0403n_1 = 150$ then $n_1 = 3722$ mol/s
The product fuel must contain at least 2.05 mol% propane (LFL) to avoid ignition
If n_2 is the flow rate of the product gas, then
Propane balance: $150 = 0.0205n_2$ then $n_2 = 7317$ mol/s
Air flow rate = 7317 – 3722 = 3595 mol/s
The minimum air flow rate is 3595 mol/s.

Flammability limits for vapours are determined in a mixture with air using the following Le Chatelier equation:

$$\mathrm{LFL_{mix}} = \frac{1}{\sum y_i/\mathrm{LFL}_i} \tag{14.8}$$

where LFL_i is the lower flammability limit for component i (vol%) and y_i is the mole fraction of component i. The same formula can be used for the $\mathrm{UFL_{mix}}$.

Example E14.5

What are the LFL and UFL of a hydrocarbon gas mixture composed of 2 vol% methane, 0.4 vol% ethane and 0.5 vol% propane and the balance is air?
The following table contains the LFL and UFL for each component in the mixture.

	LFL (vol%)	UFL (vol%)	Vol%
Methane	5.3	15	2
Ethane	3.0	12.5	0.4
Propane	2.2	9.5	0.5
Air			97.1

Solution:

Normalise the hydrocarbon vol% and assume an ideal gas mixture. The mol% for the three hydrocarbons is calculated to be 68.96 mol% methane, 13.8 mol% ethane and 17.24 mol%. The LFL can be calculated using equation (14.8):

$$\mathrm{LFL_{mix}} = \frac{1}{\sum 0.6896/5.3 + 0.1380/3.0 + 0.1724/2.2} = 3.93\%$$

Similarly, $\mathrm{UFL_{mix}} = 13.305\%$
Since the mixture contains 2.9 vol%, and the $\mathrm{LFL_{mix}}$ is 3.93%, it is not flammable. For the mixture of hydrocarbons to be flammable, the vol% of the mixture in air must be in the range 3.93–13.305%.

14.7. HAZARD ANALYSIS

Refinery processes include potential hazard risks due to excessive operating conditions such as temperature and pressure, in addition to the process hazardous material. Managing these risks is considered to save life and property from losses. An accident can be catastrophic to a plant and nearby facilities and even residents near a refinery. Recently, risk management techniques have been applied in the petroleum industry and this application has enhanced plant safety through modifications in plant design and operation.

The application of fault tree analysis (FTA) and hazard operability (HAZOP) techniques to a refining facility are conducted in a wide range. The FTA is used to identify the failure sequences which could lead to process hazards, and the analysts use these results to evaluate the impact of specific hazards on process safety.

The following questions are raised in both FTA and HAZOP techniques:

- What can happen?
- How often can it happen?
- How bad will it be?

Each of the above questions contains a lot of information and tools. The first question poses the top event scenario. The *how often* question is based on the probability of process failure. The failure data for equipment is calculated based on statistical analysis of a previously collected data bank. The last question involves the consequences of an incident and requires release models, emission inventory, gas dispersion of plumes or clouds, an evaporation material balance for hydrocarbons in a pool and also weather conditions.

14.7.1. Worst Case Scenario

Hazard analysis requires setting a worst case scenario of a hazardous top event. To completely analyse the set scenario, detailed information about the process, the piping and instrumentation diagrams (P&IDs) are required. Chemical hazardous data must be obtained on every chemical used in the process. These data are in the Material Safety Data Sheet (MSDS), which contains physical and chemical properties of the material. In addition, material handling and managing of emergency spills or exposure are all included in the MSDS. The tracing of pressure lines and the evaluation of high temperatures must be conducted. Environmental aspects for the continuous discharges of solid, liquid and vapour disposals, as well as health and toxicology exposure effects, need to be considered. It is important to establish and manage operating and maintenance procedures so they fall in line with design criteria for Safety, Health & Environment (SHE) issues. Auditing and testing the application of these procedures is the responsibility of management teams in the refinery.

14.7.2. Fault Tree Analysis

Like many facilities in the petroleum industries, substantial capital investments are raised. During the operation, the failure probability should be minimised by regular, scheduled maintenance and testing. A failure can occur and lead to catastrophic consequences. The following case study is based on a scenario of an explosion of flammable material in a crude distillation unit. The facility was in the construction phase. Several modifications were made to the facility, and a process hazard analysis was requested.

The distillation column receives crude oil and separates it into naphtha, diesel fuel and heavy residual crude. The diesel fraction is send to a side stripper to meet market specifications. This facility is composed of the following subsystems (Figure 14.1): a furnace to evaporate most of the

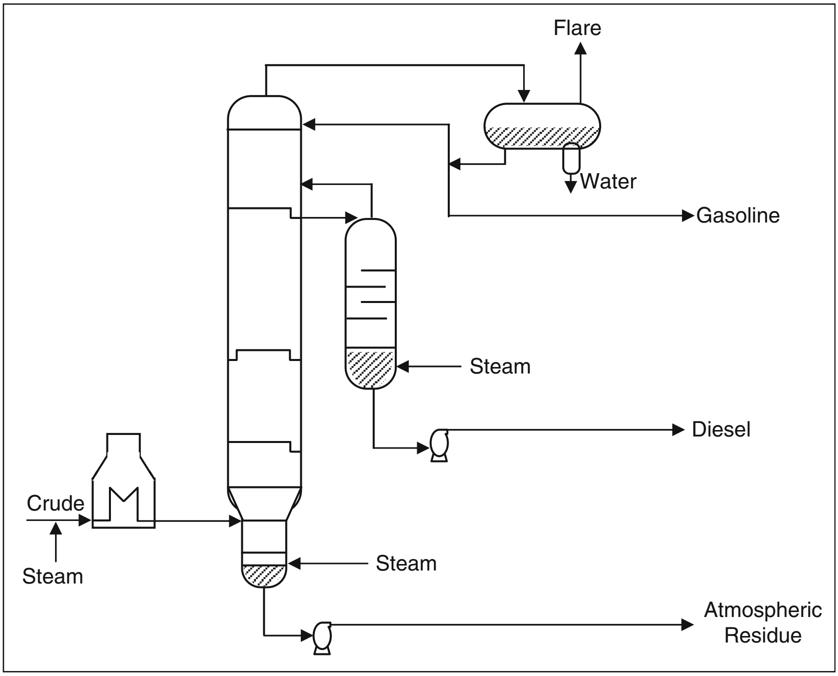


Figure 14.1 Crude distillation unit

hydrocarbons, a distillation column with a side stripper, and an overhead condenser.

To analyse the potential hazards, the system descriptions, piping and instrumentation diagrams, and process control diagrams must be reviewed. Each hazard is identified with assumptions and recommendations to highlight the hazard consequences. In general, the following are some potential problems identified in the crude distillation unit:

- Over-pressure of vessels and piping due to excessively high pump discharge.
- Explosion due to either over-pressure or overheating.
- Leak of hydrocarbon liquids or vapours to the environment via valves and pipe connections.

The temperature of the condensed naphtha is controlled by fan cooling. The controller fixes the fan speed to the desired set points. Condensed naphtha flows by gravity to the overhead collector drum. Settling naphtha in this drum assures the separation of non-condensable gases and water traces from naphtha before storage.

A worst case scenario, involving the over-pressurising of the overhead stream, is assumed as a top event. If the process gas flow exceeds the set points, the excess gas is passed to a flare system. The process flow diagram is shown in Figure 14.2.

Figure 14.3 illustrates a simplified fault tree model for the top event. At first examination, exceeding the design pressure of the overhead would seem to require two simultaneous failures: the process gas relief valve and the emergency bypass valve. The over-pressure in the condenser occurs when the relief valve to the flare system fails.

The following recommendations are requested based on the hazard analysis:

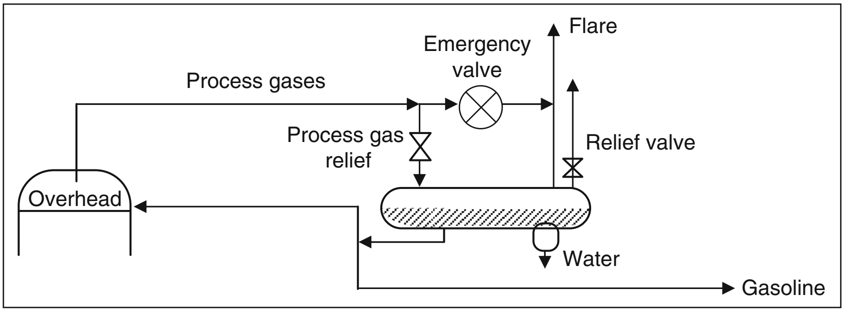


Figure 14.2 Corrective actions for process gas over-pressure

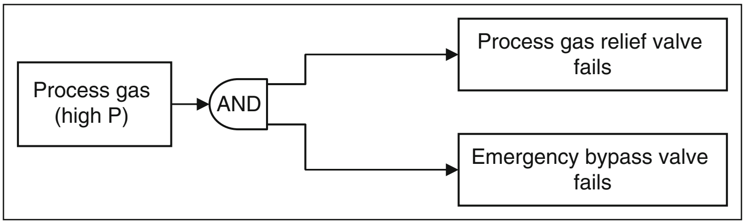


Figure 14.3 Fault tree for the case of gas over-pressurised

- Install a high pressure alarm on the crude overhead set at the maximum allowable working pressure (MAWP).
- Install a high level alarm on the overhead drum to avoid spillage of flammable naphtha and to protect the compressors.
- Install a check valve in the naphtha drain line to assure that there is no backflow.
- Install pressure safety valves on piping downstream of pumps.

14.7.3. HAZOP Case Study

HAZOP is defining hazards key words, consequences, causes and actions to be done to prevent an assumed hazardous scenario. HAZOP can be applied on units such as reactor, vessel or fractionator as a study node. In addition, HAZOP can be performed on a line in the flow sheet that includes valves and pumps. Cooling lines can be considered as HAZOP study node.

HAZOP procedure uses the following steps to complete an analysis:

- Choose a study node in the P&ID.
- Select a process parameter such as flow, pressure or temperature.
- Apply the HAZOP guide words (none, more of, less of, etc) to the process.
- Determine possible causes for each deviation of the process parameter.
- Record the consequences of the each deviation.
- Recommend an action to avoid this deviation.

Example E14.6

Consider the reactor system shown in Figure E14.6. The reaction is exothermic, so a cooling system is utilised to remove excessive heat. If the temperature rises in the reactor, the reaction rate increases and the reactor may explode due to high pressure build-up inside. Perform a HAZOP study on the cooling system.

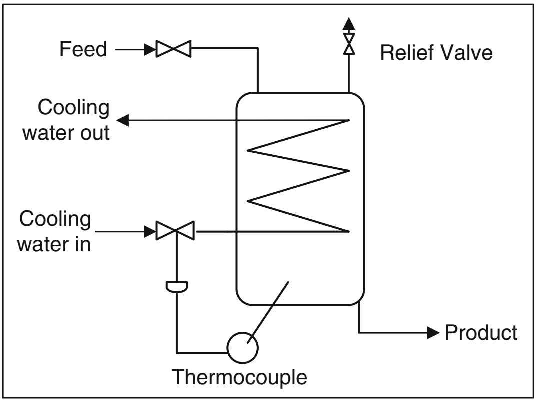


Figure E14.6 Exothermic reactor with cooling coil

Solution:

Table E14.6 shows the HAZOP results for the cooling node.

Table E14.6 HAZOP Study

Study node	Process parameter	Guide words	Possible causes	Possible consequences	Recommended action
Cooling system	Flow	No	1. control valve fails closed 2. plugged coil 3. cooling water service fails	Increase in temperature followed by increase in pressure then explosion of reactor	1. regular maintenance 2. check water service reliability
		High	1. control valve fails open		
		Low	1. control valve fails responding 2. water source failure		
	Temperature	Low	Low water supply temperature	None	
		High	High water supply temperature	Cooling system inefficient leading to reactor explosion	Install high temperature alarm

14.8. SAFETY CONSIDERATIONS IN PLANT LAYOUT

Plant layout is often a compromise between a number of factors, including safety aspects such as (Brandt et al., 1992; Meissner and Shelton, 1992):

- The geographical limitations of the site.
- The distances for transfer of materials between plant and storage units to reduce costs and risks.
- Interaction with existing or planned facilities on site such as existing roadways, drainage and utilities routings.
- The spaces for plant operability and maintainability.
- The hazardous and flammable material storages.
- Emergency services and escape routes for on-site personnel.
- The need to provide acceptable working conditions for operators.
- Preventing and/or mitigating the escalation of adjacent events (domino effect).
- Ensure that safety within on-site and off-site occupied buildings is maintained.
- Controlling the access of unauthorised personnel.

Hazard assessment of site layout is critical to minimise consequences of loss of containment and chances of escalation. The Domino effect may be by fire, explosion or toxic gas cloud causing loss of control of operations in another location.

The spread of fire from its origin to other parts of the premises can be prevented by vertical and horizontal compartments using fire-resisting walls and floors. Consideration should also be given to the spread of flammable material via drains, ducts and ventilation systems. Delayed ignition following a release may result in the spread of flames.

Protection against domino effects by convection, conduction and radiation can be achieved by inherent safety principles, that is, ensuring that the distances between plant items are sufficient to prevent overheating of adjacent plants, therefore compromising the safety of those plants. Where this is not possible due to other restrictions, other methods, such as fire walls and active or passive fire protection, may be considered.

Plant Layout design techniques applicable to the reduction of the risks from release of flammable or toxic materials include:

- Locating the storage of flammable/toxic material outside process areas.
- Locating hazardous plants away from main roadways through the site.
- Fitting remote-actuated isolation valves where high inventories of hazardous materials may be released into vulnerable areas.
- Allowing for the provision of dykes and sloping terrain to contain releases, increase the safety and reduce environmental effects.

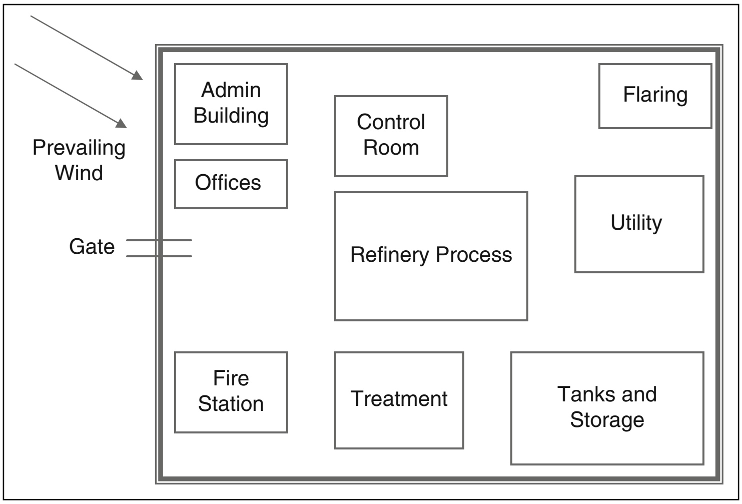


Figure 14.4 Typical refinery layout

- Siting of plants within buildings as secondary containment.
- Siting of plants in an open air environment to ensure rapid dispersion of minor releases of flammable gases and vapours and thus prevent concentration build-up which may lead to flash fires and explosions.
- Hazardous area classification for flammable gases, vapours and dusts to designate areas where ignition sources should be eliminated.

Figure 14.4 shows typical refinery layout based on the above instructions for minimising risks. The distance between occupied buildings and plant buildings will be governed by the need to reduce the dangers of explosion, fire and toxicity. In particular, evacuation routes should not be blocked by poor plant layout, and personnel with more general site responsibilities should be housed in buildings sited in a non-hazard area near the main entrance. Consideration should be given to the siting of occupied buildings outside the main fence. In all cases occupied buildings should not be sited downwind of hazardous plant areas.

14.9. SAFE OPERATION SYSTEMS

The refinery must provide a safe workplace and safe products. All accidents can be preventable. Safety regulations and procedures address employee health through working in the proper environment. In addition, the refinery is responsible for the nearby environment, which includes residents and properties. Typical systems to maintain safe operations include pressure relief, flare relief and air, water and solid emissions monitoring systems.

14.9.1. Pressure Relief Systems

Over-pressurisation can upset normal operating conditions. Relief valves are installed in the lines where over-pressurisation is possible. The relief device has a set point pressure which is below the maximum allowable working pressure (MAWP). The pressure accumulation is the percentage increase above MAWP, while the over-pressure is the percentage increase in pressure above a set point (Figure 14.5).

Physical property data and sometimes reaction rate characteristics are required for making relief sizing calculations. A designer of relief systems must be familiar with industrial standards codes and insurance requirements. Codes of particular interests are published by the American Society of Mechanical Engineers, the American Petroleum Institute (API 520, 1994) guidelines.

14.9.2. Flare Relief System

Flares are sometimes used after knockout drums. The objective of a flare is to burn the gas to produce combustion products that are neither toxic nor combustible. When operating conditions change, flares may be used as part of the process to ensure that refinery equipment is operated safely. In most cases, hydrocarbons are recovered and reused in the refining process. However, in some cases, residual hydrocarbons are burned off. The flares combust hydrocarbon vapours into water and carbon dioxide. This is the most proper method of preventing hydrocarbon vapours from escaping into the atmosphere.

The diameter of the flare must be suitable to maintain a stable flame and to prevent a blow out when vapour velocity is greater than 20% of the sonic velocity. The flare height is fixed on the basis of the heat generated and the resulting potential damage to equipment and humans. The usual design criterion is that the heat intensity (q_f) at the base of the flare is not to exceed 1500 Btu/hr/ft^2. The flare height (H) in feet can be calculated as (API, 1999):

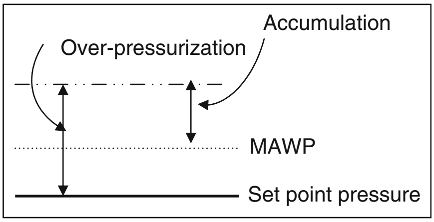


Figure 14.5 Description of over-pressurisation and accumulation

$$H = -60d_f + 0.5\sqrt{(120d_f)^2 - \left(\frac{4\pi q_f Y^2 - 960Q_m\sqrt{M}}{\pi q_f}\right)} \tag{14.9}$$

where, d_f is the flare diameter (ft), Y is the distance from the flare base, M is the fuel molecular weight and Q_m is the vapour flow rate (lb/h).

Example E14.7

Determine the flare height required to not exceed the 1500 Btu/hr/ft^2 heat intensity at a distance of 500 ft. The flare diameter is 4 ft. The fuel flow rate is 900,000 lb/h with a molecular weight of 44.

Solution:

Using equation (14.9)

$$H = -60(4) + 0.5\sqrt{(120(4))^2 - \left(\frac{4\pi(1500)(500)^2 - 960(900000)\sqrt{44}}{\pi(1500)}\right)} = 94.4 \text{ ft}$$

14.9.3. Air Emission Monitoring

The refinery maintains the commitment to reduce and eliminate emissions to the atmosphere. By running plants safely the amount of pollutants emitted into the air are reduced. Regular inspection of pumps, compressors, valves and flanges ensure that hydrocarbons do not escape into the atmosphere. To meet clean air standards, emissions from furnaces must be monitored and controlled. The calculation of fugitive emissions from pumps, valves and flanges is discussed in Chapter 17.

14.9.4. Water Emission Monitoring

Any water that comes into contact with any raw material, product, byproduct or waste is known as process water. All process water from the refinery must receive extensive treatment and be in compliance with all local regulatory requirements. Water is used to keep the refinery product streams and equipment cool. By cooling the water in large cooling towers and re-circulating it, the amount of fresh water needed is minimised.

14.9.5. Solid Waste Monitoring

At the refinery, proper waste minimisation and management is a high priority. Refinery solid wastes are typically in the form of sludge, spent process catalysts, filter clay, and incinerator ash. Sludge is generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters. Sludge is also generated from cooling waters segregated for treatment from other process or oily cooling waters. The refinery uses a variety of techniques to reduce or recycle waste and transform it into useful products as discussed in Chapter 17.

14.10. EMERGENCY ALARMS

Alarm systems alert operators to plant conditions, such as deviation from normal operating limits and to abnormal events, which require timely action or assessment. Alarm systems are not normally safety related, but they do have a role in enabling operators to reduce the demand on the safety related systems, thus improving overall plant safety. Guidelines for alarm systems are as follows (EEMUA, 2007):

- The alarm system should be designed in accordance to the designated reliability.
- The alarm system should be independent from the process control system and other alarms unless it has also been designated safety related.
- The operator should have a clear written alarm response procedure for each alarm (simple, obvious and invariant) on which he is trained.
- Each alarm should be distinguished from other alarms and remain on view at all times when active.
- The operator responsible for responding to the alarm should not be overloaded.

14.11. NOISE IN REFINERY

A noise impact assessment measures the amount of noise (a noise level) coming from a particular work and compares it against a noise limit. Noise limits are usually compared to the Environment Protection Agency (EPA) guidelines. Further, assessing noise is a complex process and involves measuring background noise so that noise limits can be determined. Then the work noise levels should be measured to see its impact on the background noise levels. Background noise is measured at various locations during the daytime, evening and night time. Background noise in a refinery is basically all the noise a person can hear, other than noise coming from the industry. For example, noise from the highway is considered background noise, but noise from a nearby factory is not. Once the background noise is measured, consultants then calculate the noise limit for each location. It is important to note that noise limits change depending on the time of the day and also on the area location and activities.

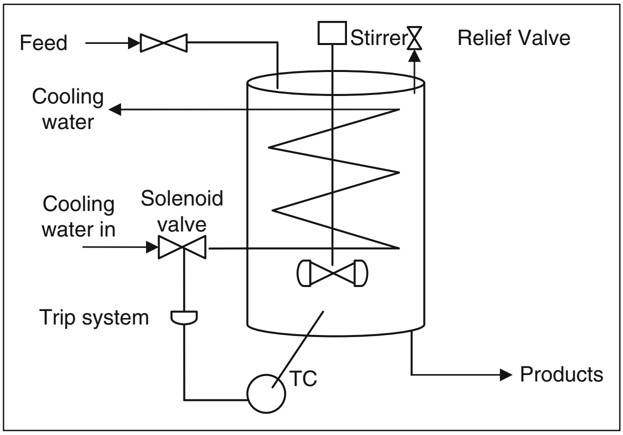
The defined noise-induced hearing loss according to noise exposure is 83 dBA (decibels of sound pressure) for a 50-year lifetime (equivalent exposure). The aim of these guidelines is to protect public health from the adverse effects of noise (WHO, 1999). When the equivalent level (L_{eq}) is greater than 100 dBA, the duration must not exceed 4 h. Hearing deficits are given as a critical effect for impulsive sounds at greater than L_{max} of 140 dBA. The average noise level within the control room shall not exceed 85 dBA during the length of the working day. Prolonged, very low or very high frequency noises should be avoided. Noise levels should not interfere with communications, warning signals and mental performance during work.

QUESTIONS AND PROBLEMS

14.1. A refinery has 50,000 full-time employees. In a particular year this plant had 280 reportable lost-time injuries with a resulting 450 lost workdays. Compute the OSHA incidence rate based on injuries and lost workdays.

14.2. A mixture of methane in the air containing 7.5 mol% CH_4 is the feed to a combustion furnace. If there is a problem in the furnace, a stream of pure air (dilution air) is added to the fuel mixture prior to the furnace inlet to make sure that ignition is not possible. If fuel flows at a rate of 50 mol/s in the original fuel gas mixture, what is the minimum molar flow rate of the dilution air?

14.3. In the reformer unit, reactors work at high pressures and temperatures. The reactor contains a stirrer to control the temperature inside. A cooling unit is also added to control temperature as shown in the attached diagram. Estimate the process failure



14.4. What are the LFL and UFL of a hydrocarbon gas mixture composed of 4.0 vol% methane, 0.5 vol% propane and 0.3 vol% butane and the balance is air?

14.5. The distillation column shown in Figure 14.1 has a side stripper, perform a fault tree analysis on this side stripper.

14.6. Determine the flare height required to not exceed the 1500 Btu/hr/ft^2 heat intensity at a distance 250 ft. The flare diameter is 5 ft. The fuel flow rate is 1×10^6 lb/hr with a molecular weight of 46.

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CHAPTER FIFTEEN

ACID GAS PROCESSING AND MERCAPTANS REMOVAL

15.1. INTRODUCTION

With increasing environmental concerns, gas emissions have become one of the leading issues in refineries and other industries. Acid gases in a refinery are carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Sour gas is the gas containing sulphur compounds, such as mercaptans and carbonyl sulphide (COS). Gas with only CO_2 is called sweet gas. Although the main gas treatment processes emit CO_2 and H_2O, CO_2 is now considered an undesired product due to its role in global warming. CO_2 is a corrosive material, non-combustible and captures solar radiation if released into the atmosphere therefore, warming the earth's atmosphere. H_2S is a highly toxic, flammable gas with an auto-ignition temperature of 292 °C (500 °F). H_2S is 1.18 times heavier than air. Therefore, it may accumulate in dangerous concentrations in drains, valve pits, vessels and tanks. A hydrogen sulphide concentration must be less than 6 mg/m^3 (43 ppm) to prevent the effect of corrosion in process equipment. Most industrial personnel gas detectors are set to 20 ppm of H_2S in air as a limit for the escape mode from an area. Table 15.1 lists the composition of sour gas and acid gas constituents. It can be observed form Table 15.1 that acid gas contains mainly H_2S.

15.2. ABSORPTION OF ACID GASES

The absorption process is used to remove a component (solute) from a gas stream by contacting the gas with a liquid solution (solvent). Absorption requires the mass transfer of a substance from the gas stream to the liquid stream. If the concentration of the vapour and liquid are in equilibrium, no driving force exist, so no mass transfer will occur. The choice of solvents depends on its physical properties, such as high solubility, and ease of recovery. Figure 15.1 shows how absorption and solvent regeneration processes for a H_2S treatment plant are oriented in the refinery.

Fundamentals of Petroleum Refining
DOI: 10.1016/B978-0-444-52785-1.00016-4

Table 15.1 Typical acid gas and sour gas constituents

	Mole fraction	
Component	Sour gas	Acid gas
CO_2	8.50	18.60
H_2S	13.54	78.71
CH_4	77.26	1.47
C_2H_6	0.21	0.09
C_3^+	0.23	0.11
COS	0.02	0.05
RSH	0.01	0.04
H_2O	0.01	0.04
N_2	0.34	0.00

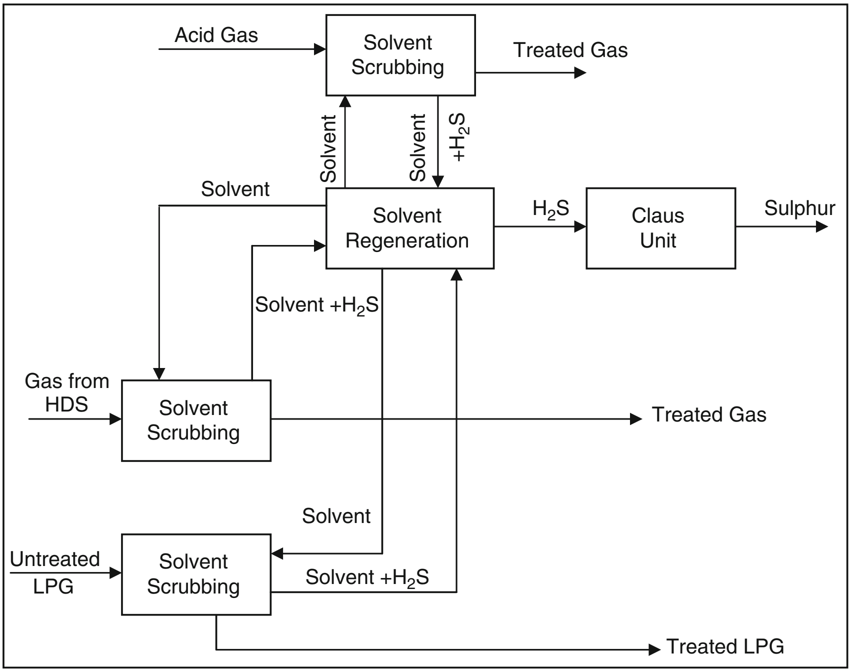


Figure 15.1 Typical H_2S removal plant in a refinery (Legrand and Castel, 2001)

15.2.1. Chemical Solvents

15.2.1.1. Amine Process

Amine gas treating, also known as gas sweetening and acid gas (AG) removal, refers to a group of processes that use aqueous solutions of various amines to remove H_2S and CO_2 from gases. Sweetening processes involve the removal of H_2S and mercaptans from refinery streams.

Amines have a functional group that contains nitrogen. Primary amines arise when one of the three hydrogen atoms in ammonia is replaced by an organic substituent. Secondary amines have two organic substituents bound to N together with one H. The most commonly used amines in gas treating are: primary monoethanolamine (MEA), secondary diethanolamine (DEA) and tertiary methyldiethanolamine (MDEA). DEA is much less corrosive to carbon steel than MEA, and DEA is less volatile than MEA. MDEA is much less reactive than either DEA or MEA. Table 15.2 shows the chemical formula of the three types of amines and their process feed rates based on acid gas flow rate. The following reactions take place in the DEA process:

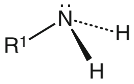
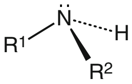
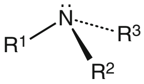
$$H_2S + R_2NH \leftrightarrows R_2NH_2^+ + HS^- \tag{15.1}$$

$$CO_2 + 2R_2NH \leftrightarrows R_2NCOO^- + R_2NH_2^+ \tag{15.2}$$

$$CO_2 + H_2O + R_2NH \leftrightarrows R_2NH_2^+ \tag{15.3}$$

A typical amine gas treating process (Figure 15.2) includes an absorber and a regenerator. In the absorber, the gas stream, which contains H_2S and CO_2, enters from the bottom. The lean amine solvent comes from the absorber top. The resultant (rich) amine is then routed into the regenerator to produce a regenerated or (lean) amine that is recycled for reuse in the

Table 15.2 Comparison of amine solvents (Abdel-Aal *et al.*, 2003)

	Primary amine	Secondary amine	Tertiary amine
Chemical formula			
Type	MEA	DEA	MDEA
Molecular weight	61	105	119
Solvent wt% in solution	15–20	20–35	40–55
Circulation (gal/mol AG)	100–165	60–125	65–110
H_2S/CO_2 selectivity	1	1	3
Steam (lb/gal)	1.0–1.2	0.9–1.1	0.9–1.1
Max. AG flow (m^3/d)	70,000	14,000	40,000

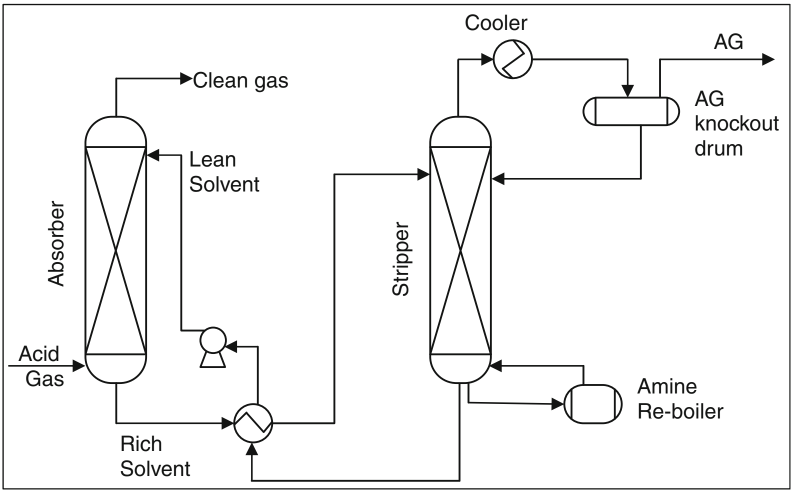


Figure 15.2 Amine absorption

absorber. The stripped overhead gas from the regenerator is concentrated H_2S and CO_2. This H_2S-rich stripped gas stream is then usually sent to a Claus process to convert it into elemental sulphur.

A typical absorber and stripper design is based on the calculation of the material balance and the derivation of the operating line for absorption. Again, these calculations are developed assuming isothermal/isobaric operation, insoluble carrier gas and a non-volatile solvent. Figure 15.3 is a representation of an absorber in which L and G are the solvent and carrier gas flow rates, respectively.

For dilute solutions, mass or mole fractions can be used for operating equations and equilibrium. The mole fraction of solute in the gas is y and the solute mole fraction in the solvent is x. For a dilute system y_1, y_2, x_1 and x_2 are small compared to 1.0. The inert carrier gas flow rate G' (i.e. free from H_2S) is:

$$G' = G_1(1 - y_1) = G_2(1 - y_2) \tag{15.4}$$

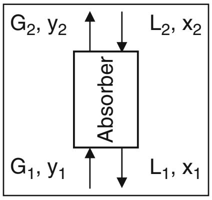


Figure 15.3 Liquid and gas notation in the absorber

The inert liquid flow rate L' is

$$L' = L_1(1 - x_1) = L_2(1 - x_2). \tag{15.5}$$

The mass balance around the column is

$$y_1 G_1 + L_2 x_2 = y_2 G_2 + x_1 L_1. \tag{15.6}$$

Initially, the gas flow rate G_1 and its concentration y_1 are known. The target outlet gas composition y_2 is also known. In addition, the solvent inlet composition x_2 is known. Therefore, the operating line that relates x and y all over the column is

$$y = \frac{L'}{G'} x + \left[y_2 - \frac{L'}{G'} x_2 \right]. \tag{15.7}$$

The above operating line equation is a straight line with slope L'/G' and intercept $(y_2 - (L'/G^{'})x_2)$.

Example E15.1

Absorption is to be used to recover H_2S from a gas mixture. Readily available pure amine will be used as the solvent. The inlet gas contains 5 mol% H_2S and 95 mol% methane. Using a basis of calculation of 100 mol/s of gas feed and assuming isothermal conditions at 1 atm, determine the exit gas mole fraction if 90% of the H_2S is recovered in the liquid phase.

Solution:

10% of the H_2S remains in the exit gas steam.
(5 mol in gas)(0.1 recovered) = 0.5 mol in the exit gas stream.
Pure solvent $x_2 = 0$.
Carrier gas = 0.95 × 100 = 95 mol/s.
The mole fraction of gas at the top of the column is

$$y_2 = \frac{0.5}{0.5 + 95} = 0.00523.$$

For a given liquid solvent flow rate, a maximum gas flow rate exists beyond which, a column floods because of the backup of liquid in the column. Therefore, the usual design limit is entrainment flooding. Entrainment of liquid is due to the carry-up of suspended droplets by rising vapour. At flooding gas velocity, u_f, the droplet is suspended such that the summation of forces on it is zero. Solving for u_f, the flooding gas velocity is (Geankoplis, 2003):

$$u_f = C\left(\frac{\rho_L - \rho_v}{\rho_v}\right)^{0.5}, \tag{15.8}$$

where ρ_v is the gas density, ρ_L is the liquid density, and

$$C = F_{st} C_F, \tag{15.9}$$

where

$$F_{st} = \text{surface tension factor} = (\sigma/20)^{0.2}, \tag{15.10}$$

C_F, the entrainment flooding capacity (ft/s), is a function of the F_{LV}:

$$\log(C_F) = -0.3078 \log(F_{LV}) + 0.0137 \text{Sp} - 1.271, \tag{15.11}$$

$$F_{LV} = \frac{LM_L}{GM_v}\left(\frac{\rho_v}{\rho_L}\right)^{0.5}, \tag{15.12}$$

where Sp is the tray spacing in inches (6–36 in.), M_L is the liquid molecular weight and M_v is the gas molecular weight.

Thus, the tower diameter D_T at 85% of the flooding velocity is

$$D_T = \left[\frac{4GM_v}{0.85 u_f \pi \rho_v}\right]^{0.5} \tag{15.13}$$

Example E15.2

Estimate the required absorber column diameter for the given data:

- Entering gas flow is 180 kmol/h, 12 mol% CO_2 and 8 mol% H_2S and the balance is CH_4. The process occurs at 66 °C and atmospheric pressure
- Entering liquid absorbent: 155 kmol/h pure MEA (20 wt% in solution)
- Required recovery 98% of H_2S
- Assume a tray spacing of 24 in., working at 80% of flooding case, and a surface tension of 70 dynes/cm.

Solution:

Based on tower bottom conditions,

$$G_1 = 180\,\text{kmol/h}, \quad y_1 = 0.08, \quad G' = 180(1 - 0.08) = 165.6\,\text{kmol/h},$$

$$L_2 = L' = 155\,\text{kmol/h}, \quad x_2 = 0.$$

For 98% recovery,

$$y_2 = \frac{0.02(0.08)(180)}{0.02(0.08)(180) + 165.6} = 0.001736,$$

$$x_1 = \frac{0.98(0.08)(180)}{0.98(0.08)(180) + 155} = 0.0835,$$

Calculating gas molecular weight M_V

$$M_v = 0.08(34) + 0.12(44) + 0.8(16) = 20.8,$$

Calculating solvent molecular weight M_L

$$\frac{1}{M_L}=\frac{0.2}{61}+\frac{0.8}{18} \quad \text{gives} \quad M_L=20.9,$$

$$\rho_v=\frac{PM_v}{RT}=\frac{101.325(20.8)}{8.314(66+273)}=0.747\,\text{kg/m}^3,$$

$\rho_L = 977.5\text{kg/m}^3$ at 30 °C (assuming the density of water for the aqueous solution),

$$F_{LV}=\frac{LM_L}{GM_v}\left(\frac{\rho_v}{\rho_L}\right)^{0.5}=\frac{155(20.9)}{165.6(20.8)}\left(\frac{0.747}{977.5}\right)^{0.5}=0.026.$$

For tray spacing = 24 in.,

$$\log(C_F)=-0.3078\log(0.026)+0.0137(24)-1.271 \text{ gives } C_F=0.35\text{ ft/s},$$

$$F_{st}=(\sigma/20)^{0.2}=(70/20)^{0.2}=1.285,$$

$$C=F_{st}C_F,$$

$$C=1.285(0.35)=0.45\text{ ft/s},$$

$$u_f=C\left(\frac{\rho_L-\rho_v}{\rho_v}\right)^{0.5}=0.45\left(\frac{977.5-0.747}{0.747}\right)^{0.5}=16.3\text{ ft/s}=4.96\text{ m/s},$$

$$D_T=\left[\frac{4GM_v}{0.8u_f\pi\rho_v}\right]^{0.5}=\left[\frac{4(165.6/3600)(20.8)}{0.8(4.96)\pi(0.747)}\right]^{0.5}=0.66\text{ m}.$$

The design of amine units can use some empirical industrial correlation to ease the design of the absorber and stripper. For 35 wt% DEA and using 0.5 mol acid gas/mol DEA, the amine circulation rate is (Abdel-Aal *et al.*, 2003):

$$q_{\text{Amine}}(\text{gpm})=126Q_{AG}X_{AG} \tag{15.14}$$

where Q_{AG} is the acid gas flow rate (MMSCFD) and X_{AG} is the AG mol fraction. The absorber diameter (in.) for this process is:

$$D_T=\left(504\frac{TZQ_{AG}}{P}\left[\left(\frac{\rho_v}{\rho_L-\rho_v}\right)C_d\right]^{0.5}\right)^{0.5} \tag{15.15}$$

where T is the temperature (°R), Z is the compressibility factor, P is the pressure (psia) and C_d is the drag coefficient that approximately equals 0.7. Usually, 20 valve trays are used with a spacing of 24 in.

Example E15.3

Acid gas flowing at 50 MMSCFD at 100 psia and 100 °F contains 2 mol% CO_2 and 2 mol% H_2S, and the balance is CH_4. Calculate the flow rate of DEA required then calculate column diameter.

Solution:

$$\text{Total AG} = 4\,\text{mol\%},$$

$$q_{\text{Amine}}(\text{gpm}) = 126\text{Q}_{\text{AG}}X_{\text{AG}} = 126(50)(4/100) = 252\,\text{gpm},$$

$$\rho_{\text{v}} = \frac{PM_{\text{v}}}{RT} = \frac{100(14)}{10.73(100+460)} = 0.233\,\text{lb/ft}^3,$$

$$\rho_{\text{L}} = 65.1\text{lb/ft}^3(\text{for water}).$$

Assuming $z = 1.0$,

$$D_{\text{T}} = \left(504\frac{TZQ_{\text{AG}}}{P}\left[\left(\frac{\rho_{\text{v}}}{\rho_{\text{L}}-\rho_{\text{v}}}\right)C_{\text{d}}\right]^{0.5}\right)^{0.5}$$

$$= \left(504\frac{(100+460)(50)}{100}\left[\left(\frac{0.233}{65.1-0.233}\right)0.7\right]^{0.5}\right)^{0.5},$$

where $D_{\text{T}} = 84$ in. $= 7$ ft.

The absorber column height is calculated based on the gas phase number of transfer units and the height transfer units H_{G} as follows (Geankoplis, 2003):

$$Z = H_{\text{G}}\left(\int_{y_1}^{y_2}\frac{\mathrm{d}y}{(y-y^*)}\right), \tag{15.16}$$

where $y*$ is the equilibrium value of the gas composition, H_{G} can be specified for the column based on the mass transfer coefficient between gas and liquid phases. The integration can be averaged as shown in Example E15.4 and E15.5 for absorber tray calculations.

Example E15.4

A tower is to be designed to absorb SO_2 from gas by using pure water at 293 K and 101.3 kPa absolute pressure. The entering gas contains 10 mol% SO_2, and the exiting gas is 2 mol%. The inert gas flow is 0.5 mol gas/s and the inert water flow is 30 mol water/s. The height transfer units (H_{G}) are 0.825 m. Calculate the SO_2 concentration in the exit liquid stream and the tower height. Equilibrium data can be represented by $y = 20x$.

Solution:

The given data are $G' = 0.5$ mol/s, $L' = 30$ mol/s, $y_1 = 0.1$, $y_2 = 0.02$ and $x_2 = 0$:

Material balance: $G'\left(\frac{y_1}{1-y_1}\right)+L'\left(\frac{x_2}{1-x_2}\right)=G'\left(\frac{y_2}{1-y_2}\right)+L'\left(\frac{x_1}{1-x_1}\right),$

$$0.5\left(\frac{0.1}{1-0.1}\right)+30\left(\frac{0}{1-0}\right)=0.5\left(\frac{0.01}{1-0.01}\right)+30\left(\frac{x_1}{1-x_1}\right).$$

Solving for $x_1 = 0.001512$, this leads to $y_1^* = 20 \times 0.001512$

$$(y-y^*)_{\mathrm{av}}=\frac{(y_1-y_1^*)-(y_2-y_2^*)}{\ln\left(\dfrac{y_1-y_1^*}{y_2-y_2^*}\right)}=\frac{(0.1-0.001512\times 20)-(0.02-0.0)}{\ln\left(\dfrac{0.1-0.001512\times 20}{0.02-0.0}\right)}=0.0358,$$

$$N_G=\frac{y_1-y_2}{(y-y^*)_{\mathrm{av}}}=\frac{0.1-0.02}{0.0358}=2.23,$$

$$Z=H_G\times N_G=0.825\times 2.23=1.84\ \mathrm{m}.$$

Example E15.5

A solvent recovery plant consists of a tray column absorber and a plate column stripper. Ninety percent of the solute in the gas stream is recovered in the absorption column. The concentration of solute in the inlet gas is 6 mol%. The solvent entering the top of the absorber contains 1 mol% of solute. Superheated steam is used to strip the solvent out of the solute. The stripped solvent stream is recycled back to the absorber unit. The solute-free solvent rate to solute-free gas rate ratio equals 2.0. Figure E15.5 shows the process flow diagram.

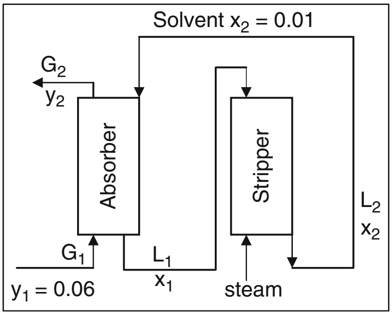


Figure E15 .5 Schematic diagram of absorber–stripper system

The equilibrium data are as follows:

In the absorber $y = 0.25x$,
In the stripper steam $y = 3.89x$.

Calculate:

(1) The theoretical number of stages in the absorber.
(2) The minimum amount of steam used in the stripper.

Solution:

(1) Given $L'/G' = 2.0$,

$$\text{if}\ \ L^{'} = 2.0\,\text{mol/h},$$
$$\text{and}\ \ G^{'} = 1.0\,\text{mol/h},$$

$$G_1 = \frac{G^{'}}{1-y_1} = \frac{1}{1-0.06} = 1.0638\,\text{mol/h}.$$

Solute in gas to absorber $= 0.06\ (1.0638) = 0.06383$ mol/h,
Solute absorbed $= 0.9\ (0.06383) = 0.05745$ mol/h,
Solute in $G_2 = 0.1\ (0.06383) = 0.006383$ mol/h,

$$y_2 = \frac{0.006383}{1+0.006383} = 0.0063427,$$

$$L_2 = \frac{L^{'}}{1-x_2} = \frac{2}{1-0.01} = 2.02\,\text{mol/h},$$

$$x_1 = \frac{0.05745 + 0.01 \times 2.02}{0.05745 + 0.01 \times 2.02 + 2} = 0.03737.$$

Absorption factor A:

$$A = \frac{L^{'}/G^{'}}{m} = \frac{\text{slope of operating line}}{\text{slope of equilibrium line}} = \frac{2}{0.25} = 8.$$

Number of theoretical trays in the absorber N (Geankoplis, 2003) is

$$N = \frac{\ln\left[\left(\frac{y_1 - mx_2}{y_2 - mx_2}\right)\left(1 - \frac{1}{A}\right) + \frac{1}{A}\right]}{\ln(A)},$$

$$N = \frac{\ln\left[\left(\frac{0.06 - 0.25 \times 0.01}{0.0063427 - 0.25 \times 0.01}\right)\left(1 - \frac{1}{8}\right) + \frac{1}{8}\right]}{\ln(8)} = 1.24.$$

(2) For the stripper unit,

$$\frac{L^{'}}{G^{'}_{\text{min}}} = \frac{y_1^{*} - \text{y}_\text{s}}{\text{x}_1 - \text{x}_2}$$

Since the stream is solute-free $y_s = 0$, then

$$\frac{L^{'}}{G^{'}_{\text{min}}} = \frac{0.03737 \times 3.89 - 0}{0.03737 - 0.01} = 5.3113;$$

$$G_{\text{min}} = \frac{2}{5.3113} = 0.3765\,\text{mol/h of steam}.$$

Example E15.6

Twenty-five MMSCFD (1245 kmol/h) gas stream of the composition shown in Table E15.6.1 enters a DEA treatment process at 30 °C and 6895 kPa.

Table E15.6.1 Feed composition

Component	N_2	CO_2	H_2S	H_2O	C_1	C_2	C_3
Mole %	0.16	4.15	1.70	0.17	87.6	3.9	0.92
Component	iC_4	nC_4	iC_5	nC_5	nC_6	nC_7	
Mole %	0.25	0.28	0.13	0.11	0.15	0.48	

The DEA flow rate is 1874 kmol/h with 28 mol% DEA in solution. Perform material balance using UNISIM software (UNISIM, 2007).

Solution:

The gas stream is first introduced to a separator to knock out water and heavy hydrocarbons as liquid stream. Then the remaining gas enters the DEA absorber as shown in Figure E15.6. The rich solvent stream goes to a distillation column to separate hydrocarbons from the solvent and recycle it back to the absorber. Table E15.6.2 shows the UNISIM results.

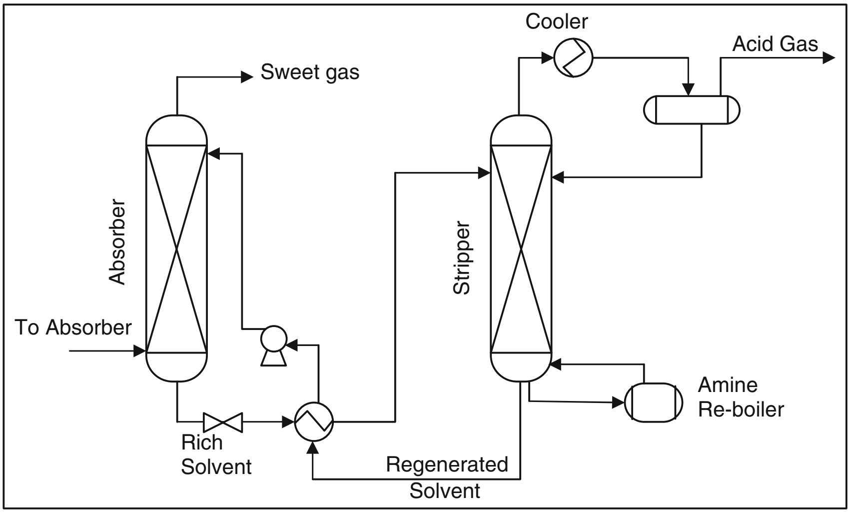


Figure E15.6 DEA treatment process

Table E15.6.2 UNISIM results for DEA process treatment

Stream	To absorber	Sweet gas	Rich solvent	Regenerated solvent	Acid gas
N_2 (mol%)	0.16	0.17	0.0	0.0	0
CO_2 (mol%)	4.15	0.219	2.58	0.1	65.2
H_2S (mol%)	1.7	0	1.08	0.0	28.33
H_2O (mol%)	0.17	0.123	90.3	93.6	6.25
C_1 (mol%)	87.6	92.8	0.0	0.0	0.22
C_2 (mol%)	3.9	4.2	0.0	0.0	0
C_3 (mol%)	0.92	0.98	0.0	0.0	0
iC_4 (mol%)	0.25	0.27	0.0	0.0	0
nC_4 (mol%)	0.28	0.30	0.0	0.0	0
iC_5 (mol%)	0.13	0.14	0.0	0.0	0
nC_5 (mol%)	0.11	0.12	0.0	0.0	0
nC_6 (mol%)	0.15	0.51	0.0	0.0	0
nC_7 (mol%)	0.48	0.12	0.0	0.0	0
DEA (mol%)	0.0	0.0	6.04	6.3	0
Flow (kmol/h)	1233	1162	1948	1874	74.2
T (°C)	30	35	60	124	49
P (kPa)	6895	6860	620	217	189.6

15.2.1.2. Carbonate Process

In this process, hot potassium carbonate (K_2CO_3) is used to remove both CO_2 and H_2S. It can also remove COS. The following reactions take place (Abdel-Aal *et al.*, 2003):

$$K_2CO_3 + CO_2 + H_2O \leftrightarrows 2KHCO_3 \tag{15.17}$$

$$K_2CO_3 + H_2S \leftrightarrows KHS + KHCO_3 \tag{15.18}$$

It can be observed that high CO_2 partial pressure, in the range of 2–6 bar (30–90 psi) and temperature between 110–116 °C (230–240 °F), are required to keep $KHCO_3$ KHS in solution. Therefore, this process cannot be used for streams that contain H_2S only because KHS is very hard to regenerate unless a considerable amount of $KHCO_3$ is present. Precipitation of $KHCO_3$ can be hindered by keeping the carbonate concentration around 35%.

The hot carbonate process, shown in Figure 15.4, includes the absorber and the stripper as in the amine process. The sweet gas coming from the top of the absorber is used to heat the sour gas feed.

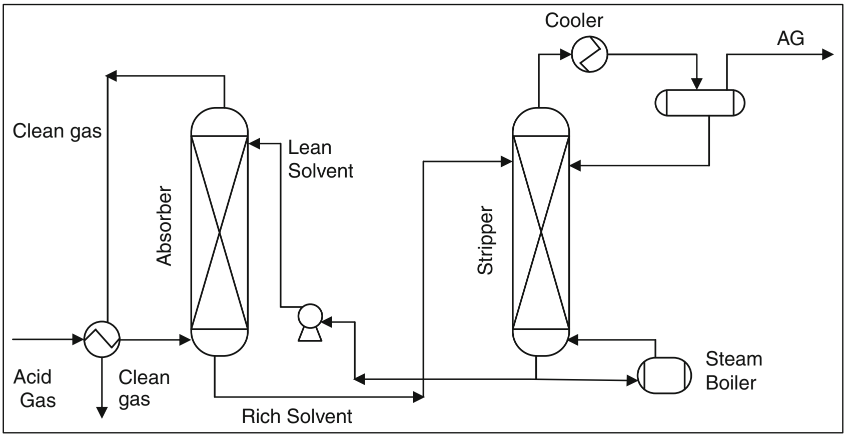


Figure 15.4 Hot carbonate process

Example E15.7

CO_2 is absorbed in a hot carbonate process at 240 °F and 1000 psia. The feed gas stream flow rate is 50 MMSCFD and contains 5 mol% CO_2. It is required to release the gas stream with 2 mol% CO_2. Assuming a circulation rate of 3.5 ft^3/gal, calculate the flow rate of hot carbonate.

Solution:

Volume of CO_2 inlet $= 50 \times 10^6/(24 \times 60)(0.05) = 1735$ ft³/min,
Amount of hot carbonate $= (1735\ \text{ft}^3/\text{min})/(\text{gal}/3.5\ \text{ft}^3) = 504$ gpm.

15.2.2. Physical Solvents

Physical solvents allow the absorption of acid compounds without any chemical reaction. Table 15.3 lists the most commonly used physical solvents in acid gas treatment. The difference in H_2S and CO_2 physical solubility gives the solvents their selectivity. Organic solvents are used in these processes to absorb H_2S more than CO_2 at high pressures and low temperatures. Regeneration is carried out by releasing the pressure. Henry's law can be applied here:

$$P_i = y_i P = H x_i. \tag{15.19}$$

The acid gas composition (x_i), absorbed in a liquid solvent, is related to the gas mole fraction (y_i) by Henry's constant (H).

Table 15.3 Physical solvent properties (Abdel-Aal *et al.*, 2003)

	Selexol	Sulphinol	Fluor
Solvent	Diethylene dimethyl ether	Sulpholane	Propylene carbonate
Molecular weight	134	120	102
Solubility (cm^3 gas/cm^3 solvent)			
H_2S	25.5		13.3
CO_2	3.6		3.3
COS	9.8		6.0

15.2.2.1. Selexol Process

Selexol is a physical solvent, unlike amine-based acid gas removal solvents that rely on a chemical reaction with the acid gases. It is dimethyl ether of polyethylene glycol. Since no chemical reactions are involved, Selexol usually requires less energy than the amine-based processes. It has high selectivity for H_2S over CO_2 that equals to 9–10. A typical process flow chart is shown in Figure 15.5.

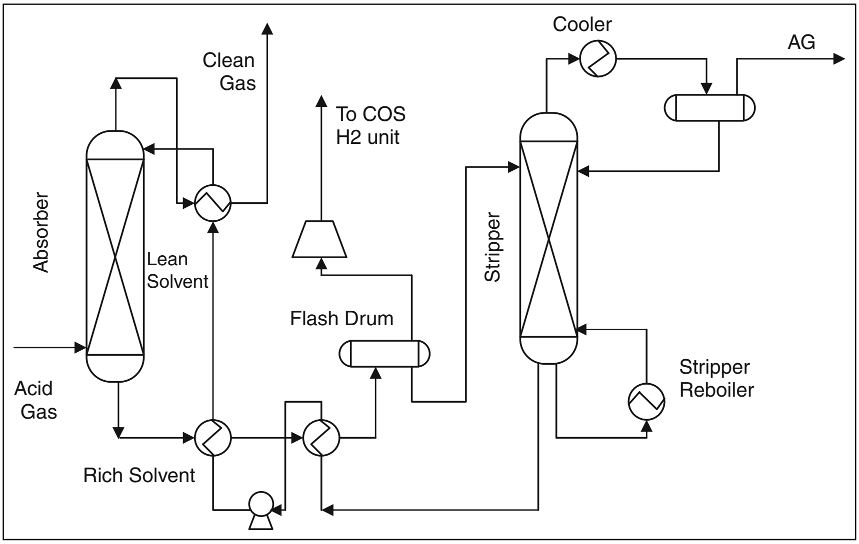


Figure 15.5 Selexol process

Example E15.8

A feed gas at a flow rate of 200 MMSCFD, 421 psia and 81 °F with the following composition (mol%): $H_2S = 1.7\%$, $CO_2 = 10\%$, is introduced to a Selexol process to treat the gas to reach 40 ppm H_2S. Calculate the percentage recovery of sulphur.

Solution:

H_2S free gas $= (200 \times 10^6/379/24)(1 - 0.017) = 21{,}614$ lbmol/h,
Amount of H_2S in the inlet gas $= (200 \times 10^6/379/24)(0.017) = 373.8$ lbmol/h,
H_2S in the exit clean gas $= (40/10^6)(21{,}614) = 0.8645$ lbmol/h,
% recovery of $H_2S = (373.8 - 0.8645)/373.8 \times 100 = 99.78\%$ of H_2S.

15.2.2.2. Morphysorb Process

The morphysorb process uses a mixture of *N*-formyl morpholine and *N*-acetyl morpholine, for the removal of acid gases (Kohl and Nielsen, 1997). This solvent is selective for the removal of H_2S, CO_2, COS, CS_2 and mercaptans. The main advantages of this process are:

- Higher solvent loading and hence a lower circulation rate.
- Lower absorption of hydrocarbons.
- Low corrosion and low environmental hazard.

A simplified flow chart for the Morphysorb process is shown in Figure 15.6.

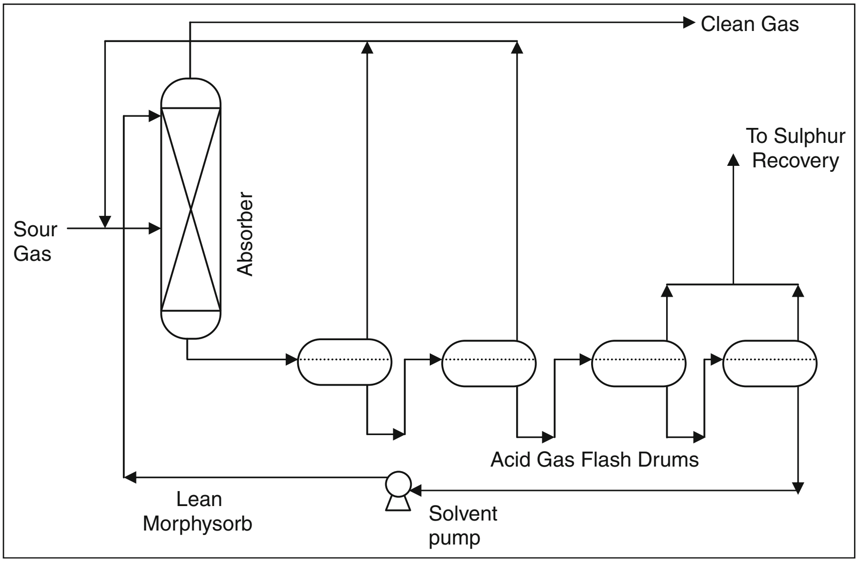


Figure 15.6 Morphysorb process

Example E15.9

An acid gas stream contains 20 mol% CO_2, 10 mol% H_2S and the balance is the carrier gas. A morphysorb solvent is used to treat this gas to 100 ppm H_2S. On the basis of 100 mol, calculate the amount of H_2S and CO_2 absorbed.

The selectivity of Morphysorb solvent = $H_2S/CO_2 = 9/1$.

Solution:

Assuming that initially no CO_2 is absorbed, the H_2S free gas is 70 mol.
H_2S in clean gas = $(100 \times 10^{-6})(70) = 0.007$ mol H_2S.
H_2S absorbed = $10 - 0.007 = 9.993$ mol.
Then for selectivity = 9, the amount of CO_2 absorbed = 1.11 mol.
CO_2 in the exit gas = $20 - 1.11 = 18.89$ mol.
Exit gas = $70 + 0.007 + 18.89 = 88.96$ mol.
H_2S in clean gas = $(100 \times 10^{-6})(88.96) = 0.008896$ mol H_2S.
H_2S absorbed = $10 - 0.0089 = 9.9911$ mol.
Then for selectivity = 9, the amount of CO_2 absorbed = 1.11 mol.

15.2.3. Membrane Absorption

Selective permeation for gases occurs depending on the solubility at the surface contact between the gas and the membrane. The rate of permeation of the gas depends on the partial pressure gradient as follows (Abdel-Aal *et al.*, 2003):

$$q_A = \frac{1}{t}(PMA_m\Delta P_A), \tag{15.20}$$

where PM is the gas permeability, A_m is the membrane surface area, t is the membrane thickness and ΔP_A is the partial pressure of gas A across the membrane.

The acid gas basically diffuses through the membrane if high pressure is maintained to ensure a high permeation rate. A membrane such as the Spiral Wound, has a high selectivity for H_2S and CO_2 over methane and other gases. For example, it has a permeation rate of 10 and 6 for H_2S and CO_2, respectively, while for methane, it is only 0.2.

Example E15.10

It is desired to capture CO_2 from a gas stream containing 10 mol% of CO_2 via a silicone rubber membrane. The membrane thickness is 1.0 mm and surface area is 3000 m^2. Calculate the required pressure difference to get a permeation rate of 6 cm^3/s.

The gas permeability for CO_2 in silicone rubber is 0.27×10^{-6} cm^3(STP) cm/(s cm^2/cmHg).

Solution:

$$q_A = \frac{1}{t}(PMA_m\Delta P_A) = 6\text{cm}^3/\text{s} = \frac{1}{0.1}(0.27 \times 10^{-6}(3000)\Delta P_A),$$

$$\Delta P_A = 740\ \text{cmHg}.$$

15.3. SULPHUR RECOVERY

Acid gas streams from hydrodesulphurization containing H_2S are sent to sulphur recovery unit (Claus unit). Furthermore, sulphur removal is carried out by tail gas clean up schemes. The purpose of removing the sulphur is to reduce the sulphur dioxide (SO_2) emissions in order to meet environmental guidelines.

15.3.1. Claus Process

The Claus process is the most significant elemental sulphur recovery process from gaseous hydrogen sulphide. Gases with an H_2S content of over 25% are suitable for the recovery of sulphur in the Claus process. Hydrogen sulphide produced, for example, in the hydrodesulphurization of refinery products is converted to sulphur in Claus plants (Yamaguchi, 2003; Topsøe *et al.*, 1996 and Chianelli, 2002). The main reaction is

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \quad \Delta H = -186.6\text{kJ/mol}. \qquad (15.21)$$

The Claus technology can be divided into two process stages (Figure 15.7): thermal and catalytic. In the thermal stage, hydrogen sulphide partially oxidized at temperatures above 850 °C (1562 °F) in the combustion chamber. This causes elemental sulphur to precipitate in the downstream process gas cooler.

If more oxygen is added, the following reaction occurs:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O \quad \Delta H = -518\ \text{kJ/mol}. \qquad (15.22)$$

Air to the acid gas is controlled such that in total, 1/3 of all hydrogen sulphide (H_2S) is converted to SO_2.

Sulphur produced in the process is obtained in the thermal process stage.

The main portion of the hot gas from the combustion chamber is cooled down. This caused the sulphur formed in the reaction step to condense.

A small portion of the process gas goes to the catalytic stage. This gas contains 20–30% of the sulphur content in the feed stream. Activated alumina or titanium dioxide is used. The H_2S reacts with the SO_2 and results in gaseous, elemental sulphur. This is called the Claus reaction:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \quad \Delta H = -41.8\ \text{kJ/mol(Sulphur vapour)} \qquad (15.23)$$

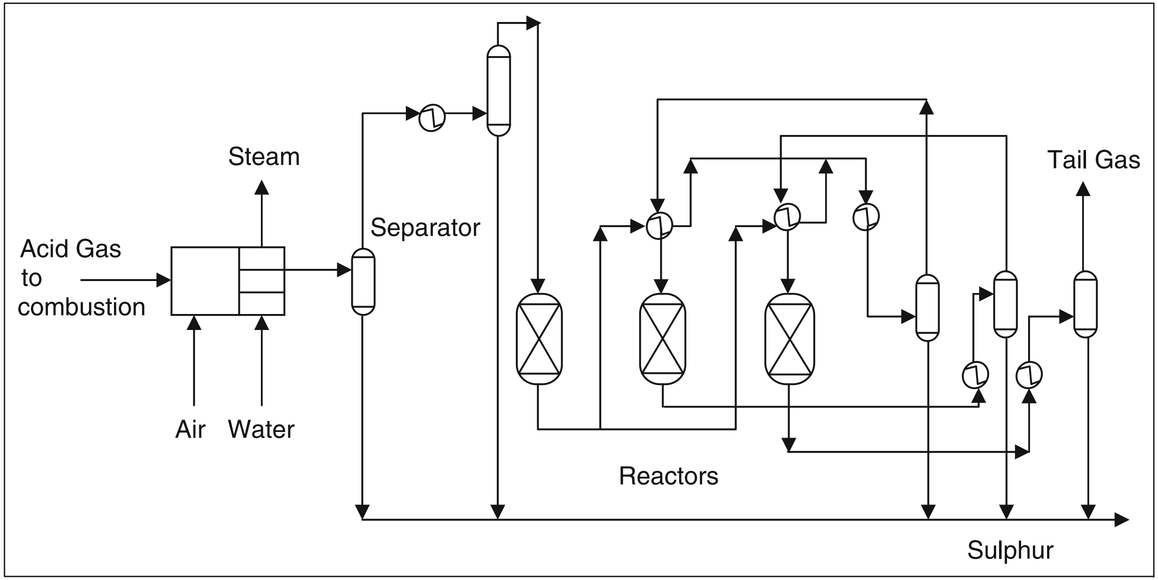


Figure 15.7 Claus process

Heating is necessary to prevent sulphur condensation in the catalyst bed which can lead to catalyst fouling.

The catalytic conversion is maximized at lower temperatures, but care must be taken to ensure operation above the dew point of sulphur.

The condensation heat is used to generate steam at the shell side of the condenser. Before storage, the liquid sulphur stream is degassed to remove any dissolved gases.

If the acid gas feed contains COS and/or CS_2 they are hydrolyzed in the catalytic reactor in the following manner:

High temperature helps to hydrolyze COS and CS_2.

$$COS + H_2O \leftrightarrows H_2S + CO_2 \tag{15.24}$$

$$CS_2 + 2H_2O \leftrightarrows 2H_2S + CO_2 \tag{15.25}$$

The tail gas from the Claus process still containing combustible components and sulphur compounds (H_2S, H_2 and CO) is either burned in an incineration unit or further desulphurized in a downstream tail gas clean-up unit (TGCU).

A typical Claus process with two catalytic stages yields 97% of the sulphur in the input stream. Over 2.6 tons of steam will be generated for each ton of sulphur yield.

Example E15.11

An acid gas has the following composition: 40.2 mol% H_2S, 54.0 mol% CO_2, 1.35 mol% CH_4, 0.15 mol% C_2H_6 and 4.3 mol% water. It is fed to a thermal stage (combustion reactor) of a Claus Process Sulphur Recovery Unit (SRU) at 40 °C, 179 kPa and 5000 kmol/h. The air feed to the SRU is at 118 °C, 179 kPa. The product stream is fed to the waste heat boiler. The product stream is then separated into sulphur and other product streams. The remaining product enters the catalytic step made of three reactors as shown in Figure E15.11. Each reactor operates at 240 °C; therefore, a heater is placed before each reactor.

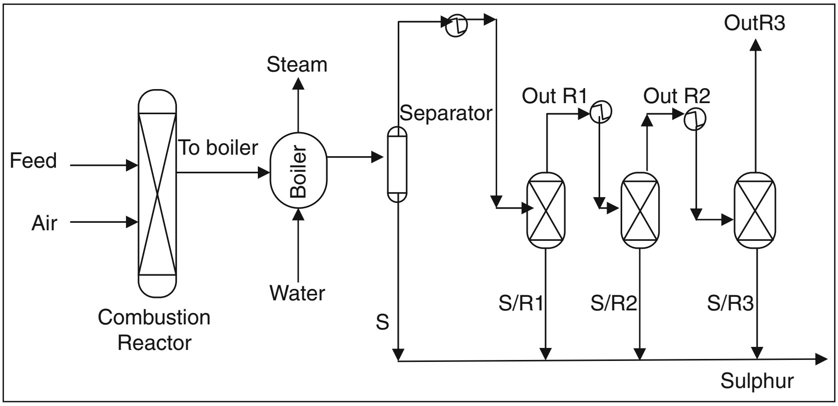


Figure E15.11 Claus process flow chart

Table E15.11 Summary results (all components in kmol/h)

	Feed	Air	To boiler	Water	Steam	Out R_1	S/R_1	Out R_2	S/R_2	Out R_3	S/R_3
H_2S	2010	0	1205.9			241.2		24		0	
CO_2	2700	0	2700			2700		2700		2700	
CH_4	67.5	0	67.5			67.5		67.5		67.5	
H_2O	215	0	1019	5505	5505	1984		1694.3		1718.4	
C_2H_6	7.5	0	7.5			7.5		7.5		7.5	
SO_2	0	0	603			120.65		12.1		0	
O_2	0	1005	0			0		0		0	
N_2	0	3781	3781			3781		3781		3781	
S	0	0	201				1447		832.2		36.17
T (°C)	40	118	833	25	100	171	171		70		212
P (kPa)	179	179	179	101	101	154	154		153		154

Total sulphur produced = 2516.4 kmol/h.
All H_2S and SO_2 are consumed.

Simulate the process on the UNISIM software and calculate material balances. Use conversion reactors for thermal and catalytic stages.

Solution:

Reactions (15.21) and (15.22) occur in the combustion reactor. Reaction (15.23) occurs in the three reactors for sulphur recovery. Table E15.11 summarizes the UNISIM results.

15.3.2. Tail Gas Clean Up

Incinerating the residual H_2S after sulphur recovery produces SO_2. Therefore, further sulphur recovery is done for the tail gases. Typical tail gas clean-up (TGCU) process can reduce SO_2 to 0.15 vol% and H_2S to 0.3 vol%. This process contains a Claus catalytic reaction followed by H_2S and SO_2 recovery section. Figure 15.8 shows a tail gas clean up scheme.

15.4. MERCAPTANS REMOVAL

The predominant sulphur compounds in refinery products that usually have an unpleasant smell are mercaptans. They are corrosive and disturb the fuel stability due to gum formation. The principle of mercaptans removal is oxidation. The mercaptan oxidation is called MEROX process. The role of MEROX in the refinery is shown in Figure 15.9.

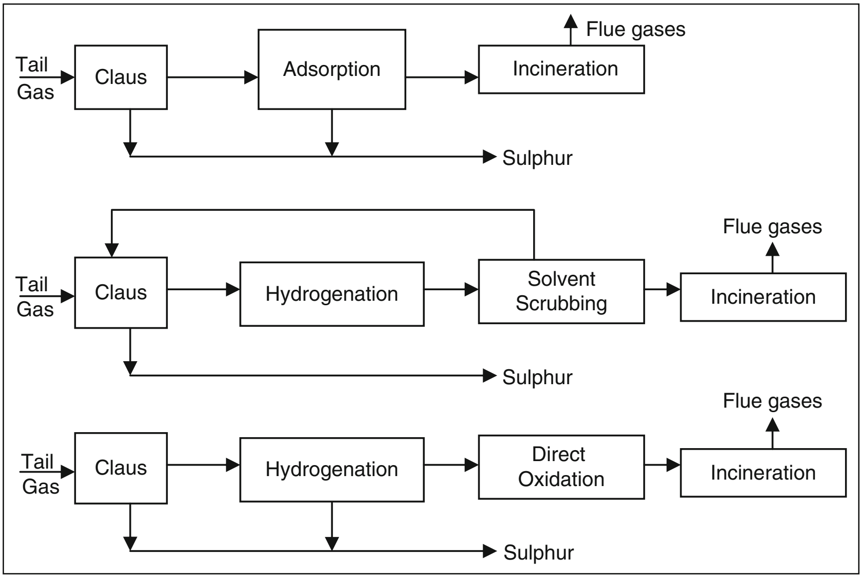


Figure 15.8 Typical Tail gas clean-up scheme (Legrand and Castel, 2001)

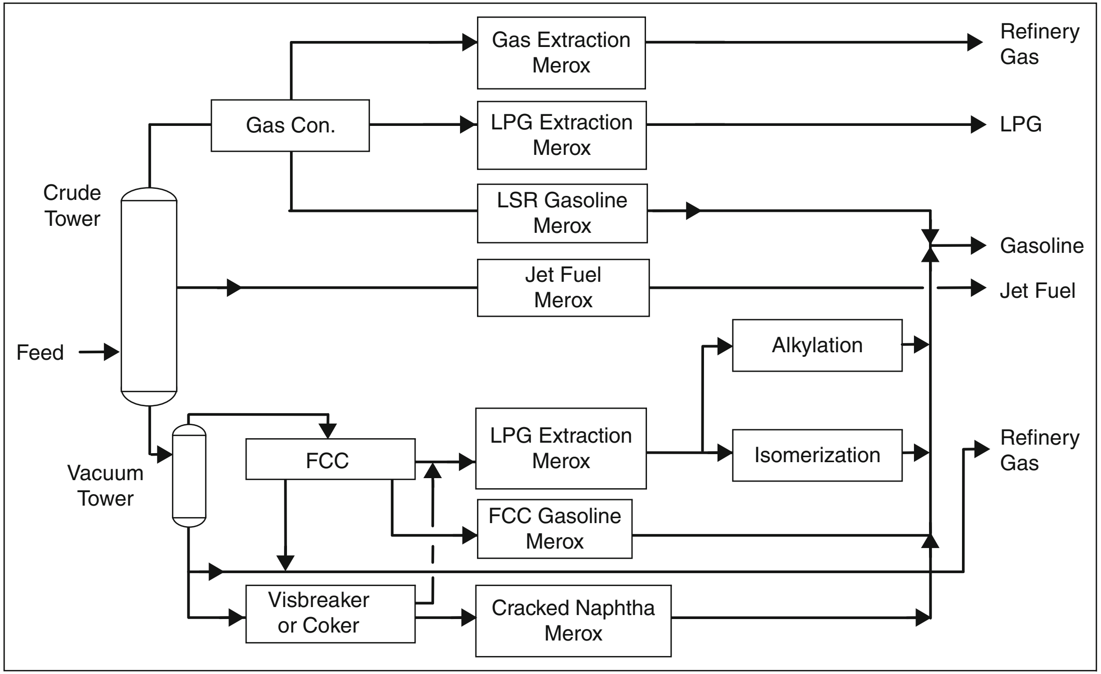


Figure 15.9 Role of MEROX in a refinery

MEROX sweetening involves the catalytic oxidation of mercaptans to disulphides in the presence of oxygen and alkalinity. Air provides the oxygen, while caustic soda provides the alkalinity. Oxygen reacts with mercaptans through the following reaction:

$$4RSH + O_2 \rightarrow 2RSSR + 2H_2O \tag{15.26}$$

Removal of mercaptans by extraction starts with dissolving them in caustic soda based on the following reaction:

$$RSH + NaOH \leftrightarrows NaSR + H_2O \tag{15.27}$$

The equilibrium occurs between the RSH oily phase and the RSH that dissolves in the aqueous phase.

Extraction equilibrium is favoured by lower molecular weight mercaptans and lower temperatures. The rich caustic soda containing the extracted mercaptans in the form of mercaptides is regenerated as shown in the equation given below:

$$4NaSR + O_2 + 2H_2O \leftrightarrows 2RSSR + 4NaOH \tag{15.28}$$

Prior to flowing to the reactor, the feedstock is passed through a caustic prewash to reduce the acid. The MEROX unit consists of a fixed-bed reactor followed by a caustic settler. Air, the source of oxygen, is injected into the feedstock upstream of the reactor. The operating pressure is chosen to assure that the air required for sweetening is completely dissolved at the operating temperature. The sweetened stream exits the reactor and flows to the reactor caustic settler.

The caustic soda settler contains a reservoir of caustic soda for use in keeping the MEROX catalyst alkaline. The solvent product leaving the water wash flows to a sand filter containing a simple bed of coarse sand that is used to remove free water and a portion of the dissolved water from the product (Figure 15.10). The regenerated caustic soda is recycled to the MEROX reactor.

15.4.1. Gasoline MEROX

MEROX as discussed above treats mercaptans (RSH) in gasoline to meet the desired specifications. The alkyl group (R) could be aliphatic, aromatic or cyclic, and saturated or unsaturated.

A dilute caustic soda solution is continuously injected into the gasoline feed prior to the addition of air. The combined stream passes through a fixed bed of MEROX catalyst where the mercaptans are oxidized to disulphides and the dilute caustic soda is coalesced. The sweetened hydrocarbon stream is essentially free of entrained caustic soda and requires no further separation. Coalesced spent caustic soda is collected and sent to the refinery's sewer, since it is minute in volume, low in NaOH concentration and partially neutralized.

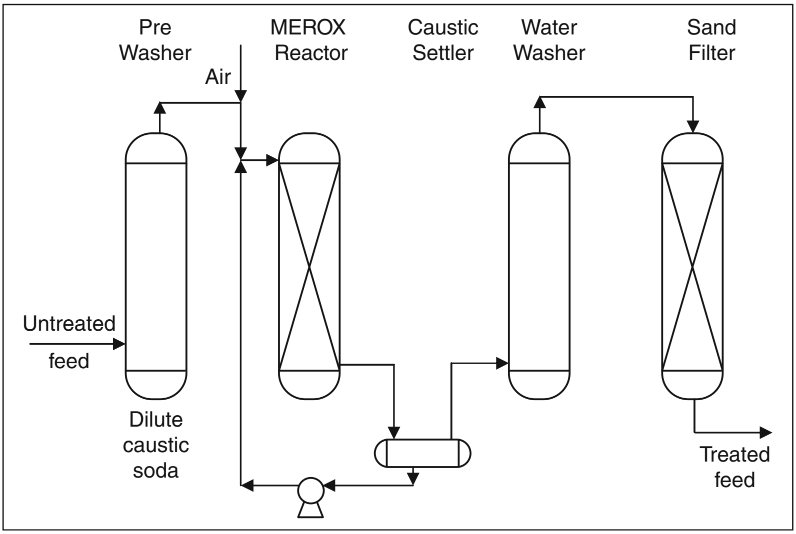


Figure 15.10 Typical MEROX flowsheet

15.4.2. Kerosene MEROX

The MEROX process for kerosene/jet fuel sweetening is one of the MEROX process applications developed for the control of mercaptans. The conventional version of this process uses air and caustic soda (NaOH) to sweeten kerosene feedstock. Pre- and post-treatment sections are included to ensure that jet fuel specifications are met.

Prior to flowing to the reactor, kerosene is passed through a caustic soda pre-wash to reduce the naphthenic acids. The reactor section of the kerosene/jet fuel MEROX unit consists of a fixed-bed reactor followed by a caustic settler. Air is injected into the feedstock upstream of the reactor. The operating pressure is chosen to assure that the air required for sweetening will be completely dissolved at the operating temperature. The kerosene leaving the caustic soda settler passes through a water wash, which removes trace quantities of caustic soda as well as water soluble surfactant.

QUESTION AND PROBLEMS

15.1. Absorption is to be used to recover H_2S from a gas mixture. Readily available pure amine will be used as the solvent. The inlet gas contains 10 mol% H_2S and 90 mol% methane. Determine the exit gas mole fraction if 95% of the H_2S is recovered in the liquid phase.

15.2. Estimate the required absorber column diameter for the given data:
- Entering gas flow is 100 kmol/h, 10 mol% CO_2 and 20 mol% H_2S and the balance is CH_4, The process occurs at 66 °C and atmospheric pressure.
- Entering liquid absorbent: 200 kmol/h pure MEA (20 wt% in solution).
- Required recovery 97% of H_2S.
- Assume a tray spacing of 24 in., working at 80% of flooding case, and a surface tension of 70 dynes/cm.

15.3. Acid gas flowing at 100 MMSCFD at 100 psia and 100 °F contains 5 mol% CO_2 and 8 mol% H_2S, and the balance is CH_4. Calculate the flow rate of DEA required, then calculate the column diameter.

15.4. A tower is to be designed to absorb SO_2 from gas by using pure water at 293 K and 101.3 kPa absolute pressure. The entering gas contains 20 mol% SO_2 and the leaving gas is 5 mol%. The tower cross-sectional area is 0.0929 m^2, and the height of transfer unit H_G is 0.825 m. Calculate the SO_2 concentration in the exit liquid stream and the tower height. Equilibrium data can be represented by $y = 20x$. Assume $L'/G' = 30$.

15.5. CO_2 is absorbed in a hot carbonate process at 240 °F and 1000 psia. The feed gas stream is 100 MMSCFD and contains 10 mol% CO_2. It is required to release the gas stream with 2 mol% CO_2. Assume the circulation rate is 3.5 ft^3/gal. Calculate the flow rate of the hot carbonate.

15.6. Perform Example E15.6 on UNISIM simulator for a feed rate of 30 MMSCFD with the same feed composition and operation conditions.

15.7. An acid gas feed flow rate is 100 MMSCFD at pressure 421 psia and at temperature 81 °F with the following composition (mol%): H_2S = 5%, CO_2 = 15%, and the balance is the carrier gas. This feed is introduced to a Selexol process to treat the gas to reach 50 ppm H_2S. Calculate the % recovery of sulphur.

15.8. An acid gas contains 30 mol% CO_2, 40 mol% H_2S and the balance is the carrier gas. A Morphysorb solvent is used to treat this gas to 50 ppm H_2S. Calculate the amount of H_2S and CO_2 absorbed.

15.9. It is desired to capture CO_2 from a gas stream containing 10 mol% of CO_2 via a silicone rubber membrane. The membrane thickness is 1.0 mm and has a surface area of 3000 m^2. The applied pressure gradient is 760 cmHg. Calculate the permeation rate.

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CHAPTER SIXTEEN

REFINERY ECONOMICS

16.1. INTRODUCTION

The supply and demand for crude oil and petroleum products are key factor in determining the status of the world economy. The increase in demand of crude oil in southeast Asia, for example, in India and China has been largely responsible for the increase in the price of crude oil to over US$ 100 per barrel in 2008. However, as the world economy started to go through a crisis in the latter half of 2008, demand has started to slow down, and supply has surpassed demand. This situation has resulted in a drastic drag of crude oils to less than US$ 40 in 2009. Since the increase in demand is due to increase in demand for petroleum products, the economics of the petroleum refining industry will undergo tremendous change. In general, refining has historically been significantly less profitable than other petroleum industry segments. Therefore, refiners have to be careful to control costs to make a profit.

In this chapter, global refining capacity is discussed. Factors affecting the refinery economics, such as costs, products prices, refinery complexity and on-stream factors, are covered.

16.2. REFINING CAPACITY

World refining capacity, as measured by crude distillation capacity, has increased from just over 1 billion tons per year in 1950 to around 4 billion tons per year or 80 million barrels per day in 1980 (1 barrel per day is approximately 50 tons per year). Due to energy-saving measures and a decrease in demand, the capacity decreased to around 73 million barrels per day in the early 1990s. The worldwide refining capacity has increased in the new millennium and it reached around 85.46 million barrels per day in 2008 as shown in Figure 16.1 (EIA, 2009). Table 16.1 lists the top refining countries in 2008.

Fundamentals of Petroleum Refining
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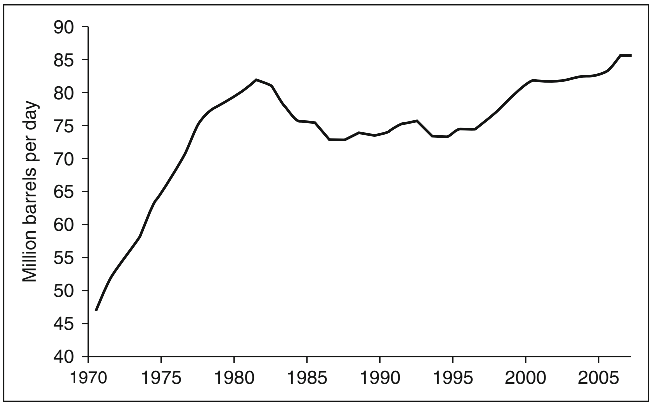


Figure 16.1 World crude oil refining capacity 1970–2008

Table 16.1 Top refining countries in 2008 (EIA, 2009)

Country	Refining capacity Million barrels per day
United States	17.594
China	6.25
Russia	5.43
Japan	4.65
South Korea	2.58
Germany	2.42
Italy	2.34
Saudi Arabia	2.08
Canada	1.97
France	1.93
Brazil	1.91
United Kingdom	1.86

16.3. REFINING COSTS

16.3.1. Capital Costs

The capital investment for a new refinery depends on its throughput, complexity and location. Added to the capital cost is the lengthy time needed for the preliminary study, obtaining the necessary permits (environmental and otherwise), designing building and commissioning. The capital cost involves the cost of the process units, utilities, security and environmental facilities, storage and handling facilities, civil work, buildings and

Table 16.2 Breakdown of capital cost of a typical European refinery (Favennec and Pegyre, 2001)

Cost item	Percent of total capital cost
Process units	45
Utilities	15
Security and environmental facilities	7
Storage and handling facilities	25
Civil works, buildings and other infrastructure	8

infrastructure. Table 16.2 gives a cost breakdown of a typical European refinery with conversion units to maximize motor gasoline production.

16.3.2. Operating Costs

The operation of the refinery requires several operating cost which are broken into variable and fixed costs.

16.3.2.1. Variable Cost

Variable cost items are directly proportional to the refinery crude oil feed rate. They include chemicals which are added during processing for corrosion prevention, oxygenates for octane number improvement, cetane number improvers, pour point depressants for gas oil, and any other additives.

Catalysts are used in hydrotreating, hydroconversion, catalytic conversion and other processing units. Some of these catalysts are very expensive since they contain noble or rare earth metals. They have a certain catalyst life and when they cannot be regenerated, they are replaced by a fresh catalyst. Average catalyst cost is a few U.S. dollars per ton of crude oil processed.

Fuel cost is a very important operating cost in the refinery. Refineries use fuel oil, natural gas and refinery waste gas as fuel sources. Converted to its energy equivalence in barrels of crude oil, fuel and other energy costs amount to between 6% and 8% of crude input, depending on the refinery size and complexity. Fuel is needed in process furnaces and for boilers in steam generation. Natural gas is needed for hydrogen production. Electrical power, if produced onsite, also requires fuel. Usually, electricity is bought from an outside utility company.

Working capital charges relate to the cost of keeping a certain level of stocks of crude oil to ensure that refinery crude feed is maintained and to meet customer demand of finished products. It amounts to \$2–3 per ton of crude oil.

16.3.2.2. Fixed Cost

- *Manpower.* The number of technical and administrative staff needed to run a refinery depends on refinery complexity, location and the level of automation incorporated in the design.

- *Maintenance*. The cost of maintenance is proportional to the capital cost. It depends on several factors, including the design of the units, the quality and reliability of the equipment, the operation practices, and preventive maintenance practices. The cost can amount to 3–4% of the initial capital cost.
- *Overhead costs*. This includes administrative costs, taxes, insurance, quality control costs, community service, advertisement, etc.
- *Cost of capital*. When a new refinery is built, it is financed totally or partially by loans from banks or financial institutions. Loans have to be repaid according to a loan plan in the form of annual capital cost repayment, which includes the interest and loan repayment. Even if the refinery is built from the refining company's own financial resources, the capital with interest has to be recovered. This constitutes the return on investment, which has to be greater than the interest paid by the banks, otherwise there would be no justification for the investment of the company's own money in building a refinery.

The breakdown for the operating cost of a refinery with deep conversion is shown in Table 16.3.

16.3.3. Factors Affecting Refinery Costs

Refining costs greatly depend on several factors:

- *Refinery complexity*. Refineries can have a simple configuration with crude distillation, catalytic reforming and product hydrotreating units or complex configuration with vacuum distillation and cracking units. Complex refineries require more capital cost and operating costs. However, they generate more profit. More details on refinery complexity will be discussed in Section 16.5.
- *Capacity utilization or stream factor*. Refineries should operate at their design throughput rate for both the crude distillation units and the downstream processing and conversion units. However, depending on product demand and prices, refineries are forced to operate at less than

Table 16.3 Typical breakdown of operating costs of a deep conversion refinery

Operating cost	Cost in $ per ton of crude feed
Variable cost	4
Fixed cost	15
Cost of capital	25
Total	44

100% stream factor. Refining capacity utilization in 2005 was around 90% in the United States and the Asia-Pacific region and around 82% in Europe. As the demand for refined products increases, the level of capacity utilization will increase. Also, the closure of old refineries in Europe and the United States has increased capacity utilization. In the future, additional refinery capacity is needed, especially in countries with developing economies like China and India.

- *Refinery size*. The capital cost of refineries is obviously dependent on its size. The most common relationship between the capital cost and capacity of process equipment, refinery units or whole refineries is given by

$$\frac{I_a}{I_b} = \left(\frac{C_a}{C_b}\right)^n, \tag{16.1}$$

  where I and C refer to capital cost and unit capacity of units a and b, respectively. The exponent n is 0.67 for refineries but can range from 0.48 to 0.84 for different process equipment or units (Favennec and Pegyre, 2001). However, operating costs per barrel decrease with increasing refinery size. This is due to the fact that fixed costs (manpower, administrative and other overhead) are independent of the size of the refinery. Furthermore, both capital and maintenance costs which depend on size, do not increase with size to the same extent that the actual rate of size increases. Therefore, there is a decrease of these costs per barrel processed.
- *Quality of the crude*. The crude oils processed in refineries are becoming heavier and contain more sulphur. If we take the USA as an example, The API gravity has decreased from an average of 33 in 1981 to around 30 in 2001, coupled with an average sulphur content increase from 0.8 to 1.4 wt%. As crude oils become heavy, additional investment have to be made in conversion and heavy oil processing units. Without these additional costs, simple or typical refineries would not be profitable.
- *Location*. The cost of building a refinery depends on its location. Refineries are usually located close to a coastal line to transport the products by tankers. Weather conditions at the location of the refinery also affect the refining costs. Refineries are usually located in oil consuming countries. Since the 1970s, oil-producing countries have developed a strategy of building export refineries to acquire a share of the refined product market in the consumer countries. The profitability of export refineries is limited due to the fact that the construction cost is higher than in consuming countries, and the cost of transporting finished products is higher than transporting crude oil. However, the majority of new refining facilities are being built in oil-producing countries like Saudi Arabia, Iran and Venezuela.

- *Environmental constraints*. Due to more strict environmental regulations regarding air, water and soil pollution, refineries have to add units and processes to make sure than the gas emissions are within the regulations. This is also applied to water discharges into rivers and the marine environment. Solid waste in the form of spent catalysts, sludge or coke has to be disposed off without harming the environment. New fuel quality specifications regarding sulphur and aromatic content require investment into deep cracking and treating processes.

16.4. REFINING MARGINS

The profitability of a refinery is determined by calculating the refining margin. Two types of margins are defined. The gross margin is the difference between the composite value of the refined products at the refinery gate and the cost of the crude oil delivered to the refinery:

$$\text{Gross margin} = \sum_{i}^{N}(\text{price of product } i \times \text{yield of product } i) - \text{crude price}, \tag{16.2}$$

where N represents all products produced. The price of product i is the spot price per barrel of product i. The yield of product i is the volume percent of product i per barrel of crude oil feed to the refinery. The crude price is the price paid by the refiner for a barrel of delivered crude oil.

The net refining margin is the gross margin less the variable refining costs, that is, chemicals, catalysts, fuel and working capital charges:

$$\text{Net margin} = \text{gross margin} - \text{variable cost}. \tag{16.3}$$

For a refinery to be profitable, the net margin has to be greater than the total fixed costs per barrel of crude oil processed. The difference between the net margin and the fixed cost per barrel of crude oil is called the cash margin and represents the profit the refinery makes per barrel of processed crude oil:

$$\text{Cash margin} = \text{net margin} - \text{fixed cost}. \tag{16.4}$$

In addition, petroleum analysts use the spread as an indicator of refining profitability. A product spread is the difference between the products price and the price of crude oil. A multiple product spread is described by the 3–2–1 crack spread, which assumes that three barrels of crude can be refined to produce two barrels of gasoline and one barrel of distillates. It is calculated as follows (EIA, 1997):

$$\begin{aligned} 3-2-1 \text{ Crack spread}(\$\,\text{bbl}^{-1}) = {} & (2 \times \text{gasoline price} + 1 \times \text{distillate price} \\ & - 3 \times \text{crude oil price})/3. \end{aligned} \tag{16.5}$$

Since the spread assumes that the crude oil can be completely converted into gasoline and distillates and that it does not include all products or the operating costs, it can be viewed as an indicator only.

Example E16.1

Calculate the gross and net margin for an average refinery in the United States using the following data:

	Product yield%	Price per barrel (US$)
Gasoline	52.3	71
Distillates	28.8	72
Other products	18.9	47.5
Crude price		57
Variable refining costs		6.4

Solution:

$$\text{Gross margin} = (71 \times 0.523 + 72 \times 0.288 + 47.5 \times 0.189) - 57 = \$9.84,$$

$$\text{Net margin} = 9.84 - 6.4 = \$3.44.$$

16.5. REFINERY COMPLEXITY

The following classification can be used to define the complexity of a refinery:

- *Simple refinery*. It has atmospheric crude distillation, a catalytic reformer to produce high octane gasoline, and middle distillated hydrotreating units.
- *Complex refinery*. It has in addition to the units of a simple refinery, conversion units such as hydrocrackers and fluid catalytic cracking units.
- *Ultra-complex refinery*. The refinery has all of the units above in addition to deep conversion units which convert atmospheric or vacuum residue into light products.

The complexity of a refinery can be assessed by calculating the complexity factor. Each unit has a coefficient of complexity (CC_i) defined as the ratio of the capital cost of this unit per ton of feedstock to the capital cost of the crude distillation unit (CDU) per ton of feedstock. The complexity factor (CF_i) of the whole refinery is then calculated from the coefficients of complexity for the units in the refinery as follows:

$$\mathrm{CF} = \sum_{i}^{N} \frac{F_i}{F_{\mathrm{CDU}}} \mathrm{CC}_i, \qquad (16.6)$$

where F_i and F_{CDU} are the feed rate to unit i and CDU, respectively.

Example E16.2

Calculate the complexity factor for a refinery which has the following unit data:

Unit	Complexity coefficient (CC_i)	Percent capacity relative to CDU capacity (F_i/F_{CDU})
Vacuum distillation unit	1.5	40
Fluid catalytic cracking	7	25
Hydrocracking	7	15
Hydrotreating	5	50
Reforming	3.4	30
Alkylation	6	5

Solution:

$$CF = 0.4 \times 1.5 + 0.25 \times 7 + 0.15 \times 7 + 0.5 \times 5 + 0.3 \times 3.4 + 0.05 \times 6 = 7.8.$$

16.6. ECONOMIC ANALYSIS

The objective of building a new refinery is to make profit. Economic analysis involves the comparison of the profit and cost of an investment proposal to determine if it is economically attractive. This subject is covered in great details in many engineering economy textbooks. Here, we will only cover the fundamentals.

16.6.1. Cash Flow Diagram

The execution of an investment project, such as building a new refinery, is viewed in terms of a timeline divided into time intervals, usually in years. The end of the cash flow diagram (CFD) corresponds to the useful lifetime of the project at which the refineries are shut down and the equipment sold as scrap. Certain events pertaining to economic activity costs (capital, operating, crude oil, chemicals, etc.) or revenues from product sales occur along this timeline.

16.6.2. Time Value of Money

When you invest money in a project, you expect that, after n periods of time in the future, your money will generate profit. Therefore the value of your money will increase with time. This situation is analogous to depositing your money in the bank with the expectation that the bank will pay you interest on your principal. The concept of compounding interest used in bank transactions is utilized in economic evaluation, where your money is compounding interest at the end of each compounding period. To develop a general formula describing the time value of money, the following letter symbols are used:

- P: Present single sum of money at time zero or at any point in time from which we choose to measure time
- F: A future single sum of money at some future date
- A: The amount of each payment in a uniform series of equal payments at the end of each period
- n: The number of interest compounding periods between the point time of P and F
- i: The period compound interest. This refers to the return on invested capital, cost of borrowed money or the minimum rate of return.

The following basic formula describes the time value of money:

$$F = P(1 + i)^n \tag{16.7}$$

or

$$P = \frac{F}{(1 + i)^n}. \tag{16.8}$$

For the uniform equal payment series of n payments, the relation between F, P and A are given by the following formulas:

$$P = A\frac{(1 + i)^n - 1}{i(1 + i)^n}, \tag{16.9}$$

$$F = A\frac{i}{(1 + i)^n - 1}. \tag{16.10}$$

As mentioned above, the CFD represents a clear visualization of each and every transaction which occurs along the timeline of the project. The discrete payments, either cost or income, are represented by an arrow at the end of the time period when the payment is made. Costs are shown as downward arrows (considered negative) and income or revenue as upward arrows (considered positive) as shown in Figure 16.2. For

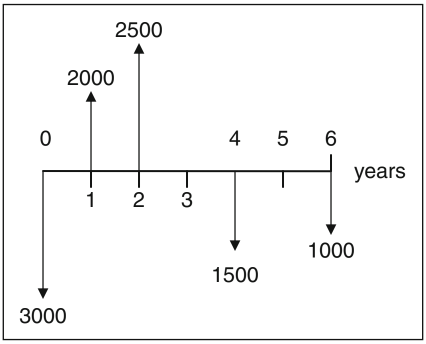


Figure 16.2 An example of a representative cash flow diagram

the economic evaluation of the investment proposal represented by the CFD, each payment must be brought backward or forward in time then compared. When this is done, the payments are called discounted payments.

Example E16.3

Calculate the value of all the payments in the CFD in Figure 16.2 at time zero and at the end of year 4. The interest rate is 8% per year.

Solution:

$$P_0 = \frac{-3000}{(1+0.08)^0} = -3000,$$

$$P_1 = \frac{2000}{(1+0.08)^1} = 1851.9,$$

$$P_2 = \frac{2500}{(1+0.08)^2} = 2143.3,$$

$$P_4 = \frac{-1500}{(1+0.08)^4} = -1102.5,$$

$$P_6 = \frac{-1000}{(1+0.08)^6} = -630.2.$$

The net present worth of all payments is the sum of all the above present values:

$$P = -3000 + 1851.9 + 2143.3 - 1102.5 - 630.3 = -737.5.$$

This means that the present value of the cost payments is more than the present value of the income payments.

The value of all the payments at the end of year 4 can be easily obtained by applying equation (16.7). The P is the value of all of the payments at time zero and n is 4 years:

$$F = -737.5(1 + 0.08)^4 = -1003.4.$$

Example E16.4

An 8 million ton per year (160,000 barrels per day) refinery with classic conversion processes has been built at a cost of $1.5 billion. The cost has been entirely financed by a loan at 8% interest, repayable over 15 years. Calculate the annual capital charge for the loan (i.e. the annual payment which has to be made to repay the loan in 15 years).

Solution:

The annual payments represent a uniform series of equal payments A. The amount of the loan occurs at time zero; therefore, it is considered as a single present value payment. Rearranging equation (16.9), the annual payment needed to repay the loan is calculated as follows:

$$A = P\frac{i(1+i)^n}{(1+i)^n - 1} = 1.5\frac{0.08(1+0.08)^{15}}{(1+0.08)^{15} - 1} = 1.8 \times 0.11683$$

$$= 0.17524 \text{ billion or } 175.24 \text{ million.}$$

This is the annual cost of capital and the refinery would need to have an operating margin of $175.24 million each year just to cover the financial obligations. This comes to $21.9 per ton (or $0.44 per barrel) of crude refined in addition to any other operating costs.

16.6.3. Inflation

The effect of inflation in the economy results in increases in the cost of equipment, labour, fuel and other operating costs. The payments shown on the CFD should reflect this inflationary effect. Due to inflation, a dollar spent in the future will purchase fewer goods and services than the same dollar would purchase today or at any arbitrary base year. Therefore, these future payments should be expressed in terms of their purchasing power as shown in the following formula:

$$F' = \frac{F}{(1+i)^n}, \tag{16.11}$$

where F' is the purchasing value of the future payment F and n is the number of year from the base year to the time this payment occurs on the CFD. When all future payments are expressed in terms of their purchasing power, the CFD is now inflation free and the calculations performed on it should be done using the inflation-free interest rate i'. The relation between the interest rate i and i' is expressed by

$$i' = \frac{1+i}{1+f} - 1, \tag{16.12}$$

where f is the annual inflation rate.

16.6.4. Taxation and After-tax Cash Flow

When estimating the annual cash flow, we must account for the effect of taxes. Taxation rates for companies depend on the country where the refinery is built. They can be in the range of 40–50%. Central to the calculation of the amount of tax to be paid is the determination of the depreciation of the equipment in the process plant. When a company builds and operates a process plant, the equipment and buildings have a finite life. The value of these assets decreases with time. The decrease in the value of the plant per year is called depreciation. When the plant is closed, the equipment may still be operational and would have a salvage value if it is sold. This salvage value would be shown as income on the CFD at the end of the project. The amount and rate at which equipment may be depreciated is set by the tax authorities in the country where the refinery is located. For tax purposes, governments allow companies to deduct the annual depreciation from the revenues for tax calculations as follows:

$$\begin{aligned} \text{Expenses} &= \text{operating costs} + \text{annual depreciation} \\ \text{Income tax} &= (\text{revenue} - \text{expenses})(\text{tax rate}) \\ \text{Net profit} &= \text{revenue} - \text{expenses} - \text{income tax} \\ \text{After-tax net profit} &= \text{net profit} + \text{depreciation}. \end{aligned} \tag{16.13}$$

16.6.5. Profitability and Project Evaluation

To access the economic feasibility of a refinery or any process units, the cash flows involved in the project, such as revenue from selling the refined products, the capital expenditures, cost of purchased crude and any other operating costs, are compared.

A new refinery project starts with preliminary studies needed before a decision can be made. This constitutes the feasibility study and involves the profitability of the project. This may take months or years, depending on the refinery owner, location and other factors. In the economic analysis of the project, the refinery site should be available either by purchase or lease, and a construction period is assumed which may be between 2 and 3 years. During this construction period, the major capital outlays occur in terms of the civil works, equipment purchase and installation, and other auxiliary facilities needed to run the refinery. Several factors affect the capital outlay and were explained in Section 16.3.3. After construction is completed, additional expenses for working capital are needed to start production. After the start-up, the refinery starts to produce finished products for sale. Then income is generated and the after-tax cash flow becomes positive.

To evaluate the profitability of a project or when comparing a project with other projects, a lifetime should be for the process plant. This is the number of the years, the process plant is believed to be operational or company want to keep it operational. The profitability of the refinery or the process plant depends on the chosen life.

There are different ways to evaluate the profitability of projects based on the following criteria (Gary and Handwerk, 2001):

- Net present value (NPV) and present value ratio (PVR)
- Discounted payback period (DPBP)
- Discounted cash flow rate of return (DCFROR)

The payments in the CFD are discounted, and thus we obtain what is called the discounted CFD. The above criteria are used to evaluate the project as follows:

Net present value (NPV) and present value ratio. These criteria are defined as:

$$\text{NPV} = \text{sum of discounted present value of all cash flows (positive and negative)}, \tag{16.14}$$

$$\text{PVR} = \frac{\text{present value of all positive cash flows}}{\text{present value of all negative cash flows}}. \tag{16.15}$$

A profitable project is the one with a positive NPV or a PVR greater than one.

Discounted payback period. This is the time required after start-up to recover the fixed capital investment required for the project with all cash flows discounted back to time zero. For the above calculations, the interest rate or the discount rate used is set by the company, and it represents the minimum rate of return that the company management finds acceptable for investing in a new plant or refinery. This minimum rate of return is affected by several factors, some of which are the rate of return on past investments, the cost of capital and the inflation rate.

Discounted cash flow rate of return. It is the interest or discount rate for which the NPV of the project is zero. The project can be considered profitable if it achieves a DCFROR greater than the minimum corporate rate of return.

16.6.6. Case Study: Refinery Economic Evaluation

A new 160,000 barrels per day simple refinery is going to be built with the following investment data in million of U.S. dollars:

Construction time: 2 years
Cost of land: $10
Capital cost during the first year: $1500
Capital cost during the second year: $500
Working (operating) capital: 10% of total capital cost or $200 at the end of year 2
Operating cost: $6.4 bbl^{-1}
Crude price: $57 bbl^{-1}
Average price of products: $66.84 bbl^{-1}
Taxation rate: 40%
Salvage value of refinery at the end of its useful life is assumed to offset its dismantling cost
Refinery life after start-up: 20 years
Depreciation per year: $2000/20 = $100

Assume that the product yield and the prices of crude oil and products and the operating costs are as shown in Example E16.1. Use a discount rate of 2.5% in your calculations.
Calculate:

- **(a)** The net present value,
- **(b)** The present value ratio,
- **(c)** The discounted payback period, and
- **(d)** The discounted cash flow rate of return.

Solution:

The cost of land would be placed at time zero on the CFD. The capital cost for the first and second year occurs at the end of each year, respectively. The working capital is at the end of year 2. The life of the project is 20 years plus the 2-year start-up period or 22 years.

The net revenues from the sales of the finished products are as calculated from the cost data in Example E16.1. Therefore,

$$\begin{aligned}
\text{Expenses} &= \text{cost of crude} + \text{operating cost} - \text{depreciation}\\
&= (57 + 6.4)\,\text{bbl}^{-1} \times 160,000\text{bbl day}^{-1} \times 365 \text{ day year}^{-1}\\
&\quad + 100,000,000 = \$3,802,560,000 \text{ year}\\
\text{Revenues} &= 66.84 \times 160,000 \times 365 = \$3,903,456,000 \text{ year}^{-1},\\
\text{Income tax} &= (3,903,456,000\text{-}380,256,000) \times 0.4 = \$40,358,400 \text{ year}^{-1},\\
\text{Net income} &= \text{revenue} - \text{expenses} - \text{income tax}\\
&= 3,903,456,000\text{-}3,802,560,000\text{-}4,358,400 = 60,537,600,\\
\text{After-tax net profit} &= \text{net income} + \text{annual depreciation}\\
&= 60,537,600 + 100,000,000\\
&= \$160,537,600 \text{ or } \$160.538 \text{ million year}^{-1}.
\end{aligned}$$

The land cost and the working capital are recovered as income at the end of the refinery life (2-year start-up plus 20 years of refinery life).

The cost items and the net profit amounts are discounted using the given discount rate and equation (16.8). An EXCEL worksheet is prepared to perform these calculations. The cash flow values are shown in the table below. The cumulative discounted cash flow gives the NPV. Therefore,

(a) NPV = \$364.352 million at end of year 22

(b) Cumulative positive cash flows = \$364.35 + \$2129 = \$2494.037 million
Cumulative negative cash flows = \$2129.685 million
PVR = 2494.037/2129.685 = 1.17

(c) The DCFROR is calculated by changing the discount rate until NPV = 0. which gives, DCFROR = 4.03%

End of year	Investment	Net profit after tax	Discounted cash flow	Cumulative cash flow
0	−10		−10.000	−10.000
1	−1500		−1463.415	−1473.415
2	−700		666.270	−2139.685
3		160.538	149.075	−1990.609
4		160.538	145.440	−1845.170
5		160.538	141.892	−1703.278
6		160.538	138.431	−1564.846
7		160.538	135.055	−1429.791
8		160.538	131.761	−1298.030
9		160.538	128.547	−1169.483
10		160.538	125.412	−1044.071
11		160.538	122.353	−921.717
12		160.538	119.369	−802.349
13		160.538	116.458	−685.891
14		160.538	113.617	−572.274
15		160.538	110.846	−461.428
16		160.538	108.142	−353.286

(continued)

(*continued*)

End of year	Investment	Net profit after tax	Discounted cash flow	Cumulative cash flow
17		160.538	105.505	−247.781
18		160.538	102.931	−144.849
19		160.538	100.421	−44.428
20		160.538	97.972	53.543
21		160.538	95.582	149.126
22	210	160.538	215.232	364.358

16.7. GLOBAL TRENDS

The future outlook of the refining industry depends on the demand for transportation fuel and the global supply of crude oil (Shore and Hackworth, 2007). It has become clear in recent years that the spare capacity for crude oil production is shrinking and that the increasing price of crude oil is driving the prices of fuels to an all time high. Economists expect that the growth of the world economy might slow down or even experience negative values if high oil prices are not controlled. This spells trouble for major economic powers like the U.S. and China and will slow down the growth of any emerging developing power like India.

There is a worldwide awareness of the effect of global warming and the need to limit carbon dioxide emission, to which petroleum-based fuels are major contributors. The nations of the world are moving towards environmentally friendly transportation fuels. New transportation fuel specifications are being put into effect. All of these factors will affect the economics of refining in the coming years.

The growth in demand manifests itself in different ways: (Swaty, 2005):

- All light product demand will increase.
- Heavy fuel oil demand is declining.
- Demand for diesel is growing, and its specifications in terms of sulphur is becoming more stringent.
- The U.S. is still a big consumer of gasoline, although the demand for diesel is growing.
- Diesel is the key fuel in Europe. Gasoline produced in Europe is being exported to the U.S.
- Refining capacity is expected to grow to 91 million barrels per day by 2010. More heavy crude oil will have to be processed.

- The majority of new refining capacity will either be in oil-producing countries like Saudi Arabia, Iran or Venezuela or in or close to major markets like China, Southeast Asia or the Caribbean countries, which are close to the U.S. market.
- The synergy between the refining and the petrochemical industries will be strengthened due to the increase in demand for petrochemical stocks like naphtha, ethylene and propylene.

Increasing oil prices and the increase in demand and price of transportation fuels have affected the refining industry. After many years of low returns during the 1990s, the industry has recently seen an increase in margins and price differentials. While historically gasoline was the largest driver of overall refining margins, distillate is playing a stronger role now. The annual average gasoline and distillate crack spreads has been increasing since 1990.

Historically, the gasoline margin has been higher than the distillate crack, but in 2005, the distillate crack spread exceeded gasoline. Even though the distillate crack averaged slightly less than the gasoline crack in 2006, it was close. Distillate is becoming a much stronger contributor to margins than in the past. The strong growth in distillate demand worldwide—and in particular in Europe—is likely to be a major driver behind this change.

The gasoline crack since 2000 is 2.3 times what is was from 1992–1999, and the distillate margin is 2.7 times over the same time period. These rises in crack spreads (and thus margins) have coincided with crude oil prices increasing from $20–25 per barrel to over $70 per barrel. Furthermore, world refining utilization has gone up by 2% from 2003 to average 86.3% worldwide.

For the refiners with bottom upgrading, the margins have become very attractive. The current light–heavy crude differential provides a very strong incentive for added bottom processing conversion capacity.

QUESTIONS AND PROBLEMS

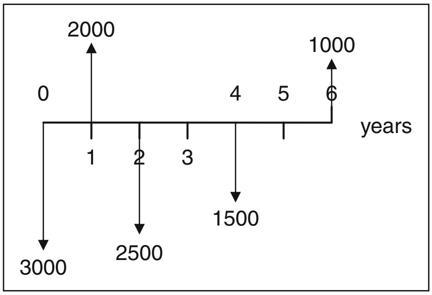
16.1. Calculate the gross and net margin for an average refinery in the U.S. Use the following data:

	Product yield (%)	Price per barrel
Gasoline	60	71
Distillates	30	72
Other products	10	47.5
Crude price		57
Variable refining costs		6.4

16.2. Calculate the complexity factor for a refinery which has the following unit data:

Unit	Complexity coefficient (CC_i)	Percent capacity relative to CDU capacity (F_i/F_{CDU})
Vacuum distillation unit	1.5	30
Fluid catalytic cracking	7	20
Hydrocracking	7	20
Hydrotreating	5	40
Reforming	3.4	40
Alkylation	6	5

16.3. Calculate the value of all the payments in the CFD in the figure below at time zero and at the end of year 6. The interest rate is 6% per year.



16.4. 200,000 barrels per day refinery with classic conversion processes has been built at a cost of $1.5 billion. The cost has been entirely financed by a loan at 6% interest, repayable over 10 years. Calculate the annual capital charge for the loan (i.e. the annual payment which has to be made to repay the loan in 10 years).

16.5. A new 200,000 barrels per day refinery is going to be built with the following investment data in millions of U.S. dollars:

Construction time: 2 years
Cost of land: $10
Capital cost during the first year: $2000
Capital cost during the second year: $750
Working (operating) capital: 10% of total capital cost
Operating cost: $6.4 bbl^{-1}
Crude price: $57 bbl^{-1}
Average price of products: $66.84 bbl^{-1}

Taxation rate: 40%

Salvage value of refinery at the end of its useful life is assumed to offset its dismantling cost.

Refinery life after start-up: 25 years

Depreciation per year: \$2000/25 = \$80

Calculate the discounted cash flow rate of return.

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CHAPTER SEVENTEEN

ENVIRONMENTAL ASPECTS IN REFINING

17.1. INTRODUCTION

The evolution of petroleum refining from simple distillation to today's sophisticated processes has created a need for environmental, health and safety management procedures and safe work practices. The safe processing of crude oil into flammable gases and liquids at high temperatures and pressures using vessels, equipment and piping requires considerable control technologies to avoid damage to the environment. Environment and health professionals assure that potential physical, mechanical, chemical and health hazards are recognized and therefore, provisions are made for safe operating practices and appropriate protective measures. These procedures should be established to assure compliance with applicable regulations and standards such as hazard communications, emission rates regulations, waste management and waste minimization.

The refinery industry has demanding environmental management challenges to protect water, soil and the atmosphere from refinery pollution. For example, petroleum refineries use relatively large volumes of water, especially for cooling systems. Table 17.1 lists typical wastes from a refinery. This chapter describes the environmental aspects of refining, including air, water and soil pollution from different units in refinery processes. In each refinery unit, the effluent gas, solid and liquid wastes are pointed out. In addition, waste treatment and waste minimization are discussed.

17.2. WASTES IN REFINERY UNITS

17.2.1. Desalter

Hydrogen sulphide is emitted to a atmosphere from the desalter when treating sour crude. Demulsifiers and other chemicals, which are used in the pretreatment process, are considered chemical hazards either during processing or in disposal. Safe material handling will minimize human exposure to these chemicals. The wash water from the desalter unit contains a large amount of chlorides, sulphides, ammonia, hydrocarbons and suspended solids. The best practices should be followed to deal with this hazardous waste.

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Table 17.1 Typical wastes from a refinery (World Bank, 1998)

Type of waste	Quantities
Wastewater from cooling systems	3.5–5 m^3 of wastewater generated per ton of crude
Polluted wastewater	Oil 100–300 mg/l (desalter water), oil 5000 mg/l in tank bottom, benzene 1–100 mg/l, heavy metals 0.1–100 mg/l
Solid waste and sludge	3–5 kg/ ton of crude (80% should be considered as hazardous waste because of the heavy metals and toxic organic substances)
VOC emissions	0.5–6 kg/ton of crude
Others emissions	Benzene, toluene and xylene (BTX) 0.75–6 g/ton of crude, sulphur oxides 0.2–0.6 kg/ton of crude, nitrogen oxides 0.006–0.5 kg/ton of crude

17.2.2. Crude Distillation

Low boiling point hydrocarbons can escape to the atmosphere from the leaky connections during distillation. Hydrogen sulphide is emitted when sour crude is processed. Wastewater contains soluble hydrocarbons, mercaptans, antifoam and anticorrosion additives.

17.2.3. Catalytic Reforming and Isomerization

Benzene is one of the most carcinogenic compounds that may be formed in an undesired reaction in catalytic reforming. Small emissions of carbon monoxide and hydrogen sulphide may occur during regeneration of a catalyst. Appropriate catalyst handling will prevent dust emissions during loading. In isomerization, there is a potential for exposure to hydrogen gas, hydrochloric acid, and hydrogen chloride and to dust when solid catalyst is used.

17.2.4. Thermal Cracking and Coking

In delayed coking units, the main point sources for air quality concerns are the coker furnace stack emissions and the flare system where off gas is rejected from the unit and burned. Complete combustion in both the furnace and the flare assures minimum hydrocarbon emissions to the atmosphere. To reduce furnace stack emissions, it is important to operate coker furnaces at optimum conditions; installing air pre-heaters and advanced process controls can increase the overall furnace efficiency.

Water, which is used for cooling, is considered waste since it contains coke and hydrocarbons. Wastewater may be highly alkaline and contain oil, sulphides, ammonia, and/or phenol. Large quantities of water are used during coke drum cleaning. Coke handling and dewatering operations use the optimum water quantities to reduce water pollution. Typically, all coke handling water is recycled within the unit.

The exposure to hazardous gases, such as hydrogen sulphide, carbon monoxide, and trace polynuclear aromatics (PNA), is associated with coking operations. Handling hot coke with care will minimize human exposure to hazardous emissions. Safe work practices and the use of appropriate personal protective equipment may be needed for exposure to chemicals and other hazards, such as heat and noise, and during process sampling, inspection, and maintenance.

17.2.5. Hydrocracking

Low boiling point hydrocarbons, hydrogen and hydrogen sulphide can leak during hydrocracking. Improper catalyst regeneration may lead to carbon monoxide and hydrocarbon emissions. Steam stripping and regeneration of the catalyst create waste streams containing sour water and ammonia.

17.2.6. Hydrotreating

Hydrogen sulphide and ammonia are hazardous emissions that are released into the atmosphere during hydrotreating. The hydrogen required in hydrotreating reactions should be handled with care to avoid explosions.

17.2.7. Fluid Catalytic Cracking (FCC)

Catalyst regeneration produces emissions to the atmosphere upon burning the deposited coke. When the catalyst is stripped with steam, condensate is produced that needs to be treated before disposing since it contains heavy metals such as nickel and vanadium.

Carbon monoxide (CO) results from the incomplete combustion of coke in the regenerator. Combustion promoters with a noble metal base (Pd or Pt) are added to the catalyst. Particulate matters emissions are controlled by applying more resistant catalyst and improve cyclone designs as well as installing third stage cyclone, electrostatic precipitations and wet scrubbers downstream from the FCC regenerator.

Control of SO_2 emissions has been also widely applied by adding metallic oxides (MO) to the catalyst. Nitrogen oxides (NO_x) is produced in FCC from the combustion of nitrogen compounds present in the coke deposited on the catalyst during regeneration. The addition of Pt-based composition promoters to remove CO results in the increase of NO_x because originally, CO could have react with NO_x. A summary of FCC environmental control methods is given in Table 17.2.

Table 17.2 Control methods of waste in FCC

Carbon monoxide CO
Carbon combustion/CO prompter
CO boiler (CO incinerator)
Particulates
Third stage separation
Electrostatic precipitation
Flue gas scrubbing
Sulphur oxides (SO_x)
Feed desulphurization
Flue gas scrubbing
SO_x catalyst additives
Nitrogen oxides (NO_x)
Selective catalytic reduction
Selective non-catalytic reduction
NO_x catalyst additives
Counter current regeneration

17.2.8. Alkylation

Sulphuric acid and hydrofluoric acid are potentially hazardous chemicals. Material handling should be based on available material safety data sheets for both acids. Water contamination with these acids is hazardous and may lead to an explosion. Furthermore, appropriate skin and respiratory personal protective equipment is needed for potential exposure to liquid spillage of the acids.

17.2.9. Asphalt Production, Solvent Extraction and Dewaxing

Phenol, amines and other solvents used in deasphalting processes are considered hazardous chemicals. If a spill or release occurs, there is a potential for exposure to residues and asphalt. The potential for exposure to hydrogen sulphide and sulphur dioxide exists in the production of asphalt. Solid waste effluent should be treated with care since it contains large quantities of hazardous chemicals.

17.2.10. Hydrogen Production

The produced hydrogen is considered the most potentially hazardous gas. Carbon monoxide and carbon dioxide are produced with hydrogen from methane gas. Carbon monoxide is toxic gas and needs to be kept within ambient guidelines. An amine solvent should be handled according to its exposure guidelines.

17.3. WASTE MANAGEMENT

Pollution associated with petroleum refining, as discussed in Section 17.2, typically includes volatile organic compounds (VOCs), carbon monoxide (CO), sulphur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH_3), hydrogen sulphide (H_2S), metals, spent acids and numerous toxic organic compounds.

These pollutants may be discharged as air emissions, wastewater or solid waste. All of these wastes are treated. However, air emissions are more difficult to capture than wastewater or solid waste. Thus, air emissions are the largest source of untreated wastes released to the environment. The categories for pollution management of waste are:

- Estimation of emissions
- Waste treatment and control
- Waste minimization and prevention

17.3.1. Gas Waste

Air emissions include point and non-point sources. Point sources are emissions that exit stacks and flares which can be monitored and treated. Non-point sources are fugitive emissions which are difficult to locate and capture. Fugitive emissions in refineries arise from valves, pumps, tanks, pressure relief valves, flanges, and so on. For example, steam generators are potential sources of SO_x, NO_x, CO, particulates and hydrocarbons emissions. When operating properly and when burning cleaner fuels, such as refinery fuel gas, fuel oil or natural gas, these emissions are relatively low. If, however, combustion is not complete, emissions can be significant for non-burn hydrocarbons.

The gas streams from each unit in the refinery are collected and sent to the gas treatment and sulphur recovery units. Emissions from the sulphur recovery unit typically contain H_2S, SO_x and NO_x. Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units and hydroprocessing units can contain high concentrations of hydrogen sulphide mixed with light refinery fuel gases.

Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system. These blowdown systems handle liquid and gas safely. The gaseous component is either discharged directly to the atmosphere or combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulphur oxides when flared. Table 17.3 lists some typical US-EPA emission regulations in petroleum refineries.

Table 17.3 Emission regulations for US petroleum refineries (EPA-NESHAP, 2007)

Emission source	Emission	Proposed regulation
Catalytic cracker unit	Organic HAP[a]	Below 20 ppmv or 98 wt%
Catalytic cracker	Inorganic HAP	CO 500 ppmv (dry) Particulate emissions below 1 lb/1000 lb of coke burn-off or nickel emissions below 0.029 lb/h
Catalytic reformer coke burn off or catalyst regeneration	Hydrochloric acid	Below 30 ppmv or 92 wt% removal efficiency

[a] Hazardous Air Pollutants

17.3.1.1. Emission Estimation

Mass balance involves the quantification of total materials into and out of a process. The differences between their inputs and outputs are accounted for in terms of releases to the environment or as part of the facility waste. Mass balance is particularly useful when the input and output streams can be quantified, and this is most often the case for individual process units and operations.

Example E17.1

Fuel containing 4 wt% sulphur is burned in a furnace to heat the crude oil before introducing it to the crude distillation unit. Calculate the amount of SO_2 emitted from the furnace stack per 100 kg of fuel burned. Calculate the amount of air required for combustion.

Solution:

Amount of sulphur in fuel = 4 kg
This will produce = (4/32) × 64 = 8 kg SO_2 based on the following reaction

$$S + O_2 \rightarrow SO_2$$

8 kg SO_2 required = 4/32 = 0.125 kmol oxygen
The amount of air required = 0.125/0.21 = 0.595 kmol = 17.28 kg air

In general, emission factors are developed for emission rate estimation. The emission rate is calculated by multiplying the emission factor by the flow rate of the activity. The formula is

$$\text{Emission rate (mass per time)} = \text{Emission factor (mass per unit of activity)} \times \text{Activity data (unit of activity per time)} \tag{17.1}$$

Table 17.4 lists typical emission factors for refinery units.

Table 17.4 Significant refinery emission factors (US EPA Document AP-42, 1998)

Refinery process	Air pollutant	Emission factor lb/1000 bbl feed
Catalytic cracking (fluid bed)	Particulates	242
	Carbon monoxide	13,700
	Sulphur dioxide	493
	Nitrogen oxides	71
	Hydrocarbons	220
	Aldehydes	19
	Ammonia	54
Catalytic cracking (moving bed)	Particulates	17
	Carbon monoxide	3800
	Sulphur dioxide	60
	Nitrogen oxides	5
	Hydrocarbons	87
	Aldehydes	12
	Ammonia	6
Catalytic reforming	Hydrocarbons	25
	Inorganic chlorine	4450
Sulphur recovery plant	Sulphur dioxide	359 lb/ton sulphur recovered
	Reduced Sulphur	0.65 lb/ton sulphur recovered
Storage vessels	Hydrocarbons	No single emission factor
Fluid coking	Particulates	523
Wastewater streams	Hydrocarbons	0.097
Cooling towers	Hydrocarbons	0.0048
Equipment leaks	Hydrocarbons	0.034
Blowdown system	Hydrocarbons	580
Vacuum distillation	Hydrocarbons	50
Steam boiler, furnace or process heater (below 100 MBtu/h capacity)	Particulates	2 lb/1000 gallon distillate oil
	Nitrogen oxides	20 lb/1000 gallon distillate oil
	Carbon monoxide	5 lb/1000 gallon distillate oil
	Sulphur oxides	142 × sulphur percentage in fuel/1000 gallon distillate oil
Steam boiler, furnace or process heater (above 100 MBtu/h capacity)	Particulates	2 lb/1000 gallon fuel oil
	Nitrogen oxides	24 lb/1000 gallon fuel oil
	Carbon monoxide	5 lb/1000 gallon fuel oil
	Sulphur oxides	157 wt% S in fuel/1000 gallon fuel
Compressor engine (reciprocating)	Hydrocarbons	1.4 lb/1000 cubic feet gas fuel
	Carbon monoxide	0.43 lb/1000 cubic feet gas fuel
	Nitrogen oxides	3.4 lb/1000 cubic feet gas fuel
	Sulphur oxides	2 wt% S in fuel/1000 cubic feet gas

(continued)

Table 17.4 (*continued*)

Refinery process	Air pollutant	Emission factor lb/1000 bbl feed
Compressor engine (gas turbine)	Hydrocarbons Carbon monoxide Nitrogen oxides Sulphur oxides	0.02 lb/1000 cubic feet gas fuel 0.12 lb/1000 cubic feet gas fuel 0.3 lb/1000 cubic feet gas fuel 2 wt% S in fuel /1000 cubic feet gas
Vessel loading (barge)	Hydrocarbons	3.4 lb/1000 gallons transferred
Vessel loading (ship)	Hydrocarbons	1.8 lb/1000 gallons transferred

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Example E17.2

10,000 BPD crude oil containing 4 wt% sulphur is burned in a furnace of an 80 MBtu/h steam boiler. Calculate the amount of SO_2 emitted form the furnace stack using the emission factors.

Solution:

The emission factor from Table 17.4 is 142 wt% S/1000 gal crude
Crude feed rate is 10,000 BPD = 420,000 gal/day
Emission rate of SO_2 = 142 (0.04)(420,000)/1000 = 2385.6 lb/day SO_2

The trace element in particulate emissions can be estimated using the weight fractions presented in Table 17.5, combined with the following equation:

$$ER = TSP(wt\%/100) \qquad (17.2)$$

Table 17.5 Trace elements (wt%) in catalyst from two typical refinery processes (USEPA, 1993)

	FCC	Fluid coking
Manganese	0.022	0.004
Nickel	0.088	0.038
Copper	0.020	0.001
Zinc	0.017	0.003
Arsenic	0.002	0.144
Selenium	0.002	0.002
Antimony	0.035	0.005
Lead	0.046	0.003
Cobalt	0.002	–
Cadmium	0.009	–
Mercury	0.010	0.002

where ER is the emission rate of the specified metal from the relevant source (kg/h), TSP (kg/h) is the total suspended particulates as calculated from emission factors in Table 17.4 and wt% is the appropriate weight percent of species provided in Table 17.5.

Example E17.3

10,000 BPD is fed to a FCC unit. In the regenerator of spent catalyst, the flue gas has some amount of escape catalyst. Calculate that amount of particulate (catalyst) escaping into the atmosphere and estimate the amount of nickel in that particulate stream.

Solution:

From Table 17.4 the particulate emission factor 242 lb/1000 bbl feed

Then amount of catalyst emission feed = (242/1000)(10,000/24)

= 100.83 lb/h = 45.83 kg/h

Nickel in FCC particulate emission = 0.088 wt% from Table 17.5

Then amount of nickel in particulate (ER)= (0.088/100) (45.83) = 0.0403 kg/h

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17.3.1.1.1. Stack and Flare Emissions Flaring has become more complicated than just lighting up waste gas. Concern about flaring efficiency has been increasing. The Occupational Safety & Health Administration (OSHA) and Environmental Protection Agency (EPA) have become more active in this field, resulting in tighter regulations on both safety and emission control. These regulations have resulted in higher levels of involvement in safety and emissions matters, smoke, noise, glare and odour. A properly designed flare works as an emission control system with greater than 98% combustion efficiency. The appropriate use of steam, natural gas and air assisted flare tips can result in smokeless combustion.

The combustion of hydrocarbons releases many gases into the atmosphere. Gases such as CO_2, CO, NO_x and H_2O affect the natural balance that exists in the atmosphere. Typical constituents of flared gas are listed in Table 17.6. High pressure flares are usually ground flares with high concentration of methane. Most of flared gas is methane (CH_4). Upon combustion, each mole of carbon atoms is converted to one mole of CO_2. This means that one mole of CH_4 yields one mole of CO_2 when complete combustion takes place and one mole of C_2H_6 (ethane) results in two moles of CO_2 and so on. Incomplete combustion can also occur if insufficient air is supplied. The following reactions are typical in the flaring system:

Table 17.6 Typical constituents of the flared gas

Component	High *P* (mol%)	Low P (mol%)	Heat of combustion (kJ/mol)
C_1	72.8	52.1	−890.36
C_2	14.3	21.3	−1559.9
C_3	6.3	13.8	−2220.0
iC_4	1.1	2.8	−2865.8
nC_4	1.7	4.6	−2878.5
iC_5	0.4	1.1	−3529.2
nC_5	0.5	1.3	−3536.1
C_6	0	0	−4194.8

$$\left.\begin{array}{l} CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \\ C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O \\ C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \end{array}\right\} \text{complete combustion} \tag{17.3}$$

$$\left.\begin{array}{l} CH_4 + 1.5O_2 \rightarrow CO + 2H_2O \\ C_2H_6 + 2.5O_2 \rightarrow 2CO + 3H_2O \\ C_3H_8 + 3.5O_2 \rightarrow 3CO + 4H_2O \end{array}\right\} \text{incomplete combustion} \tag{17.4}$$

Therefore, with the known composition and amount of each hydrocarbon, the total moles of CO_2 can be calculated. The same procedure can be repeated to calculate the percentage of fuel that goes to incomplete combustion reactions.

The estimated emission factors for the combustion products are listed in Table 17.7.

Table 17.7 Flaring emission factors (kg/ton of hydrocarbon) (USEPA, 1995)

CO_2	CH_4	N_2O	NO_x	CO	VOC
2690	35	0.081	1.5	8.7	15

Example E17.4

100 kg/h high pressure flare gas of the composition shown in Table 17.6 is burned. Assuming complete combustion, calculate the CO_2 emission rate based on the material balance and compare it with the CO_2 emission factors listed in Table 17.7.

Solution:

Calculating the molecular weight of the gas = 0.728 (14) + 0.143 (30) + 0.063 (44) + 0.011 (58) + 0.017 (58) + 0.004 (72) + 0.005 (72) = 19.526 kg/kmol

100 kg/h fuel = 5.1213 kmol/h

Based on the complete combustion reactions listed in equation (17.3)

Amount of CO_2 in the flue gas =

$$5.1213[0.728(1) + 0.143(2) + 0.063(3) + 0.028(4) + 0.009(5)] = 6.965\ \text{kmol/h} = 306.45\ \text{kg/h}$$

Emissions based on emission factor = 2690 kg CO_2/ton fuel

Amount of CO_2 in the flue gas = (2690/1000) (100 kg/h) = 269 kg/h

It can be observed that emission factors can be used for easy and fast estimates. However, if full data are available, material balance gives exact estimates.

17.3.1.1.2. Tank Emissions

Atmospheric storage tanks and pressure storage tanks are used throughout the refinery for storage of crude, intermediate products (between the processes) and finished products. Tanks are also provided for fire water, process and treatment water, acids, additives and other chemicals. The type, construction, capacity and location of tanks depend on their use and materials stored.

There are three significant types of hydrocarbon emissions from fixed roof tanks.

- *Breathing loss* is the expulsion of vapour from a tank as a result of vapour expansion, which is caused by changes in temperature and pressure.
- *Working loss* is due to changes in the tank's liquid level.
- *Flashing loss* occurs when dissolved gas flashes out of the liquid stream due to the pressure drop between the production line and the tank.

The following equations have been identified by the US-EPA to quantify hydrocarbon emissions from oilfield tanks.

Breathing loss:

$$L_B = 0.0226 M_v \left(\frac{P}{P_a - P}\right)^{0.68} D^{1.73} H^{0.51} \Delta T^{0.5} F_p C K_c R(1 - \text{EFF}) \tag{17.5}$$

Working loss:

$$L_w = 2.4 \times 10^{-5} M_v P V N K_N K_c R(1 - \text{EFF}) \tag{17.6}$$

The flashing loss:

$$L_F = A(\mathrm{GOR})D_G R(1 - \mathrm{EFF}) \tag{17.7}$$

Total hydrocarbon emissions from the tank are:

$$L = L_B + L_w + L_F \tag{17.8}$$

where:

A = annual throughput (bbl oil/year)

C = adjustment factor for small diameter tanks = $0.0771\ D - 0.0013\ D^2 - 0.1334$

D = tank diameter (ft)

D_G = vapour density (lb/scf) = $(14.7\ M_v)/(18.73\ T_s\ ^\circ\mathrm{R})$

F_p = paint factor (dimensionless) = 1.4 (medium grey colour)

GOR = gas oil ratio (scf/bbl)

H = average vapour space (ft) = 0.5 tank height

K_c = product factor (dimensionless) = 0.65 (crude oil)

L_B = breathing loss (lb/year)

L_F = flashing loss (lb/year)

L_w = working loss (lb/year)

M_v = molecular weight of vapour in storage tank (lb/lb mol)

N = number of turnovers per year = annual throughput/tank capacity

P_A = atmospheric pressure at tank location (psia) = 14.7 psia

P = true vapour pressure at bulk liquid conditions (psia)

R = vapour reactivity (defined as the reactive non-methane hydrocarbons in the tank vapours divided by the total hydrocarbons in the tank vapours)

ΔT = average ambient diurnal temperature change (°F)

V = tank capacity (gallons)

EFF = vapour recovery efficiency = 0.95 if connected to vapour recovery, 0 if no vapour recovery

Calculating the amount of hydrocarbon release from a storage tank in refinery based on factors can be done. The estimated emissions are 400 mg of hydrocarbons/liter of liquid per tank amount in litres (EPA–NESHAP).

Example E17.5

Calculate the total hydrocarbon emissions from a tank using the specifications in Table E17.5. Compare with hydrocarbon emissions calculated from emission factors for tanks.

Solution

Using the specifications in Table E17.5, the total hydrocarbon emissions are calculated as the summation of L_B, L_W and L_F. The result is 6,648,400 lb/yr which equals 3022 ton/yr.

Table E17.5 Typical sample calculation on storage tank

Data	Symbol	Value	Units
Tank diameter	D	86.00	ft
Tank volume	V	40,000	bbl
Average outage	H	20.0	ft
Adjustment factor	C	1.0 (large)	
Average daily temperature change	T	20.0	°F
Average storage temperature	T_s	85	°F
Paint factor	F_p	1.4	
Molecular weight	M_v	70.0	lb/lb mol
True vapour pressure	P	9.2	psia
Crude oil factor			
Breathing	k_{cb}	0.65	
Working	k_{cw}	0.84	
Annual throughput	A	41,924,492	bbl
Annual turn over (A/V)	N	1048	
Turnover factor	k_n	0.46	
Efficiency of control system	EFF	0.00	
Gas/oil ratio	GOR	0.451	scf/bbl
Gas density	DG	0.1008	lb/scf
Vapour reactivity	R	0.912	
Hours per day of operation	HPD	24.0	h
Days per year of operation	DPY	365.0	days
Calculated L_B		85,289	lb/yr
Calculated L_W		6,476,202	lb/yr
Calculated L_F		86,909	lb/yr
Total hydrocarbon emissions		6,648,400	lb/yr

If using the amount of fuel listed in Table E17.5, then the result is 2730 tonnes hydrocarbon/year, and this value is comparable with the 3022 tonnes hydrocarbons/year calculated from the detailed tank emissions.

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*17.3.1.1.3. **Fugitive Emissions*** Valves, flanges and fittings can emit hydrocarbons into the atmosphere. These emissions are usually the result of improper fit, wear and tear, and corrosion. The hydrocarbon emissions can be estimated for existing facilities using a factor that is multiplied by the number of active equipment pieces. Generally, fugitive emissions are less than 1% of the total emissions from tanks and flares.

Where no screening values are available for particular equipment types, average emission factors should be used. This methodology involves applying the following equation to estimate emissions from all sources in a stream:

$$\mathrm{EVOC} = \mathrm{FA} \times \mathrm{WFVOC} \times N \tag{17.9}$$

where EVOC is the emission rate of VOC from all sources in kg/year, FA is the applicable average emission factor, WFVOC is the average weight fraction of VOC in the stream, and N is the number of pieces of equipment grouped in the relevant category according to weight fraction of VOC.

The following steps for fugitive emission calculation are:

1. *Develop an inventory of the number and type of fugitive sources*: The number and service type of each equipment in the refinery must be determined.
2. *Group the inventory into streams*: To simplify calculations, it is recommended that the equipment/service mode combinations identified in Step 1 (i.e. valves in gas service) be grouped into streams according to the approximate weight fraction of VOC in each stream.
3. *Note operational hours*: The number of operational hours needs to be estimated.
4. *Use emission factors to estimate emission rates*: Use the relevant emission factors and the equation given above to calculate the emissions from each equipment type. These emissions should then be added to derive a total emission rate for all equipment pieces quantified using this methodology. Table 17.8 presents the emission factors required to estimate emissions using the steps discussed above.

Example E17.6 illustrates the application of the average emission factor approach.

Example E17.6

In the calculations of fugitive emissions from a refinery site, the following inventory steps are carried out:

1. A particular section of a refinery has a count of 300 valves (Step 1)
2. It is ascertained that 200 of these are in gas service (Step 1)
3. Within these valves in gas service, it is ascertained that 100 ($N = 100$) valves are with 80 wt% (non-methane hydrocarbons) (WFVOC = 0.8) and 20 wt% methane. Therefore, the rest of the valves do not emit any VOCs and will not be included (Step 2)
4. It is estimated that this group of valves operates for 5500 h/year (Step 3)
5. The appropriate emission factor for valves in gas service is FA = 0.0268 kg/h/source (from Table 17.8) (Step 4).

Calculate the emission rate of VOC.

Solution:

The final emission estimate for the group of 100 valves specified above is calculated from equation (17.9)

EVOC = (0.0268) (0.8) (100) (5500) = 11,790 kg VOC/year.

Table 17.8 Average fugitive emission factors (API, 1991)

Equipment	Service	Emission factor (kg/h/source)
Connectors	Gas	2.50×10^{-4}
	Light liquid	2.50×10^{-4}
	Heavy liquid	4.34×10^{-3}
Flanges	Gas	2.5×10^{-4}
	Light liquid	2.5×10^{-4}
	Heavy liquid	4.68×10^{-3}
Compressor seals	Gas	0.636
Pump seals	Light liquid	0.114
	Heavy liquid	3.49×10^{-3}
Valves	Gas	0.0268
	Light liquid	0.0109
	Heavy liquid	0.87×10^{-3}
Open-ended lines	All	2.30×10^{-3}
Pressure relief valves	Gas	0.16
Sampling connections	All	0.015
Drains	All	0.032

17.3.1.1.4. Gas Dispersion Air pollution models constitute a set of formulas that take into account:

- Sources of pollution in a given area
- The amounts of pollutants emitted by each source
- Chemical reaction transformations
- Different meteorological conditions and topographical features
- Other factors that affect dispersion of pollutants

The short term concentration model for pollutant sources uses the steady-state Gaussian plume equation for a continuous elevated source. For each source and each hour, the origin of the source's coordinate system is placed at the ground surface at the base of the source. The x-axis is positive in the downwind direction, which the y-axis is crosswind (normal) to the x-axis, and the z-axis extends vertically. The fixed receptor locations are related to each source's coordinate system. The hourly concentrations calculated for each source at each receptor are summed to obtain the total concentration for all sources.

The hourly concentration at downwind distance x (meters) and cross-wind distance y (meters) is given by (Wark and Warner, 1981)

$$C(x, y, z) = \frac{Q}{(2\pi)\sigma_y \sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right]\left\{\exp\left[\frac{-(z-\overline{H})^2}{2\sigma_z^2}\right] + \exp\left[\frac{-(z+\overline{H})^2}{2\sigma_z^2}\right]\right\} \tag{17.10}$$

where Q is the pollutant emission rate (mass per unit time), σ_y, σ_z are the standard deviation of lateral and vertical concentration distribution (m), $\sigma_y = 104\ X^{0.894}$ (at neutral stability class), $\sigma_z = 61\ X^{0.911}$ (at neutral stability class), X is the downwind distance (km), u is the mean wind speed (m/s) at release height, and $\overline{H}$ is the source height (m).

Equation (17.10) includes a vertical term, a decay term, and dispersion parameters. It should be noted that the vertical term includes the effects of source elevation, receptor elevation, plume rise, limited mixing in the vertical, and the gravitational settling and dry deposition of larger particulates.

Example E17.7

1000 kg/h fuel is burned in a furnace. The fuel contains 4 wt% sulphur. The furnace stack is 35 m high. A residential area is about 1 km downwind from the stack. On a day of 5 m/s wind, calculate the amount of SO_2 that reaches the residential area.

Solution:

Emission rate of SO_2 from the furnace stack = (1000 kg/h) (0.04 S) (64/32) = 80 kg/h SO_2

$Q = 22.2$ g/s

$Y = 0$ since the residential area is downwind

$Z = 0$ since residential area is at ground level

$X = 1.0$ Km, then

$\sigma_y = 104\ X^{0.894} = 104$ m

$\sigma_z = 61\ X^{0.911} = 61$ m

$$C_{SO_2} = \frac{Q}{(\pi)\sigma_y \sigma_z u}\left\{\exp\left[\frac{-(H)^2}{2\sigma_z^2}\right]\right\} = \frac{22.2(10^6)}{\pi(104)(61)(5)}\left\{\exp\left[\frac{-(35)^2}{2(61)^2}\right]\right\} = 189\frac{\mu g}{m^3}$$

This 189 µg/m^3 is equivalent to 72.3 ppb which is greater than the standard daily average of SO_2 concentration of 60 ppb.

17.3.1.2. Treatment and Control

Pollution control equipment should be designed and operated in such a way that the substances released from the equipment have the minimum influence on the environment. Table 17.9 lists typical air emissions and suggested reduction methods for each pollutant. In general, pollution control equipment should be kept running during start-up and shutdown for as long as is necessary to ensure compliance with release limits.

Table 17.9 Potential BAT[a] air emission reduction requirements for refineries (CONCAWE, 1999)

Process	Air emissions	Emission reduction method
Incinerator	SO_x, CO_2 and particulates	Use refinery or natural gas fuel
Incinerator	NO_x	Use low NO_x burner (<100 mg/Nm^3)
HDS unit	H_2S	Use alkanolamine adsorption
Gas processing	VOCs, H_2S	Maintenance
Sulphur recovery plant	H_2S, SO_x	Maintenance
Catalytic reformer	NO_x	Use low NO_x burner and flue gas recirculation (<100 mg/Nm^3)
Alkylation unit	HF	Maintenance and continuous monitoring of emissions
Fluid catalytic cracking	SO_x	Hydrogenate the vacuum distillate and install FGD[b] (<100 mg/Nm^3)
Fluid catalytic cracking	NO_x	Use SCR system (<100 mg/Nm^3)
Fluid catalytic cracking	CO	Install CO boiler (<100 mg/Nm^3)
Thermal cracking (visbreaking)	NO_x	Use low NO_x burner (<100 mg/Nm^3)
Storage tanks	VOCs	Install double seals on floating roofs
Steam boilers (gas fuel)	SO_x	Use refinery or natural gas fuel
Steam boilers (gas fuel)	NO_x	Use low NO_x burner (<100 mg/Nm^3)
Steam boilers (residual fuel)	SO_x	Install FGD system
Steam boilers (residual fuel)	NO_x	Use SCR[c] system (<100 mg/Nm^3)

[a] best available techniques;
[b] flue gas desulphurization;
[c] selective catalytic reduction.

To ensure continued optimum performance, all equipment should have regular preventative maintenance according to operational requirements. Since the main air pollutants in a refinery are the sulphur compounds, such as sulphur oxides and hydrogen sulphide, Chapter 15 discusses acid gas processing and treatment technology in detail.

17.3.1.2.1. NO_x Emission Treatment The major NO_x emission sources in a petroleum refinery are combustion processes. NO_x emissions are usually the result of the reaction between oxygen and nitrogen at temperatures above 1093 °C (2000 °F) in the air/fuel combustion flame. NO_x emission control technologies applicable to these sources include combustion controls, Selective Catalytic Reduction (SCR) systems, Selective Non Catalytic Reduction (SNCR) systems and a combination of these techniques.

Most SCR systems use anhydrous ammonia as a reducing agent to convert any NO_x in a flue gas stream into nitrogen over a catalyst. The reactions are:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{17.11}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{17.12}$$

Catalysts are usually oxides of titanium, tungsten, vanadium and molybdenum or in combination. The catalyst operates at temperatures in the range of 127–232 °C (260–450 °F). Zeolite catalysts have been applied successfully in SCR systems at 232 °C (450 °F). Over 95% NO_x emission reduction can be achieved. In SCR operation care should be taken to reduce fouling and corrosion that poison the catalyst (Jaafar *et al.*, 2003).

Example E17.8

Flue gas at a flow rate of 200 kmol/h from the FCC catalytic regenerator contains 35 mol% NO_2, 12 mol% NO and 47 mol% CO_2. The flue gas enters SCR with 95% conversion of nitrogen oxides. The following two reactions take place at 232 °C and atmospheric pressure:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$$

Ammonia and oxygen are added to reactor. The reactor products are then cooled using a flash drum to 50 °C and separated to collect water from the bottoms and N_2 goes to the stack. Use UNISIM simulator, perform the material balance on the process.

Solution:

The process flow chart is shown in Figure E17.8, and a summary of results is shown in Table E17.8.

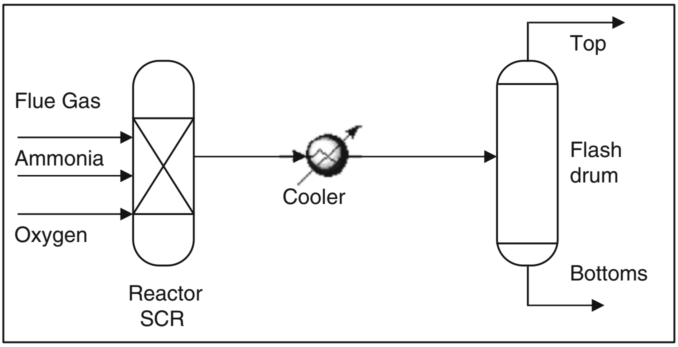

Figure E17.8 Process flow chart

Table E17.8 Summary of results

	Feed to reactor	Top from flash drum	Bottoms from flash drum
NO_2 (kmol/h)	70	3.4	0.095
NO (kmol/h)	24	1.2	0
CO_2 (kmol/h)	106	103.5	3.05
O_2 (kmol/h)	50	11	0
NH_3 (kmol/h)	160	1.146	2.5
H_2O (kmol/h)	0	34.73	198.96
N_2 (kmol/h)	0	122.55	0
T (°C)	232	50	50
P (kPa)	101	96	96

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*17.3.1.2.2. **VOC Emission Treatment*** VOC emissions from refinery units are controlled by incineration in a CO boiler, carbon adsorption, flares, catalytic oxidation and condensation. Adsorption systems have been applied to the control of VOC emissions from catalytic reformer purge gas streams. All of these VOC emission control systems are capable of controlling 95–99% of the emissions from oil refinery sources.

*17.3.1.2.3. **CO Emission Treatment*** CO incinerators or boilers generally oxidize 95% or more of the CO emissions to carbon dioxide. Wet gas scrubbing (WGS) technology allows refiners to meet FCC emission regulations. WGS advantages are:

- Replaces costly CO boiler
- Reduces particulate and SO_x emission
- Produces environmentally safe wastewater discharge
- Collects catalyst

After effective separation from the scrubbing liquid, the clean flue gas is vented to the atmosphere and the liquid containing the particulates. SO_2 and NO_x are disposed in an environmentally acceptable manner. Figure 17.1 shows the WGS unit in the FCC process.

Seawater scrubbing uses the natural alkalinity of the seawater to remove SO_2. The achieved environmental benefits of SO_2 recovery can be as high as 99%. The sulphur content of the effluent seawater is increased by approximately 3%. Special maintenance should be carried out to minimize corrosion.

17.3.1.2.4. Particulate Emission Control WGS is very efficient (>90%) for removal of particulates (4–10 μm) from the FCC regenerator exit (Figure 17.1). Cyclones could be the first choice clean-up device for particulates. As a particulate emission control, cyclones are situated inside

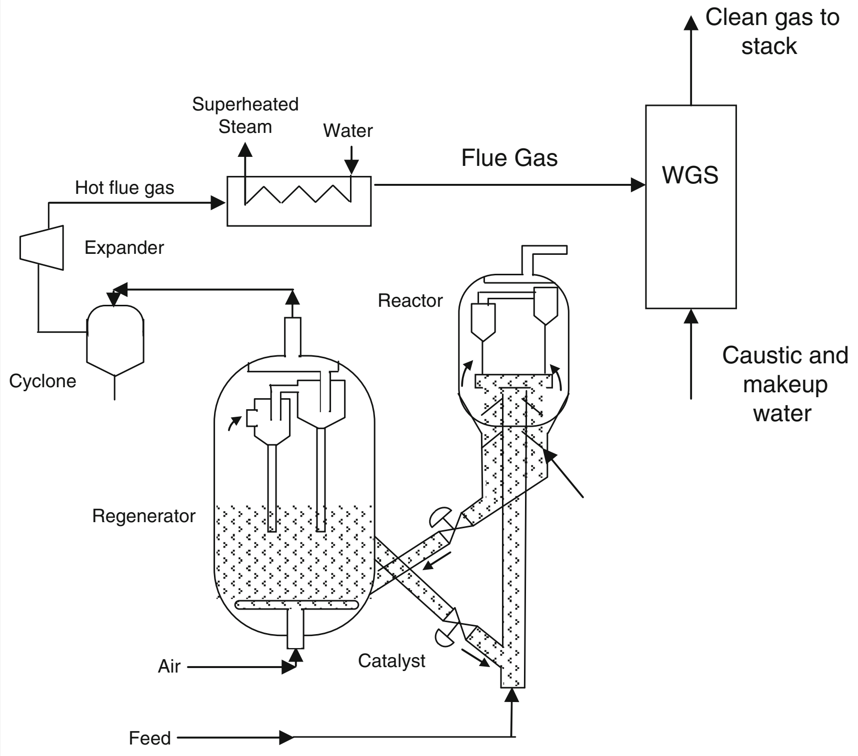

Figure 17.1 Treatment of FCC flue gases by WGS

the FCC reactor and regenerator. They are high-velocity devices which return recovered catalyst to a dust hopper. Cyclones are efficient at removing particles in the range of 10–40 µm and above. Efficiencies can range from 30 to 90%. Cyclones are more effective for coarser particles.

On the other hand, electrostatic precipitators (ESP) employ an electrostatic field to apply a charge to particulate emissions and then collect them on grounded metal plates. ESP units are very efficient (99.8%) for removing finer (4–10 µm) particulates from FCC regenerator gas. Typical particulate emission levels achieved with ESP is <50 mg/Nm^3. As a consequence of the particulate reduction, the metals in the flue gas can be reduced to less than 1 mg/Nm^3. Particulate emissions from the FCC can thus be reduced to 1.1–2.3 kg/h. In the regenerator, the spent catalyst is regenerated by burning off the coke by utilizing air for combustion (Figure 17.2). The flue gas from the regenerator is usually routed through multistage cyclone separators, power and heat recovery equipment, particulate emission control equipment and then released to the atmosphere via the stack. The flue gas from flue gas cooler passes through the ESP unit and the particulates flowing through an electrostatic charged field are reduced to acceptable limits. Clean gas from the ESP is vented to the atmosphere via the stack. The catalyst fines are collected in hoppers below the ESP. Periodically, the hoppers are drained and the catalyst fines are removed for further disposal (CONCAWE, 2006).

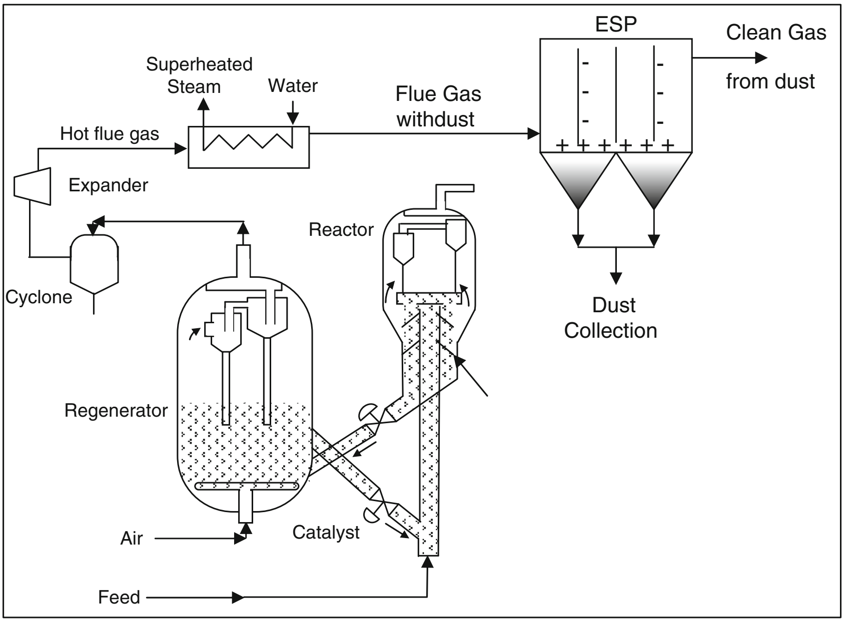

Figure 17.2 Treatment of FCC flue gases by ESP

The ESP design basically depends on the gas flow velocity V_g, the electric field and the drift velocity ω. The very high voltage differential between electrodes causes electrons to pass at the high rate from the centre wire into the passing gas stream. The electrons attach themselves to the gas particulates. The particulates with negative ions migrate to the collecting plates, which have either a positive charge or grounded. The migration or drift velocity ω is calculated (Wark and Warner, 1981) as:

$$\omega = \frac{2.2 \times 10^{-14} E^2 d_p}{\mu_g} \tag{17.13}$$

where E is the electric voltage per distance (V/m), d_p is the particulate diameter (μm) and μ_g is the gas viscosity (kg/m h). The ESP efficiency η is calculated based on plate spacing S, gas and drift velocities:

$$\eta = 1 - \exp\left(-\frac{L\omega}{V_g S}\right) \tag{17.14}$$

Example E17.9

ESP with plates spacing of 23 cm is attached to 50 kV of electric power. The flue gas flows at 1.5 m/s and carries particulates with 0.5 μm at 100 °C. Calculate the plate length to capture 95% of the particulates.

Solution:

Since the electric power is applied midway between plates, the distance from wire to plate is 0.23/2 = 0.115 m.

$$\omega = \frac{2.2 \times 10^{-14} E^2 d_p}{\mu_g} = \frac{2.2 \times 10^{-14} (50,000/0.115)^2 (0.5)}{0.0863} = 0.024 \text{ m/s}$$

$$0.95 = 1 - \exp\left(-\frac{0.024L}{1.5(0.115)}\right) \quad \text{gives} \quad L = 21.5 \text{ m}$$

If we increase the efficiency to 99%, the length will increase to 33 m.

17.3.1.2.5. Emission Monitoring

Continuous emission monitoring is recommended for petroleum refinery air emission point sources for gas temperature and gas flow rate as well as for NO_x, SO_x, CO, VOC and total reduced sulphur concentration. In refinery steam boilers, process heaters and process furnaces, it is required to monitor CO, NO_x and SO_x emissions. Catalytic cracking units have to monitor both NO_x and SO_x in certain locations. The refinery must show evidence that the released emissions are prevented or minimized through continuous monitoring.

17.3.1.3. Waste Minimization and Prevention

The recent trend on this subject is to investigate pollution prevention opportunities other than end-of-pipe treatment. Pollution prevention provides a wide range of options for reducing emissions to levels well below those provided by treatment methods. The highest priority in pollution prevention is given to source reduction, while the end-of-pipe treatment is usually kept as the last and unfavourable option. The main advantage of the pollution prevention approach is that it improves production and reduces the adverse impacts of pollution before they happen.

Pollution prevention options are source reduction and recycle/reuse. Source reduction includes actions to reduce the quantity or the toxicity of the waste at the source. Examples include equipment modification, design and operational changes of the process, redesign of products, substitution of raw materials and use of environmental friendly chemicals. On the other hand, recycle/reuse involves the use of pollutant-laden streams within the process. Typically, separation technologies are key elements in recycle/reuse systems to recover valuable materials such as solvents, metals, inorganic species and water.

17.3.2. Wastewater

Wastewater includes condensed steam, stripping water, spent caustic solutions, a cooling tower and boiler blowdown, wash water, alkaline and acid waste neutralization water, and other process-associated water. Wastewater typically contains hydrocarbons, dissolved materials, suspended solids, phenols, ammonia, sulphides, and other compounds. Water usage in the refinery generates large volumes of water contaminated with oil and other chemical impurities. Part of this water can be reused while the remainder is discharged to water bodies. The discharged part must meet the environmental regulations in its contents of metals and pollutants.

17.3.2.1. Emission Estimation

The first refining step is desalting in which a hot water wash extracts the salts. If the feedstock contains aromatics with good solubility such as benzene or toluene then some will be in the desalted effluent.

Process wastewater arises from desalting crude oil, steam stripping operations, pump cooling, product fractionator reflux drum drains and boiler blow down. Table 17.10 shows typical wastewater coming from refinery units.

Recirculated cooling water must be treated to remove dissolved hydrocarbons. Because the water is saturated with oxygen from being cooled with air, the chances for corrosion are increased. One means of corrosion prevention is the addition of a material to the cooling water that forms a protective film on pipes and other metal surfaces. Therefore, the effluent water from at the cooling tower contains dissolved hydrocarbons, anticorrosive chemicals and corrosion material.

Table 17.10 Typical refinery waste water effluents before treatment (CONCAWE, 1999)

	Oil	H_2S	NH_3	Phenols	TOC	CN-	TSS
Distillation	XX	XX	XX	X	XX	–	XX
Hydrotreater	XX	XXX	XXX	–	XX	–	–
Visbreaker	XX	XX	XX	XX	XX	X	X
FCC	XX	XXX	XXX	XX	XX	X	X
Hydrocracker	XX	XXX	XXX	–	X	–	–

X $<$ 50 mg/l; 50 $<$ XX $<$ 500 mg/l; XXX $>$ 500 mg/l. TOC is total organic carbon.

Point Source Discharge In the petroleum refining industry, the dissolved organic carbon (DOC) of refinery effluents is a known parameter. Hence, the emission factors for organic compounds in Table 17.11 are based on the DOC. Trace elements and inorganic compound emissions factors are also expressed in Table 17.11.

Table 17.11 Typical emissions in refinery effluent (Ontario Ministry of Environment, 1994)

Component	wt% of DOC
Toluene	9.2×10^{-4}
Benzene	9.1×10^{-4}
Xylene	1.4×10^{-3}
Phenol	6.9×10^{-4}
1,2-Dichloroethane	2.7×10^{-4}
Hexachlorohexane	4.4×10^{-4}
PAH	1.6×10^{-3}
Styrene	1.0×10^{-4}
Ethylbenzene	1.2×10^{-4}
1,1,2-Trichloroethane	3.6×10^{-3}
Chloroform	2.5×10^{3}
Elements	**Emission factor (kg/m^3)**
Zinc	4.4×10^{-4}
Phosphorous	4.1×10^{-7}
Arsenic	6.7×10^{-6}
Chromium	7.7×10^{-6}
Selenium	3.1×10^{-6}
Nickel	3.6×10^{-6}
Copper	2.9×10^{-6}
Antimony	5.8×10^{-7}
Cobalt	1.6×10^{-6}
Mercury	1.1×10^{-8}
Cadmium	3.3×10^{-7}
Lead	1.9×10^{-6}
Cyanide	1.3×10^{-6}

These factors are applied to the following effluent parameter:

$$\text{WWE} = \text{DOC}(\text{wt\%}/100)(\text{Flow}) \tag{17.15}$$

where WWE is the wastewater emission of a component from the treatment plant (kg/h), DOC is the dissolved organic carbon of the treated effluent discharged (kg/m^3), wt% is the weight percent of the component as provided in Table 17.11, and Flow is the wastewater flow rate discharged to the receiving body of water (m^3/h).

Example E17.10

Calculate the benzene and nickel emission rates from 1000 m^3/h typical refinery wastewater effluent. A typical DOC in this effluent is 0.1 kg/m^3.

Solution:

From Table 17.11, for benzene DOC wt% $= 9.1 \times 10^{-4}$

Benzene emission rate $= (0.1\ \text{kg/m}^3)\ (9.1 \times 10^{-4}/100)\ (1000\ \text{m}^3/\text{h}) = 9.1 \times 10^{-4}\ \text{kg/h}$

Nickel emission rate $= (1000\ \text{m}^3/\text{h})\ (3.6 \times 10^{-6}\ \text{kg/m}^3) = 3.6 \times 10^{-3}\ \text{kg/h}$

Example E17.11

The effluent wash water in a desalter will contain salts removed from the crude oil. Calculate the effluent salt content of the effluent, considering the following operating conditions:

Crude oil = 25,000 BPD
Inlet salt content = 100 lb/1000 bbl
Outlet salt content in crude = 3 lb/1000 bbl
Outlet water content in crude = 0.3 vol%
Water in crude oil = 0.5 vol%
Wash water = 5 vol% on crude

Solution:

$$\begin{aligned}\text{Salt removed} &= 100 - 3 = 97\ \text{lb}/1000\ \text{bbl}\\ &= 97\ (25) = 2430\ \text{lb/day}\end{aligned}$$

$$\begin{aligned}\text{Effluent water} &= (0.05 + 0.003)\ (25{,}000) = 1325\ \text{bbl/day}\\ &= (1325\ \text{bbl/day})\ (42\ \text{gal/bbl})\ (35.3145\ \text{ft}^3/264.17\ \text{gal})\ (62\ \text{lb/ft}^3)\\ &= 463{,}000\ \text{lb/day}\end{aligned}$$

$$\begin{aligned}\text{Salt in effluent water} &= (2430\ \text{lb/day})/(463{,}000\ \text{lb/day})\ (100) = 0.53\ \text{wt\%}\\ &= 5300\ \text{ppm}\end{aligned}$$

Example E17.12

10,000 BPD of 30 API crude oil and a wash water rate of 5 vol% on the crude are used in a desalter. The crude oil contains 100 ppm of sulphides and the wash water contains 100 ppm of sulphides. Using a water/oil partition coefficient of 4, calculate the sulphide concentration in the wash water effluent.

Solution:

Crude oil of 30 API = 10,000 BPD = 128,000 lb/h

Wash water used = 0.05 (10,000 bbl/day) (42 gal/bbl) (35.3145 ft^3/264.17 gal) (62 lb/ft^3) (day/24 h) = 7252 lb/h

$$\text{Total sulphides entering the process} = [100 \times 10^{-6}(128{,}000) + 100 \times 10^{-6}(7252)] = 13.525 \text{ lb/h}$$

Let x be the sulphide content in effluent water and the water oil partition coefficient equal 4 then,

$$4 = \frac{\text{sulfide in water}}{\text{sulfide in oil}} = \frac{(x/7252)}{(13.525 - x)/128,000} \quad \text{gives x} = 2.5 \text{ lb/hr}$$

The sulphides concentration in the wash water effluent = (2.5/(7252)) (10^6) = 345 ppm

---

17.3.2.2. Treatment and Control

Petroleum refineries typically utilize primary and secondary wastewater treatments. Table 17.12 shows typical effluents after treatment.

Table 17.12 Typical water effluent composition (World Bank, 1996; USEPA, 1995)

	Primary treatment effluent composition (mg/l)	Secondary treatment effluent composition (mg/l)	USEPA standard emissions (kg/day)
Oil	40	0.05–9.8	99
Chemical oxygen demand (COD)	300	30–225	2371
Biological oxygen demand (BOD)	150	2–50	338
Total suspended solids (TSS)	10–20	2–8	270
Phenols	12	0.03–1.0	2.1
Sulphide	5	0.01–1.0	1.8
MTBE	0–3	<1	
PAH	0.1	0.005–0.05	
BTX	5	<0.001	
Metals	1	0.1–1.0	

Primary Treatment Primary treatment is the separation of hydrocarbons from wastewater. API separators gravity separation and settling chambers remove suspended hydrocarbons, oily sludge and solids by gravity separation, skimming and filtration. Some oil–water emulsions must be heated to assist in separating the oil and water. Acidic wastewater is neutralized using ammonia or soda ash. Alkaline wastewater is treated with sulphuric acid, carbon dioxide-rich flue gas or sulphur. Figure 17.3 shows a schematic diagram of API separator.

Secondary Treatment Oily water is segregated into two streams: low (160–250 ppm) and high oil content (>250 ppm). The low stream is made up primarily of stripped sour water and requires no further treatment. A high oil stream is treated using API oil/water separator followed by dissolved air floatation (DAF) separator.

Activated carbon is used to remove heavy hydrocarbons from light organic gas streams in the refinery. Furthermore, by using a catalyst combined with hydrogen peroxide, it is possible to reduce the chemical oxygen demand (COD) and the biological oxygen demand (BOD). Besides, phenols are transformed into less biodegradable compounds which can be removed by subsequent coagulation and precipitation. Removal of soluble and insoluble organic and inorganic contaminants from refinery wastewater streams is performed by employing ultra-filtration and membrane separation.

The high oil content water goes into a second stage, which utilizes physical or chemical methods to separate emulsified oils from the wastewater. Physical methods include settling ponds with a long retention time. In DAF, air is bubbled through the wastewater, and both oil and suspended solids are skimmed off the top. Chemicals, such as ferric hydroxide or aluminium hydroxide, can be used to coagulate impurities into sludge, which can be more easily skimmed off the top. Table 17.13 shows the influent and effluent data for API and DAF processes.

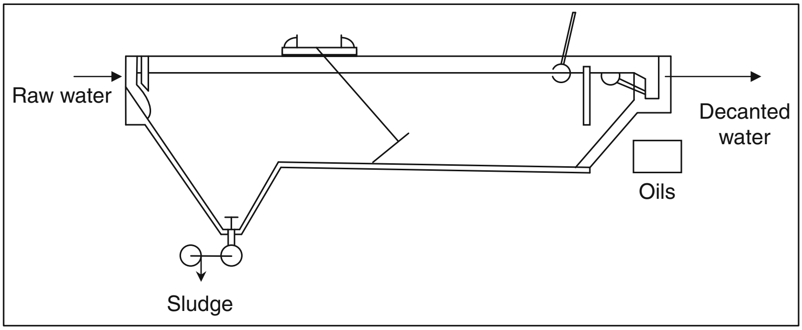

Figure 17.3 Schematic diagram of API separator

Table 17.13 Typical operating data for secondary treatment (Parakash, 2003)

	API		DAF	
	Influent	**Effluent**	**Influent**	**Effluent**
TSS (ppm)	500	500	500	20
Total oil (ppm)	410	180	21,640	13
COD (ppm)	1000	500	640	300
BOD (ppm)	620	310	320	150
Phenols (ppm)	3	3	3	1.8
Sulphides (ppm)	10	10	10	8

Tertiary Treatment Operations These treatments include chlorination, ozonation, ion exchange and activated carbon adsorption. Compressed oxygen is diffused into wastewater streams to oxidize certain chemicals or to satisfy regulatory oxygen-content requirements. Wastewater that is to be recycled may require cooling to remove heat and/or oxidation by spraying or air stripping to remove any remaining phenols, nitrates and ammonia.

Figure 17.4 summarizes the wastewater schemes through primary, secondary and tertiary treatment.

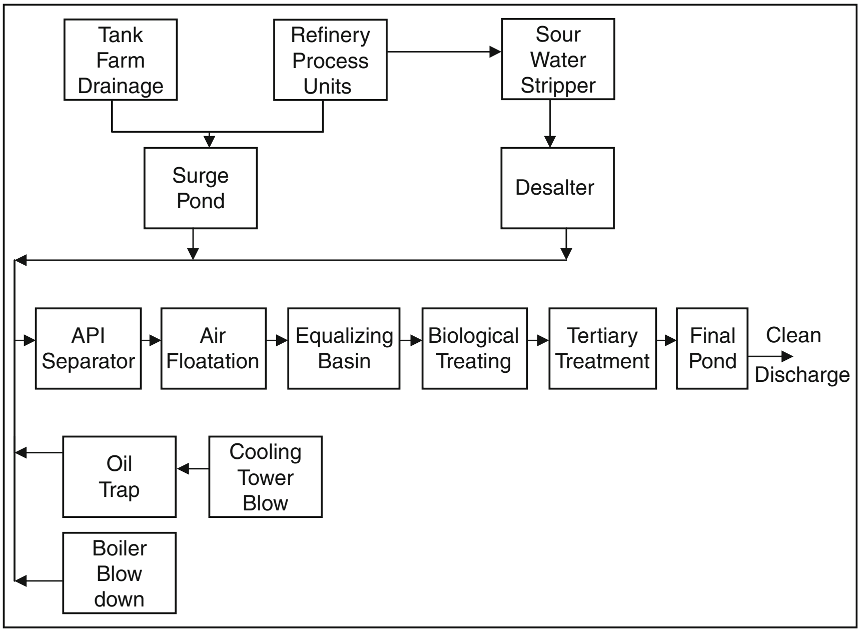

Figure 17.4 Typical refinery wastewater system

Example E17.14

A sour water at 37 °C and 275 kPa is heated to 93.3 °C and then stripped in a column to separate H_2S and NH_3 from water. Sour water contains 0.7 mol% H_2S and 0.5 mol% NH_3, and the balance is water. The feed flow is 331.22 m^3/h. The heat exchanger uses stripped water from the column in the shell side to heat the sour water feed which enters the heat exchanger tube side. The preliminary specifications for the column are a reflux ratio of 10 and the ammonia at the reboiler is 10^{-5} mol fraction. Use UNISIM simulator to do the material balance for all streams (UNISIM, 2007).

Solution:

Figure E17.14 shows a simplified flow chart for the process. Table E17.14 summarizes the material balance and operating conditions.

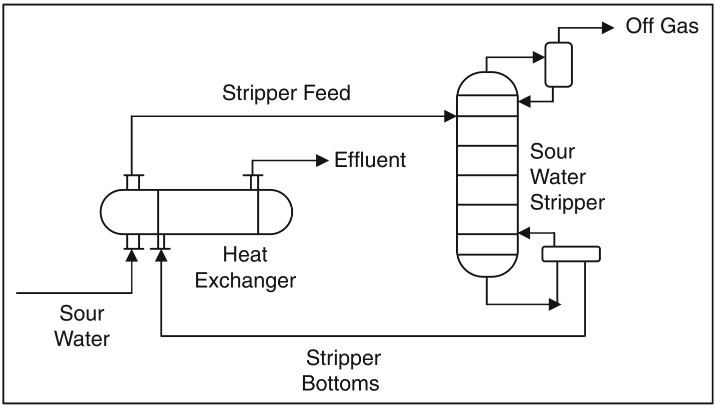

Figure E17.14 Sour-water treatment

Table E17.14 Summary of results

	Sour water	Effluent	Stripped feed	Off gas	Stripped bottoms
H_2S mol%	0.7	0	0.3712	16.95	0
NH_3 mol%	0.5	0.001	0.5305	24.18	0.001
H_2O mol%	98.8	99.999	99.0983	58.87	99.999
Temperature (°C)	37.8	67.8	93.3	105.4	124
Pressure (kPa)	275.8	156.5	206.8	197.9	225.5
Flow (m^3/h)	331.22	321.4	331.22	9.82	321.4

17.3.3. Solid Waste

Refinery solid wastes are typically in the form of sludge, spent process catalysts, filter clay and incinerator ash. Sludge is generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters. It is also generated from cooling waters segregated for treatment from other process or oily cooling waters. Storage tank bottoms are mixtures of iron rust from corrosion, sand, water, emulsified oil and wax, which accumulate at the bottom of tanks. Tank bottom sludge is removed during the periodic cleaning of tanks for inspection.

Both hazardous and non-hazardous solid wastes are generated, treated and disposed. Treatment of these wastes includes incineration, land treating off-site, land filling on-site, land filling off-site and other treatment methods. Figure 17.5 shows the refinery sludge paths. Table 17.14 shows typical sludge and solid waste in refinery units.

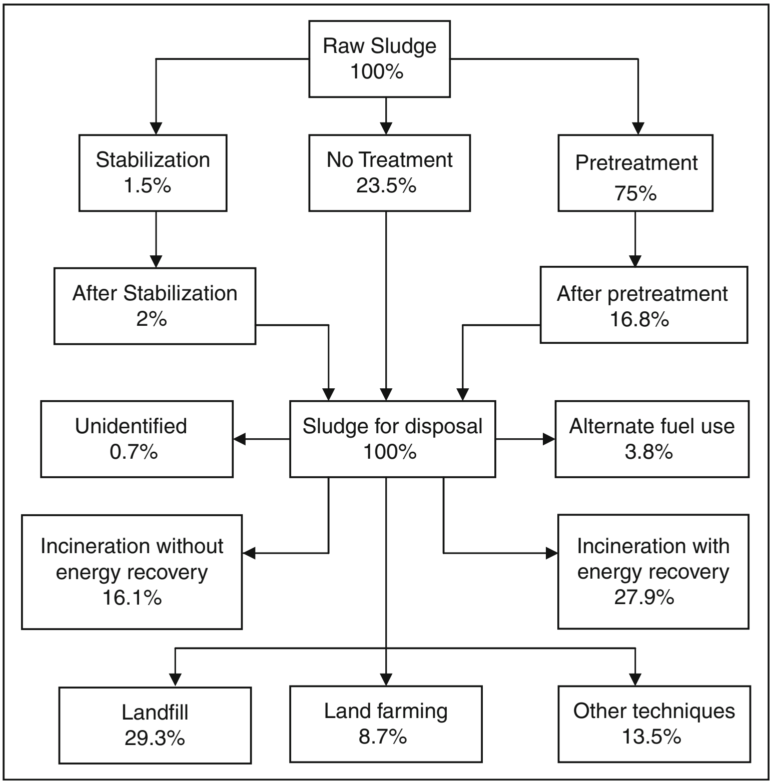

Figure 17.5 Refinery sludge routes (CONCAWE, 1999)

Table 17.14 Solid waste percentages in refinery processes (CONCAWE, 1999)

Type of waste	wt%
Sludge	
API/DAF	41.8
Wastewater bio-treatment	30.2
Boiling fresh water	13.0
Tank bottom	7.2
Miscellaneous	6.7
Desalter	0.8
Acid alkylation	0.3
Other solid waste	
Contaminated soil	26.3
FCC catalyst	19.4
Other wastes	15.5
Miscellaneous oily waste	8.9
Incinerator ash	6.0
Spent caustic	6.0
Other catalysts	4.7
Desulphurization catalyst	3.2
Spent clay	2.7
Tank scales	2.4
Sorbents	1.9
Flue gas desulphurization	1.3
Spent chemicals	1.2
Reformer catalyst	0.4
Acid tar	0.2

The toxicity and amount of de-oiled and de-watered sludge is reduced through thermal treatment. Thermal sludge treatment units use heat to vaporize the water and volatile components in the feed and leave behind a dry solid residue. The vapours are condensed for separation into hydrocarbon and water components. Non-condensable vapours are either flared or sent to the refinery amine unit for treatment and then used as refinery fuel gas.

QUESTIONS AND PROBLEMS

17.1. Fuel containing 3 wt% sulphur is burned in a furnace to heat crude before introducing it to the crude distillation unit. Calculate the amount of SO_2 emitted form the furnace stack per 1000 kg fuel burned. Calculate the amount of air required for combustion.

17.2. 10,000 BPD crude oil is fed to the crude distillation unit. Fuel containing 3 wt% sulphur is burned in a furnace to heat that crude before introducing it to the CDU. Calculate the amount of SO_2 emitted from the furnace stack using the emission factors.

17.3. 70,000 BPD is fed to FCC unit. The regenerator of spent catalyst flue gas has some amount of escape catalyst. Calculate that amount of particulate and all flue gas emissions such as CO, SO_2 and others.

17.4. 100 kg/h fuel contains the mole % of gases shown in the low-pressure flare gas in Table 17.6. It is burned in a flare. Calculate the CO_2 emission rate based on a material balance and on emission factors listed in Table 17.7 and compare.

17.5. It is ascertained that 200 valves are with 90 wt% (non-methane hydrocarbons) and 10 wt% methane in a pipeline of a plant. Valves operate for 5000 h/year. Calculate the fugitive emission rate.

17.6. 1000 kg/h fuel is burned in a furnace with 95% efficiency. The fuel contains 2.5 wt% sulphur. The furnace stack is 50 m high. If there is a residential area about 1 km downwind from the stack, calculate the amount of SO_2 that reaches the residential area at a day of 3 m/s wind.

17.7. Solve example E17.8 by hand calculation and compare with the UNISIM results.

17.8. ESP with a plates spacing of 25 cm is attached to 50 kV of electric power. The dirty gas flows at 2 m/s and carries particulates with 0.4 μm at 100 °C. Calculate the plate length to capture 98% of the particulates.

17.9. Calculate the phenol and lead flow rates from 1000 m^3/h typical refinery wastewater effluent. A typical DOC in this effluent is 0.2 kg/m^3.

17.10. The effluent wash water in a desalter will contain salts removed from the crude oil. Calculate the effluent salt content of the effluent considering the following operating conditions:
Crude oil = 50,000 BPD
Inlet salt content = 100 lb/1000 bbl
Outlet salt content in crude = 5 lb/1000 bbl
Outlet water content in crude = 0.2 vol%
Water in crude oil = 0.5 vol%
Wash water = 5 vol% on crude

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CHAPTER EIGHTEEN

OVERALL REFINERY CASE STUDY

18.1. INTRODUCTION

In this chapter, a typical case study is taken to consider most of the CDU product streams into more process downstreams such as reformer, fluid catalytic cracking, delayed coker and alkylation. Hydroprocessing is mainly used to remove sulphur to meet the market product specifications.

The capacity of a crude distillation unit (CDU) is 100,000 barrels per stream day (BPSD). The unit produces raw products, which have to be processed in the downstream unit to produce products of a certain specification. This involves the removal of undesirable components like sulphur, nitrogen and metal compounds, and limiting the aromatic content. Typical products from the CDU are:

- Gases
- Light straight run naphtha (also called light gasoline, light naphtha)
- Heavy gasoline (also called military jet fuel)
- Kerosene (also called light distillate or jet fuel)
- Middle distillates called diesel or light gas oil (LGO)
- Heavy distillates called atmospheric gas oil (AGO) or heavy gas oil (HGO)
- Crude column bottoms called atmospheric residue or topped crude

18.2. THE CASE STUDY

In this case study 100,000 BPD crude oil, with an API of 26, is introduced to a distillation column. The produced naphtha cut (190–380 °F) is hydrotreated to remove sulphur and then fed to a reformer to produce a C_5^+ cut of 94 RON. The produced hydrogen in the reformer is used in the hydrotreater units.

The gas oil cut (580–650 °F) is hydrotreated to remove sulphur and then fed to the FCC unit of 75% conversion to produce gasoline, gases, gas oil and coke. Fluidized catalytic cracking (FCC) is the heart of the refinery and is where heavy, low value petroleum streams are upgraded into lighter products

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mainly gasoline and C_3/C_4 olefins, which can be used in the alkylation unit to produce ultra-clean gasoline (C_7–C_8 alkylates).

The residue cut (1050+ °F) produced from the CDU is fed to a delayed coker unit to produce gasoline, gases, gas oil and coke. Coking is the process of carbon rejection from the heavy residues producing lighter components lower in sulphur, since most of the sulphur is retained in the coke.

Gas streams are split to separate isobutane (iC_4) and butene ($C_4^=$) from other gases. iC_4 and $C_4^=$ are fed to an alkylation unit with an addition of make-up iC_4 to produce alkylate. Alkylation is the process of producing gasoline range material (alkylates) from olefin butylenes ($C_4^=$) and isobutane. Butylene is the most used olefin because of the high quality of the alkylate produced.

The typical flow chart of the full process is shown in Figure 18.1. The crude TBP-vol% analysis is shown in Table 18.1.

The crude TBP and API as a function of accumulated liquid volume % (LV%) are calculated as follows:

$$\mathrm{TBP}(^\circ\mathrm{R}) = \left\{\left(2.2\ln\left(\frac{100}{100-\mathrm{LV\%}}\right)\right)^{2.7}+1\right\}490 \tag{18.1}$$

$$\mathrm{API} = -0.0004(\mathrm{LV\%})^3 + 0.05(\mathrm{LV\%})^2 - 2.4(\mathrm{LV\%}) + 80 \tag{18.2}$$

Material balance and property calculations are performed for each product streams using the methods outlined in Chapter 3 to 8 and 10. The details are as follows:

Considering the crude distillation unit:

190–380 °F cut

Substituting in equation (18.1) to get LV% at IBP and EBP

$$\text{Cut vol\%} = 33.05 - 25.92 = 7.134\%$$
$$\text{Cut mid volume} = 29.485$$

Substituting the cut mid volume in equation (18.2) to get API = 42.45

$$\text{Cut volume} = 0.07134(100{,}000) = 7134\ \text{BPD}$$
$$\text{Cut amount} = 7134(11.87) = 84{,}681\ \text{lb/h}$$

Calculation of sulphur content:

$$M = 42.965[\exp(2.097\times10^{-4}T_\mathrm{b} - 7.78712\ \mathrm{SG} + 2.08476\times 10^{-3}T_\mathrm{b}\mathrm{SG})]\,T_b^{1.26007}\mathrm{SG}^{4.98308}$$

$$T_\mathrm{b} = ((190+380)/2-32)/1.8+273 = 413\ \mathrm{K}$$

$$\mathrm{SG} = 0.812$$

$$M = 109\ \mathrm{lb/lb\ mol}$$

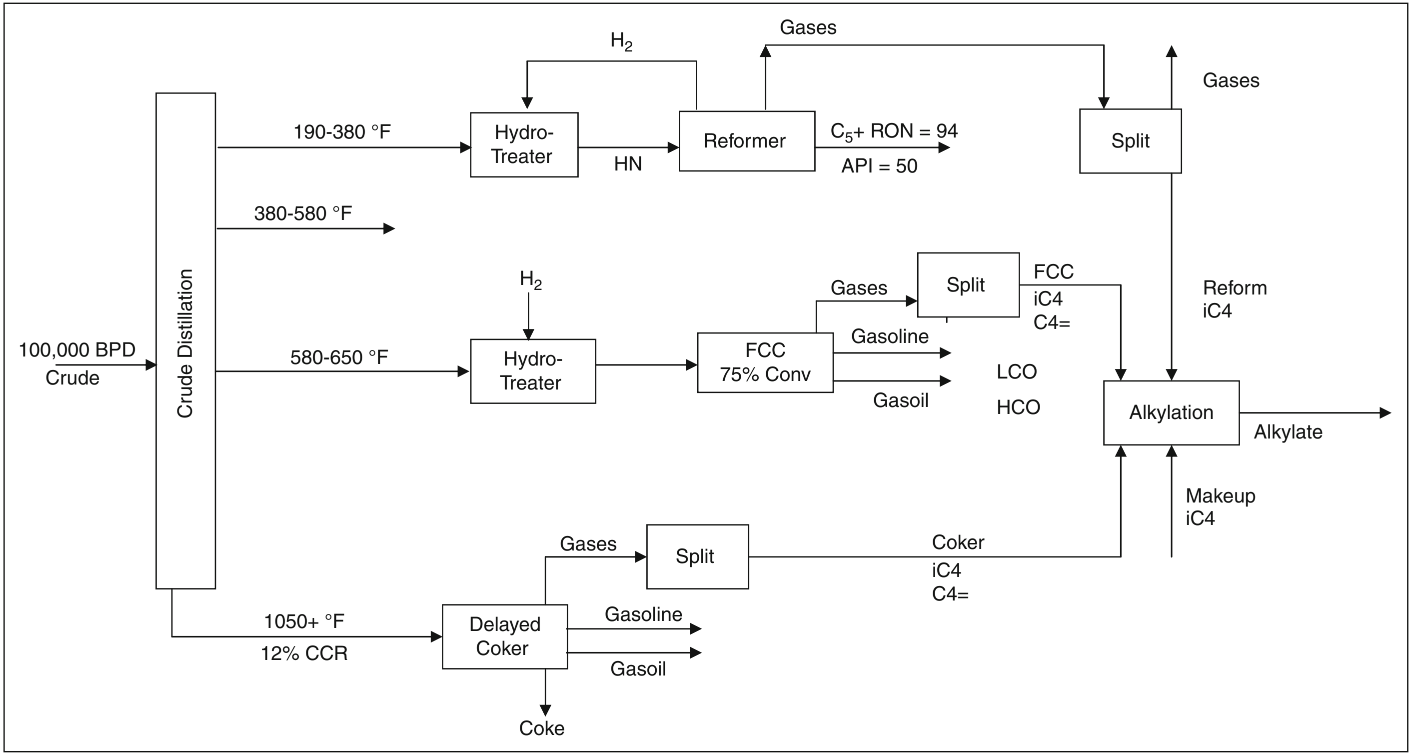

Figure 18.1 Process flow chart

Table 18.1 TBP-vol% analysis

Fraction No.	Cut temp. (°F)	vol%	SG
0	86	0.0	
1	122	0.5	0.6700
2	167	1.2	0.6750
3	212	1.6	0.7220
4	257	2.7	0.7480
5	302	3.1	0.7650
6	347	3.9	0.7780
7	392	4.7	0.7890
8	437	5.7	0.8010
9	482	8.0	0.8140
10	527	10.7	0.8250
11	584	5.0	0.8450
12	636	10.0	0.8540
13	689	7.8	0.8630
14	742	7.0	0.8640
15	794	6.5	0.8890
Residuum	–	20.8	0.9310

$$I = 2.266 \times 10^{-2}\exp(3.905 \times 10^{-4} T_\mathrm{b} + 2.468\mathrm{SG} - 5.704 \times 10^{-4} T_\mathrm{b}\mathrm{SG})\, T_b^{0.0572}\mathrm{SG}^{-0.72} = 0.2632$$

$$n = \left(\frac{1+2I}{1-I}\right)^{1/2} = 1.439$$

$$R_\mathrm{i} = n - \frac{d}{2} = 1.033$$

$$m = M(n - 1.475) = -3.924$$

since $M < 200$

$$\text{sulphur wt\%} = 177.448 - 170.946\, R_\mathrm{i} + 0.2258\, m + 4.054\,\mathrm{SG} = 1.36\ \text{wt\%}$$

$$\text{sulphur amount} = 0.0136(84{,}681) = 1152\ \text{lb/h}$$

580–650 °F cut

Substituting in equation (18.1) to get LV% at IBP and EBP

$$\text{Cut vol\%} = 39.1 - 37.77 = 1.33\%$$

$$\text{Cut mid volume} = 38.435$$

Substituting the cut mid volume in equation (18.2) to get API = 30.0

$$\text{Cut volume} = 0.0133(100{,}000) = 1330\ \text{BPD}$$

$$\text{Cut amount} = 1330(12.77) = 16{,}984\ \text{lb/h}$$

Calculation of sulphur content:

$$M = 42.965[\exp(2.097 \times 10^{-4} T_b - 7.78712\,\mathrm{SG} + 2.08476 \times 10^{-3} T_b \mathrm{SG})]$$
$$T_b^{1.26007} \mathrm{SG}^{4.98308}$$

$$T_b = ((580 + 650)/2 - 32)/1.8 + 273 = 597\ \mathrm{K}$$

$$\mathrm{SG} = 0.83$$

$$M = 265\mathrm{lb/lb\ mol}$$

$$I = 2.266 \times 10^{-2} \exp(3.905 \times 10^{-4} T_b + 2.468\mathrm{SG} - 5.704 \times 10^{-4} T_b \mathrm{SG})$$
$$T_b^{0.0572} \mathrm{SG}^{-0.72} = 0.2757$$

$$n = \left(\frac{1 + 2I}{1 - I}\right)^{1/2} = 1.4635$$

$$R_i = n - \frac{d}{2} = 1.0485$$

$$m = M(n - 1.475) = -3.0475$$

since $M > 200$

$$\text{sulphur wt\%} = -58.02 + 38.463\ R_i - 0.023\ m + 22.4\ \mathrm{SG} = 3.3\ \text{wt\%}$$

$$\text{sulphur amount} = 0.033(16{,}984) = 560.5\ \mathrm{lb/h}$$

Considering the naphtha hydrotreater unit:

$$K = \frac{(T_b)^{1/3}}{\mathrm{SG}} = \frac{\left(\frac{190 + 380}{2} + 460\right)^{1/3}}{0.812} = 11.164$$

$$\mathrm{SCFB\ H_2} = 191 S_f - 30.7 = 191(1.36) - 30.7 = 229.06\ \mathrm{SCFB}$$

Since the feed is 7134 BPD:
Required hydrogen is 359.3 lb/h

$$\Delta\mathrm{API_p} = 0.01(\mathrm{SCFB\ H_2}) + 0.036(\mathrm{API_f}) - 2.69 = 1.1288$$

$$\mathrm{API_p} = 42.45 + 1.1288 = 43.58$$

$$\text{Parrafin vol\%} = 12.8 K_f^2 - 229.5 K_f + 1330 = 28.27$$

$$\text{Naphthenes vol\%} = -78.5 K_f^2 + 1776.6 K_f - 9993.7 = 56.42$$

$$\text{Aromatics vol\%} = 38.4 K_f^2 - 894.3 K_f + 5219.4 = 21.414$$

$$\text{Normalizing}: P\ \text{vol\%} = 26.64, \quad N\ \text{vol\%} = 53.8, \quad A\ \text{vol\%} = 20.18$$

Considering the reformer unit:

$$\text{Reformer feed} = 7134\ \text{BPD}$$

$$\text{API} = 43.58$$

$$\text{Amount of feed to reformer} = 7134(11.79) = 84,110\ \text{lb/h}$$

$$\begin{aligned} C_5^+\ \text{vol\%} &= 142.7914 - 0.77033 \times \text{RON}_\text{R} + 0.219122 \times (N + 2A)_F \\ &= 142.7914 - 0.77033 \times 97 + 0.219122 \times (53.8 + 2(20.18)) \\ &= 90.876 \end{aligned}$$

$$H_2\ \text{wt\%} = -12.1641 + 0.06134 \times C_5^+\ \text{vol\%} + 0.099482 \times \text{RON}_\text{R} = 2.76$$

$$C_1\ \text{wt\%} = 11.509 - 0.125 \times C_5^+\ \text{vol\%} = 0.1495$$

$$C_2\ \text{wt\%} = 16.496 - 0.1758 \times C_5^+\ \text{vol\%} = 0.52$$

$$C_3\ \text{wt\%} = 24.209 - 0.2565 \times C_5^+\ \text{vol\%} = 0.9$$

$$C_4\ \text{wt\%} = 27.024 - 0.2837 \times C_5^+\ \text{vol\%} = 1.243$$

$$nC_4\ \text{wt\%} = 0.585 \times \text{total}\ C_4\ \text{wt\%} = 0.727$$

$$iC_4\ \text{wt\%} = 0.415 \times \text{total}\ C_4\ \text{wt\%} = 0.516$$

Hydrogen produced = 0.0276 (84,110) = 2321 lb/h > 359.3 lb/h, this means that the hydrogen produced in the reformer is more than the required hydrogen in the hydrotreating reformer feed.

Considering the gas oil hydrotreater unit:

Middle distillate HT

$$\text{SCFB}\ H_2 = 110.8\ S_\text{f} + 10.2(\text{HDS\%}) - 659$$

Assume 100% severity of the hydrotreater

$$\text{SCFB}\ H_2 = 110.8(3.3) + 10.2(100) - 659 = 726.64\ \text{SCFB}$$

Since the feed is 1330 BPD:

Amount of H_2 required = 212.5 lb/h (This can be supplied from the reformer unit.)

$$\Delta\text{API}_\text{p} = 0.00297(\text{SCFB}\ H_2) - 0.11205(\text{API}_\text{f}) + 5.5419 = 4.3385$$

$$\text{API}_\text{p} = 30 + 4.3385 = 34.3385$$

$$\text{Feed to FCC} = 1330(12.45) = 16,559\ \text{lb/h}$$

Considering the FCC unit:

Conversion = 75%

$$\text{Coke wt\%} = 0.05356 \times \text{CONV} - 0.18598 \times \text{API} + 5.966975 = 3.5977$$

$$\text{LCO LV} = 0.0047 \times \text{CONV}^2 - 0.8564 \times \text{CONV} + 53.576 = 15.7835$$

$$\text{Gases wt\%} = 0.0552 \times \text{CONV} + 0.597 = 4.737$$

$$\text{Gasoline LV\%} = 0.7754 \times \text{CONV} - 0.7778 = 57.3772$$

$$iC_4\ \text{LV\%} = 0.0007 \times \text{CONV}^2 + 0.0047 \times \text{CONV} + 1.40524 = 5.7$$

$$nC_4\ \text{LV\%} = 0.0002 \times \text{CONV}^2 + 0.019 \times \text{CONV} + 0.0476 = 2.6$$

$$C_4^{=}\ \text{LV\%} = 0.0993 \times \text{CONV} - 0.1556 = 7.3$$

$$C_3\ \text{LV\%} = 0.0436 \times \text{CONV} - 0.8714 = 2.4$$

$$C_3^{=}\ \text{LV\%} = 0.0003 \times \text{CONV}^2 + 0.0633 \times \text{CONV} + 0.0143 = 6.45$$

$$\text{Gasoline API} = -0.19028 \times \text{CONV} + 0.02772 \times (\text{Gasoline LV\%}) + 64.08 = 51.4$$

$$\text{LCO API} = -0.34661 \times \text{CONV} + 1.725715 \times (\text{Feed API}) = 33.26$$

Products	BPD	(lb/h)/BPD	lb/h
Gases			784.4
iC_4	75.81	8.22	623.2
nC_4	34.58	8.51	294.3
$C_4^{=}$	97.1	8.76	850.5
C_3	31.9	7.42	237
$C_3^{=}$	85.8	7.61	653
Gasoline	763	11.29	8614.3
LCO	210	12.53	2631.2
HCO			1275.3
Coke			595.7

1050+ °F cut

Substituting in equation (18.1) to get LV% at IBP and EBP

$$\text{Cut vol\%} = 100 - 44.9 = 55.1\%$$

$$\text{Cut mid volume} = 72.45$$

Substituting the cut mid volume in equation (18.2) to get API = 16.45

$$\text{Cut volume} = 0.551(100,000) = 55,100\ \text{BPD}$$

$$\text{Cut amount} = 55,100(13.96) = 769,196\ \text{lb/h}$$

Considering the delayed coker unit:

$$\text{Gas}(C_4^-)\text{wt\%} = 7.8 + 0.144 \times (\text{wt\% CCR}) = 9.528$$

$$\text{Naphtha wt\%} = 11.29 + 0.343 \times (\text{wt\% CCR}) = 15.406$$

$$\text{Coke wt\%} = 1.6 \times (\text{wt\% CCR\%}) = 19.2$$

$$\text{Gas oil wt\%} = 100 - \text{wt\% Gas} - \text{wt\% Napthta} - \text{wt\% Coke} = 55.866$$

$$\text{Amount of gases produced} = 0.09528(769,196) = 73,289\text{lb/h}$$

Assume the average molecular weight for the gases is 22.12 lb/lb mol

$$\text{Gases} = 73,289/22.12 = 3313\ \text{lbmol/h}$$

$$C_4^= = 0.024(3313)(56) = 4453\ \text{lb/h}$$

$$iC_4 = 0.01(3313)(58) = 1922\ \text{lb/h}$$

$$nC_4 = 0.026(3313)(58) = 4996\ \text{lb/h}$$

Considering the alkylation unit:

$$\begin{aligned}\text{Amount of olefins} &= C_4^=\text{coker} + C_4^=\text{FCC}\\ &= 4453 + 850.5 = 53035\ \text{lb/h}\end{aligned}$$

$$\begin{aligned}\text{Amount of i}C_4 &= iC_4\ \text{coker} + iC_4\ \text{FCC} + iC_4\ \text{Reformer}\\ &= 1922 + 623.2 + 611.5 = 3156.71\ \text{b/h}\end{aligned}$$

$$\frac{\text{lb}iC_4}{\text{lb olefin}} = 1.1256$$

$$\text{Required } iC_4 = 1.1256(5303.5) = 5969.6\ \text{lb/h}$$

$$\text{Make-up } iC_4 = 5969.6 - 3156.7 = 2813\ \text{lb/h}$$

$$\text{BPD olefin} = 5303.5/8.76 = 605.42\ \text{BPD}$$

$$\text{BPD}i\ C_4 = 5969.6/8.22 = 726.23\ \text{BPD}$$

$$\text{Total feed to alkylation} = 605.42 + 726.23 = 1331.65\ \text{BPD}$$

$$\text{Volume of product} = 1331.65/1.2 = 1109.71\ \text{BPD}$$

$$\text{Alkylate amount produced} = 0.8236(1109.71) = 914\ \text{BPD}$$

Summary of the case:

$$\begin{aligned}\text{Total gasoline produced} &= \text{Coker gasoline} + \text{FCC gasoline} + \text{reformer gasoline}\\ &= 0.15406(769,196) + 8614.3 + 0.90876(7134)(11.37)\\ &= 118,502 + 8614.3 + 73,712.7\\ &= 200,829\ \text{lb/h}\end{aligned}$$

Appendices: Appendix A

A. CONVERSION FACTORS

A.1. Length

1 m = 100 cm = 1000 mm = 10^6 μm = 39.37 in = 3.2808 ft = 1.0936 yd
1 ft = 12 in = 1/3 yd = 0.3048 m = 30.48 cm

A.2. Mass

1 kg = 1000 g = 0.001 metric ton = 2.20462 lb_m = 35.27392 oz
1 lb_m = 16 oz = 5×10^{-4} ton = 453.593 g

A.3. Volume

1 m^3 = 1000 L = 10^6 cm^3 = 35.3145 ft^3 = 220.83 imperial gallon = 264.17 gal
1 ft^3 = 1728 in^3 = 7.4805 gal = 0.028317 m^3 = 28.317 L = 28.317 cm^3 = 7.48 gal
1 barrel = 42 gal (oil) = 5.62 ft^3
Ideal gas occupies 379.5 ft^3 at (P = 14.7 psia and T = 60 °F)
Ideal gas occupies 224 liter at (P = 14.7 psia and T = 32 °F)

A.4. Density

Density of water = 1000 kg/m^3 = 1 g/cm^3 = 62.4 lb/ft^3
Specific gravity (SG) = density of oil/density of water

$$\text{API} = \frac{141.5}{\text{SG}} - 131.5$$

A.4. Force

1 N = 1 kg m/s^2 = 10^5 dyne = 10^5 g cm/s^2 = 0.22481 lb_f
1 lb_f = 32.174 lb m ft/s^2 = 4.4482 N = 4.4482×10^5 dyne

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A.5. Pressure

$1\ \text{atm} = 1.01325 \times 10^5\ \text{N/m}^2\ (\text{Pa}) = 101.325\ \text{kPa} = 1.01325\ \text{bar}$
$= 1.01325 \times 10^5\ \text{dyne/cm}^2 = 760\ \text{mmHg at } 0\ ^\circ\text{C} = 10.33\ \text{m H}_2\text{O at } 4\ ^\circ\text{C}$
$= 14.7\ \text{lbf/in}^2\ (\text{psi}) = 33.9\ \text{ft H}_2\text{O at } 4\ ^\circ\text{C} = 29.921\ \text{in Hg at } 0\ ^\circ\text{C}$

A.6. Energy

$1\ \text{J} = 1\ \text{N m} = 10^7\ \text{ergs} = 10^7\ \text{dyne cm} = 2.778 \times 10^{-7}\ \text{kW h}$
$= 0.23901\ \text{cal} = 0.7376\ \text{ft lb}_\text{f} = 9.486 \times 10^{-4}\ \text{Btu}$

A.7. Power

$1\ \text{W} = 1\ \text{J/s} = 0.23901\ \text{cal/s} = 0.7376\ \text{ft lb}_\text{f}/\text{s}$
$= 9.486 \times 10^{-4}\ \text{Btu/s} = 1.341 \times 10^{-3}\ \text{hp}$

A.8. Standard Acceleration of Gravity

$g = 9.80665\ \text{m/s}^2 = 980.665\ \text{cm/s}^2 = 32.174\ \text{ft/s}^2$

A.9. Dynamic Viscosity

$1\ \text{cp} = 10^{-2}\ \text{g/cm s (poise)} = 2.4191\ \text{lb}_\text{m}/\text{ft h} = 6.7197 \times 10^{-4}\ \text{lb}_\text{m}/\text{ft s}$
$= 10^{-3}\ \text{Pa s} = 10^{-3}\ \text{kg/m s} = 10^{-3}\ \text{N s/m}^2 = 2.0886 \times 10^{-5}\ \text{lb}_\text{f}\ \text{s/ft}^2$
$1\ \text{Pa s} = 1\ \text{N s/m}^2 = 1\ \text{kg/m s} = 1000\ \text{cp} = 0.67197\ \text{lb}_\text{m}/\text{ft s}$

A.10. Kinematic Viscosity

$1\ \text{cSt} = 0.01\ \text{stoke} = 0.01\ \text{cm}^2/\text{s} = 1.07 \times 10^{-5}\ \text{ft}^2/\text{s}$

A.11. Heat Capacity

$1\ \text{Btu/lb}_\text{m}\ ^\circ\text{F} = 4.1868\ \text{kJ/kg K} = 1\ \text{cal/g}\ ^\circ\text{C} = 2326\ \text{J/kg}$
$1\ \text{kcal/gmol} = 4.1840 \times 10^3\ \text{kJ/kg mol}$

A.12. Temperature

$^\circ\text{C} = (^\circ\text{F} - 32)/1.8$
$^\circ\text{F} = 32 + 1.8(^\circ\text{C})$
$^\circ\text{R} = ^\circ\text{F} + 459.67$
$^\circ\text{K} = ^\circ\text{C} + 273.15$
$1.0\ \text{K} = 1.0\ ^\circ\text{C} = 1.8\ ^\circ\text{F} = 1.8\ ^\circ\text{R}$

A.13. Gas Law Constant

1.9872 g cal/gmol K = 1.9872 Btu/lb mol °R = 82.057 cm^3 atm/gmol K
8324.34 J/kmol K = 82.057 × 10^{-3} m^3 atm/kgmol K
10.731 ft^3 $\mathrm{lb_f/in}^2$ lb mol °R = 0.7302 ft^3 atm/lb mol °R
1545 ft $\mathrm{lb_f}$/lb mol °R = 8314.34 m^3 Pa/kg mol K

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APPENDIX B

B. DEFINITION OF TERMS

Absorption	The disappearance of one substance into another so that the absorbed substance loses its identifying characteristics, while the absorbing substance retains most of its original physical aspects. Used in refining to selectively remove specific components from process streams.
Acid treatment	A process in which unfinished petroleum products, such as gasoline, kerosene and lubricating oil stocks, are treated with sulphuric acid to improve color, odour and other properties.
Adsorption	Adhesion of the molecules of gases or liquids to the surface of solid materials.
Aliphatic hydrocarbon	Hydrocarbons characterized by open-chain structures: ethane, butane, butene, acetylene, and so on.
Alkylation	A process using sulphuric or hydrofluoric acid as a catalyst to combine olefins (usually butylene) and isobutane to produce a high-octane product known as alkylate.
Aniline point	The minimum temperature for complete miscibility of equal volumes of aniline and a test sample. This test is an indication of paraffinicity and the ignition quality of diesel.
API gravity	An arbitrary scale expressing the density of petroleum products.
Aromatics	Hydrocarbon compound that contains atleast one benzene ring.
Asphaltenes	The asphalt compounds soluble in carbon disulphide but insoluble in paraffin naphthas.
ASTM distillation	A standardized laboratory batch distillation for naphthas and middle distillate at atmospheric pressure.
Atmospheric tower	A distillation unit operated at atmospheric pressure.
Benzene	An unsaturated, six-carbon ring, basic aromatic compound.
Blending	The process of mixing two or more petroleum products with different properties to produce a finished product with desired characteristics.
Blowdown	The removal of hydrocarbons from a process unit, vessel or line on a scheduled or emergency basis by the use of pressure through special piping and drums provided for this purpose.

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Boiling range	The range of temperature (usually at atmospheric pressure) at which the boiling (or distillation) of a hydrocarbon liquid commences, proceeds and finishes.
Bottoms	Tower bottoms are residues remaining in a distillation unit after the highest boiling point material to be distilled has been removed. Tank bottoms are the heavy materials that accumulate in the bottom of storage tanks, usually comprised of oil, water and foreign matter.
Catalyst	A material that aids or promotes a chemical reaction between other substances but does not react itself. Catalysts increase reaction speeds and can provide control by increasing desirable reactions and decreasing undesirable reactions.
Catalytic cracking	The process of breaking up heavier hydrocarbon molecules into lighter hydrocarbon fractions by use of heat and catalysts.
Caustic wash	A process in which distillate is treated with sodium hydroxide to remove acidic contaminants that contribute to poor odour and stability.
Cetane number	The percentage of pure cetane in a blend of cetane and alpha methyl naphthalene which matches the ignition quality of a diesel fuel sample.
Coke	A high carbon-content residue remaining from the destructive distillation of petroleum residue.
Coking	A process for thermally converting and upgrading heavy residual into lighter products and by-product petroleum coke. Coking is also the removal of all lighter distillable hydrocarbons that leave a residue of carbon in the bottom of units or as build-up or deposits on equipment and catalysts.
Condensate	The liquid hydrocarbon resulting from cooling vapours.
Conradson carbon	A test used to determine the amount of carbon residue left after the evaporation and pyrolysis of an oil under specified conditions.
Cracking	The breaking up of heavy molecular weight hydrocarbons into lighter hydrocarbon molecules by the application of heat and pressure with or without the use of catalysts.
Crude assay	A procedure for determining the general distillation and quality characteristics of crude oil.
Crude oil	A naturally occurring mixture of hydrocarbons that usually includes small quantities of sulphur, nitrogen and oxygen derivatives of hydrocarbons as well as trace metals.
Cycle gas oil	Cracked gas oil returned to a cracking unit.
Deasphalting	Process of removing asphaltic materials from reduced crude using liquid propane to dissolve non-asphaltic compounds.
Debutanizer	A fractionating column used to remove butane and lighter components from liquid streams.

Dehydrogenation	A reaction in which hydrogen atoms are eliminated from a molecule. Dehydrogenation is used to convert ethane, propane and butane into olefins (ethylene, propylene and butenes).
Desalting	Removal of mineral salts (most chlorides, e.g. magnesium chloride and sodium chloride) from crude oil.
Desulphurization	A chemical treatment to remove sulphur or sulphur compounds from hydrocarbons.
Dewaxing	The removal of wax from petroleum products (usually lubricating oils and distillate fuels) by solvent absorption, chilling and filtering.
Diethanolamine	A chemical ($C_4H_{11}O_2N$) used to remove H_2S from gas streams.
Distillate	The products of distillation formed by condensing vapours.
Dry gas	Natural gas with so little natural gas liquids, that it is nearly all methane with some ethane.
Feed stock	Stock from which material is taken to be fed into a processing unit.
Flash point	Lowest temperature at which a petroleum product will give off sufficient vapour so that the vapour–air mixture above the surface of the liquid will propagate a flame away from the source of ignition.
Flashing	The process in which a heated oil under pressure is suddenly vaporized in a tower by reducing pressure.
Flexicoking	Thermal process in which coke is gasified into fuel gas using steam and air.
Fouling	Accumulation of deposits in condensers, exchangers, and so on.
Fractionating tower	Process unit that separates various fractions of petroleum by simple distillation, with the column tapped at various levels to separate and remove fractions according to their boiling ranges.
Fuel gas	Refinery gas used for heating.
Gas oil	Middle distillate petroleum fraction with a boiling range of about 350–750 °F, usually includes diesel fuel, kerosene, heating oil and light fuel oil.
Gasoline	A blend of naphthas and other refinery products with sufficiently high octane and other desirable characteristics to be suitable for use as fuel in internal combustion engines.
Hydrocracking	A process used to convert heavier feedstock into lower boiling, higher value products. The process employs high pressure, high temperature, a catalyst and hydrogen.

Hydrodesulphurization	A catalytic process in which the principal purpose is to remove sulphur from petroleum fractions in the presence of hydrogen.
Hydrogenation	The chemical addition of hydrogen to a material in the presence of a catalyst.
Isomerization	A reaction that catalytically converts straight-chain hydrocarbon molecules into branched-chain molecules of substantially higher octane number. The reaction rearranges the carbon skeleton of a molecule without adding or removing anything from the original material.
Iso octane	A hydrocarbon molecule (2,2,4-trimethylpentane) with excellent antiknock characteristics on which the octane number of 100 is based.
Kerosene	A middle distillate product composed of material of 300–550 °F boiling range.
Knockout drum	A vessel wherein suspended liquid is separated from gas or vapour.
Lean oil	Absorbent oil fed to absorption towers in which gas is to be stripped. After absorbing the heavy ends from the gas, it becomes fat oil. When the heavy ends are subsequently stripped, the solvent again becomes lean oil.
LPG	Liquefied petroleum gas. Liquefied light end gases used for home heating and cooking. The gas contains 95% propane, and the balance is a split between ethane and butane.
MON	Motor octane number. A measure of resistance to self-ignition (knocking) of gasoline. It is 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.
Napthenes	Hydrocarbons (cycloalkanes) with the general formula C_nH_{2n}, in which the carbon atoms are arranged to form a ring.
Naphtha	A general term used for low boiling hydrocarbon fractions that are a major component of gasoline. Aliphatic naphtha refers to those naphthas containing less than 0.1% benzene and with carbon numbers from C_3 to C_{16}. Aromatic naphthas have carbon numbers from C_6 to C_{16} and contain significant quantities of aromatic hydrocarbons such as benzene (>0.1%), toluene and xylene.
Octane number	A number indicating the relative antiknock characteristics of gasoline.
Olefins	A family of unsaturated hydrocarbons with one carbon–carbon double bond and the general formula C_nH_{2n}.
Paraffins	A family of saturated aliphatic hydrocarbons (alkanes) with the general formula C_nH_{2n+2}.

Pour point	The lowest temperature at which a petroleum oil will flow or pour when it is chilled without disturbance at a controlled rate.
Quench oil	Oil injected into a product leaving a cracking or reforming heater to lower the temperature and stop the cracking process.
Raffinate	The product resulting from a solvent extraction process and consisting mainly of those components that are least soluble in the solvents. The product recovered from an extraction process is relatively free of aromatics, naphthenes and other constituents that adversely affect physical parameters.
Reactor	The vessel in which chemical reactions take place during a chemical conversion type of process.
Reboiler	An auxiliary unit of a fractionating tower designed to supply additional heat to the lower portion of the tower.
Recycle gas	High hydrogen-content gas returned to a unit for reprocessing.
Reduced crude	A residual product remaining after the removal by distillation of an appreciable quantity of the more volatile components of crude oil.
Reflux	The portion of the distillate returned to the fractionating column to assist in attaining better separation into desired fractions.
Reformate	An upgraded naphtha resulting from catalytic or thermal reforming.
Reforming	The thermal or catalytic conversion of petroleum naphtha into more volatile products of higher octane number. It represents the total effect of numerous simultaneous reactions such as cracking, polymerization, dehydrogenation and isomerization.
Regeneration	In a catalytic process, the reactivation of the catalyst sometimes done by burning off the coke deposits under carefully controlled conditions of temperature and oxygen content of the regeneration gas stream.
RON	Research octane number: same definition of MON except the engine operates here at 600 rpm.
RVP	Reid vapour pressure. The vapour pressure at 100 °F of a product determined in a volume of air four times the liquid volume.
Salt content	Salts in solution that are emulsified with the crude.
Scrubbing	Purification of a gas or liquid by washing it in a tower.
Severity	The degree of intensity of the operating conditions of a process unit.
Smoke point	A test measuring the burning quality of jet fuels, kerosene and illuminating oils. It is defined as the height of the flame.
Solvent extraction	The separation of materials of different chemical types and solubility by selective solvent action.

Sour gas	Natural gas that contains corrosive, sulphur-bearing compounds such as hydrogen sulphide and mercaptans.
Stabilization	A process for separating the gaseous and more volatile liquid hydrocarbons from crude petroleum or gasoline and leaving a stable (less-volatile) liquid so that it can be handled or stored with less change in composition.
Straight-run gasoline	Gasoline produced by the primary distillation of crude oil. It contains no cracked, polymerized, alkylated, reformed or visbroken stock.
Stripping	The removal (by steam-induced vaporization or flash evaporation) of the more volatile components from a cut or fraction.
Sulphuric acid treating	A refining process in which unfinished petroleum products such as gasoline, kerosene and lubricating oil stocks are treated with sulphuric acid to improve their colour, odour and other characteristics.
Sulphurization	Combining sulphur compounds with petroleum lubricants.
Sweetening	Processes that either remove obnoxious sulphur compounds (primarily hydrogen sulphide, mercaptans and thiophens) from petroleum fractions or streams, or convert them, as in the case of mercaptans, to odourless disulphides to improve odour, colour and oxidation stability.
Tail gas	The lightest hydrocarbon gas released from a refining process.
Thermal cracking	The breaking up of heavy oil molecules into lighter fractions by the use of high temperature without the aid of catalysts.
Turn around	A planned complete shutdown of an entire process or section of a refinery or of an entire refinery to perform major maintenance, overhaul and repair operations and to inspect, test and replace process materials and equipment.
Vacuum distillation	The distillation of petroleum under vacuum which reduces the boiling temperature sufficiently to prevent cracking or decomposition of the feedstock.
Visbreaking	A low-temperature cracking process used to reduce the viscosity or pour point of straight-run residuum.
Wet gas	A gas containing a relatively high proportion of hydrocarbons that are recoverable as liquids.

Appendix C

C. PROCESS SIMULATOR (UNISIM) MANUAL

Process simulation is the use of a computer program to quantitatively model the characteristic equations of a process flowsheet by utilizing:

- Mass and energy balance
- Equilibrium relationships
- Rate correlations (reaction and mass/heat transfer)

To obtain quickly an estimate of:

- Stream flow rates, compositions and properties
- Operating conditions
- Equipment sizes
- Steady state process simulation
- Rigorous petroleum simulation
- Petroleum/crude oil handling
- Data regression, data fit and optimization

Some time models are used in:

- Improving current processes
- Answering ''What If'' scenarios
- Determining optimal process conditions within given constraints
- Assisting in locating constraining parts of a process (de-bottlenecking)

UNISIM, licensed by Honeywell Process Solutions, provides the user with an intuitive and interactive approach towards process modelling, simulation and optimization. This software lets you create detailed high fidelity plant simulations for analyzing and optimizing your plant's operation. Through the completely interactive UNISIM interface, you have access to a fine level of equipment geometry, performance detail as well as the ability to completely customize your simulation using its OLE extensibility capability.

At any time, you can access help information by pressing F1. You can also look at the entire help structure by clicking the UNISIM Help Topics command in the Help menu.

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In the following sections, we will introduce flowsheeting concepts and some UNISIM simulator program features.

The simulation basis manager is the main view of the simulation environment. One of the important concepts is that UNISIM is based upon environments. The simulation basis environment allows you to input or access information within the simulation basis manager, while the other areas of UNISIM are put on hold, avoiding unnecessary flowsheet calculations. Once the simulation environment is entered, all changes that were made in the simulation basis environment will take effect at the same time. Conversely, all thermodynamic data are fixed and will not be changed as manipulations to the flowsheet take place in the simulation environment.

The minimum required inputs to run a simulation are:

- Set-up
- Components
- Properties
- Streams
- Blocks

Simulator operation procedure:

Step 1: Opening a new case is shown in Fig. C.1

Step 2: Entering components (Fig. C.2)

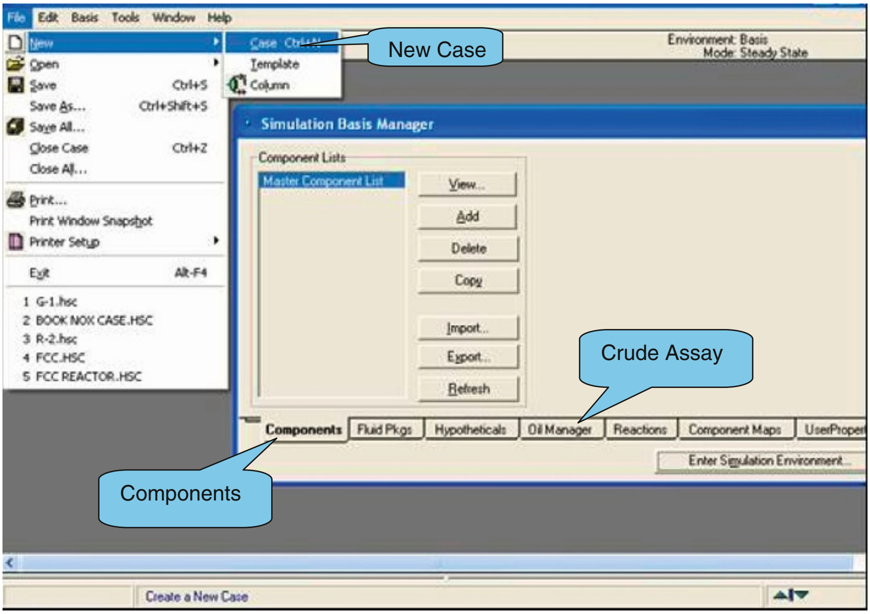
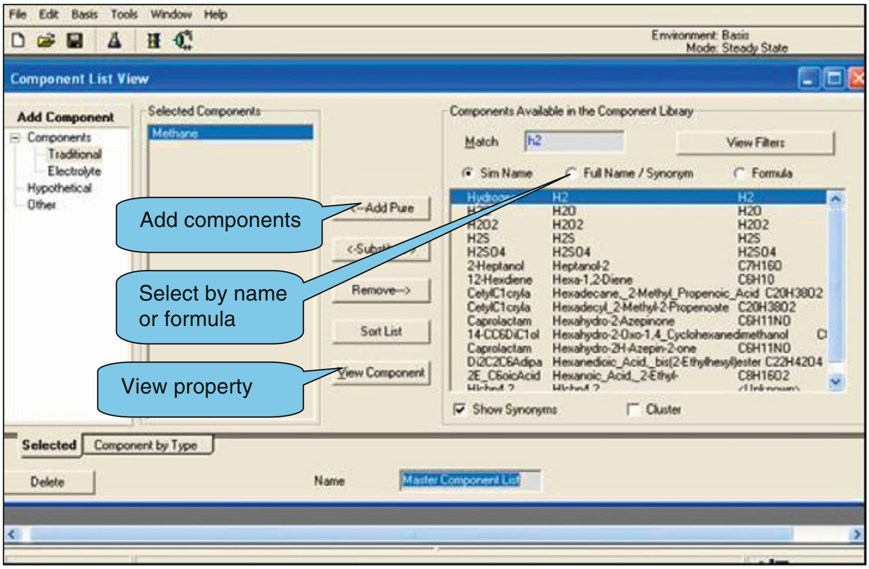


Figure C.1 Opening a new case



Add components

Select by name or formula

View property

Match: h2

● Sim Name ○ Full Name / Synonym ○ Formula

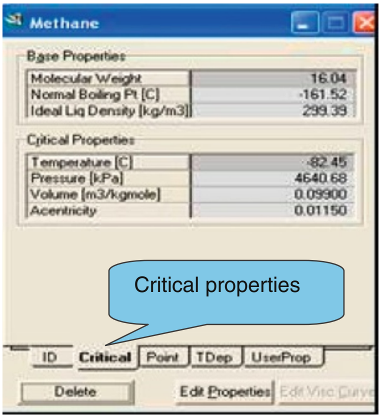
Hydrog	H2	H2
[illegible]	H2O	H2O
H2O2	H2O2	H2O2
H2S	H2S	H2S
H2SO4	H2SO4	H2SO4
2-Heptanol	Heptanol-2	C7H16O
12-Hexdiene	Hexa-1,2-Diene	C6H10
CetylC1cryla	Hexadecane,_2-Methyl_Propenoic_Acid	C20H38O2
CetylC1cryla	Hexadecyl_2-Methyl-2-Propenoate	C20H38O2
Caprolactam	Hexahydro-2-Azepinone	C6H11NO
14-CC6DiC1ol	Hexahydro-2-Oxo-1,4_Cyclohexanedimethanol	C
Caprolactam	Hexahydro-2H-Azepin-2-one	C6H11NO
Di2C2C6Adipa	Hexanedioic_Acid,_bis(2-Ethylhexyl)ester	C22H42O4
2E_C6oicAcid	Hexanoic_Acid,_2-Ethyl-	C8H16O2

☑ Show Synonyms ☐ Cluster

Name: Master Component List

Figure C.2 Adding component list

- The component ID is used to identify the component in simulation inputs and results
- Each component ID can be associated with a databank component as either:
  - Formula: Chemical formula of component
  - Name: Full name of component
  - View component property in the databank as shown in Fig. C.3.



Base Properties

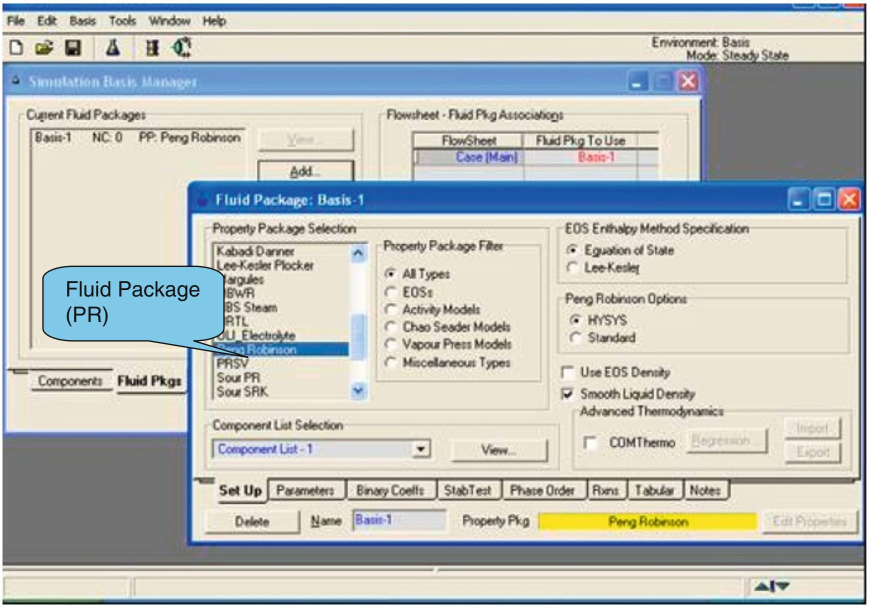
Molecular Weight	16.04
Normal Boiling Pt [C]	-161.52
Ideal Liq Density [kg/m3]	299.39

Critical Properties

Temperature [C]	-82.45
Pressure [kPa]	4640.68
Volume [m3/kgmole]	0.09900
Acentricity	0.01150

Critical properties

Figure C.3 Viewing component properties



Environment: Basis
Mode: Steady State

Basis-1 NC: 0 PP: Peng Robinson

Case (Main) Basis-1

● All Types

● Equation of State

● HYSYS

☑ Smooth Liquid Density

Component List - 1

Name Basis-1 Property Pkg Peng Robinson

Fluid Package (PR)

Figure C.4 Selection of fluid package for all property types

Step 3: Entering fluid package for thermo-physical property model (Fig. C.4)

The choice of the thermodynamic property model depends on:

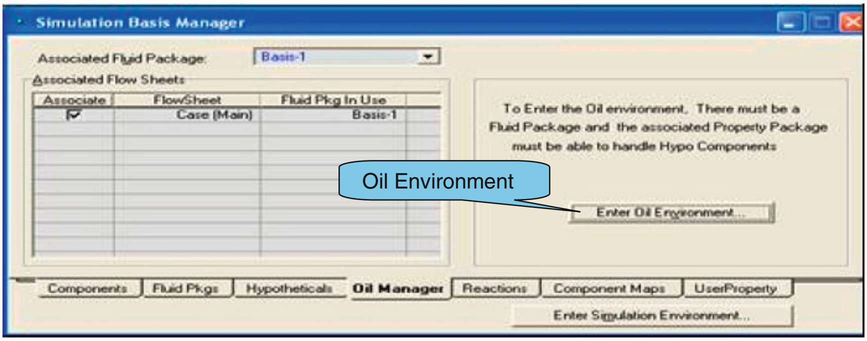
- Degree of non-ideal behaviour of components
- Range of operating conditions in the process

Samples of the fluid package are:

- Equation of State Methods: Peng–Robinson (PR) and Soave–Redlich–Kwong (SRK)
- Activity Coefficient Methods: Non-random two liquid (NRTL), unified functional activity coefficient (UNIFAC), universal quasi-unified activity coefficient (UNIQUAC)

Step 4: Petroleum handling assay characterization

- Entering oil environment (Fig. C.5)
- Edit crude assay data such as TBP/vol%, ASTM or others (Fig. C.6)
- Calculate the assay properties
- Plot the distribution of cuts (Fig. C.7)
- The more "pseudo" or hypothetical components cut properties are calculated



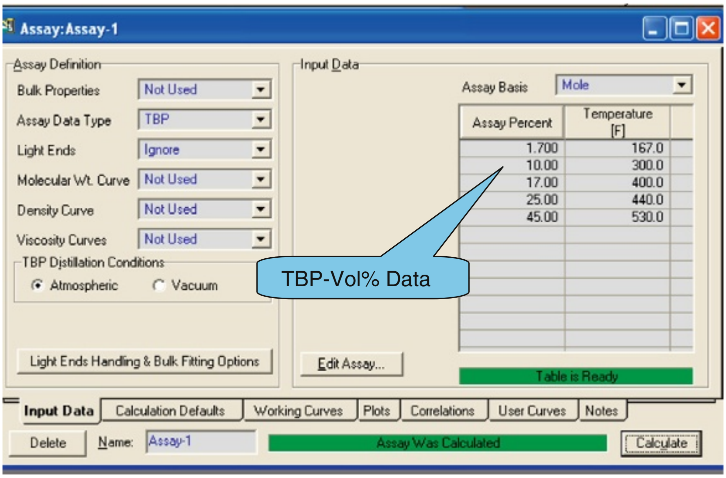
Associated Fluid Package: Basis-1

Associated Flow Sheets

Associate	FlowSheet	Fluid Pkg In Use
☑	Case (Main)	Basis-1

To Enter the Oil environment, There must be a Fluid Package and the associated Property Package must be able to handle Hypo Components

Figure C.5 Oil environment from oil manager



Assay Definition

Bulk Properties: Not Used
Assay Data Type: TBP
Light Ends: Ignore
Molecular Wt. Curve: Not Used
Density Curve: Not Used
Viscosity Curves: Not Used

TBP Distillation Conditions: ● Atmospheric ○ Vacuum

Input Data

Assay Basis: Mole

Assay Percent	Temperature [F]
1.700	167.0
10.00	300.0
17.00	400.0
25.00	440.0
45.00	530.0

Table is Ready

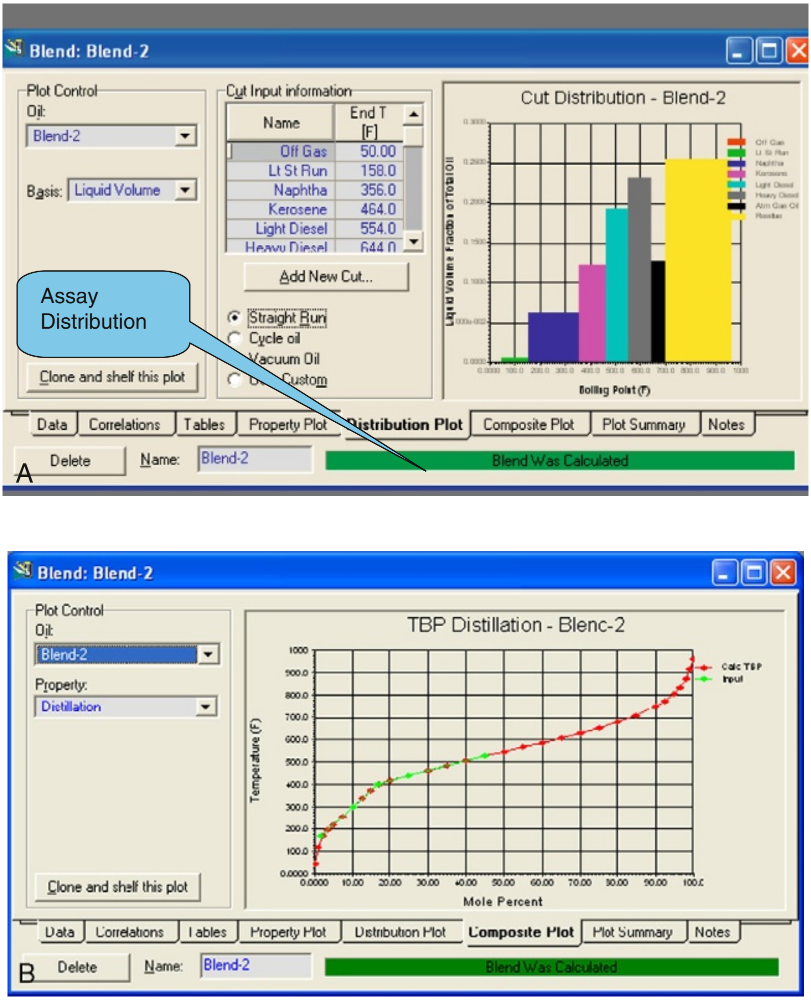
Name: Assay-1

Assay Was Calculated

Figure C.6 Entering crude assay data

Step 5: Simulation environment

- Figure C.8 shows the simulation environment containments
- Figure C.9 shows the required data for each input stream in the flowsheet such as name, temperature, pressure, composition (mole, mass or volume fractions) of components, quality and others, if any.



Oil: Blend-2

Basis: Liquid Volume

Name	End T [F]
Off Gas	50.00
Lt St Run	158.0
Naphtha	356.0
Kerosene	464.0
Light Diesel	554.0
Heavy Diesel	644.0

● Straight Run
○ Cycle oil
○ Vacuum Oil
○ Custom

Name: Blend-2

Blend Was Calculated

Oil: Blend-2

Property: Distillation

Name: Blend-2

Blend Was Calculated

Figure C.7 (A) Calculation of crude assay data and TBP distillation fit; (B) Calculation of crude assay data and TBP distillation fit

Some unit operation models require additional specification forms (e.g. reactors)

- Reactions stoichiometry entered as equilibrium or conversion reaction (Fig. C.10)
- Entering the design connection stream data (Fig. C.11)

Recycle stream:

- Flow (total and component), pressure and enthalpy are manipulated by iteration

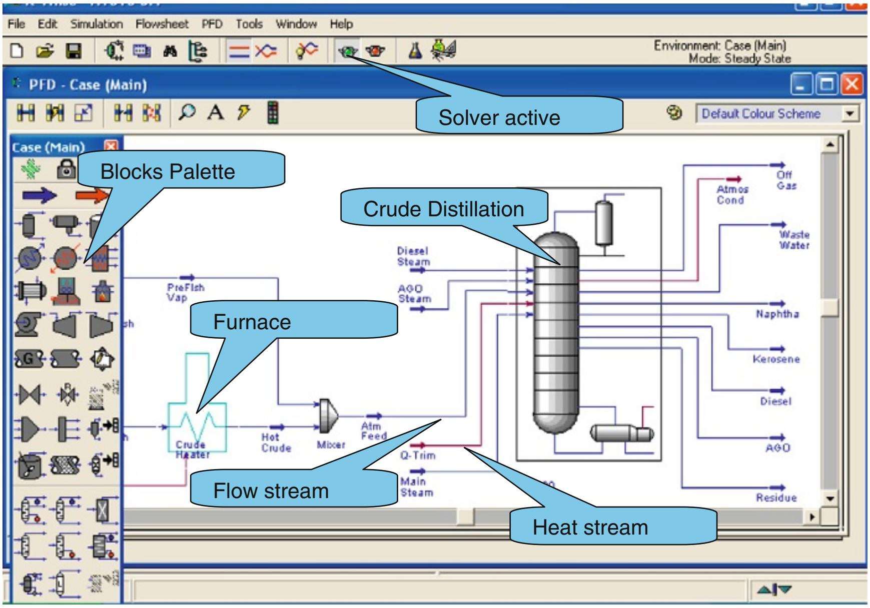
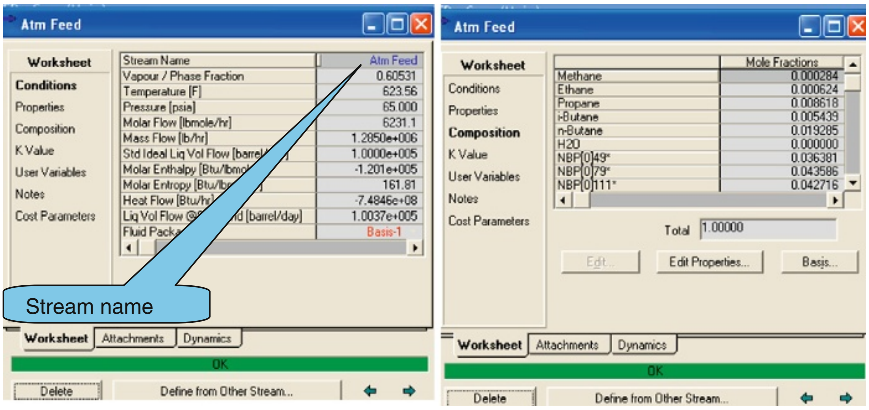


Figure C.8 Simulation environment



Stream Name	Atm Feed
Vapour / Phase Fraction	0.60531
Temperature [F]	623.56
Pressure [psia]	65.000
Molar Flow [lbmole/hr]	6231.1
Mass Flow [lb/hr]	1.2850e+006
Std Ideal Liq Vol Flow [barrel/]	1.0000e+005
Molar Enthalpy [Btu/lbmol	-1.201e+005
Molar Entropy [Btu/lb]	161.81
Heat Flow [Btu/hr]	-7.4846e+08
Liq Vol Flow @ d [barrel/day]	1.0037e+005
Fluid Packa	Basis-1

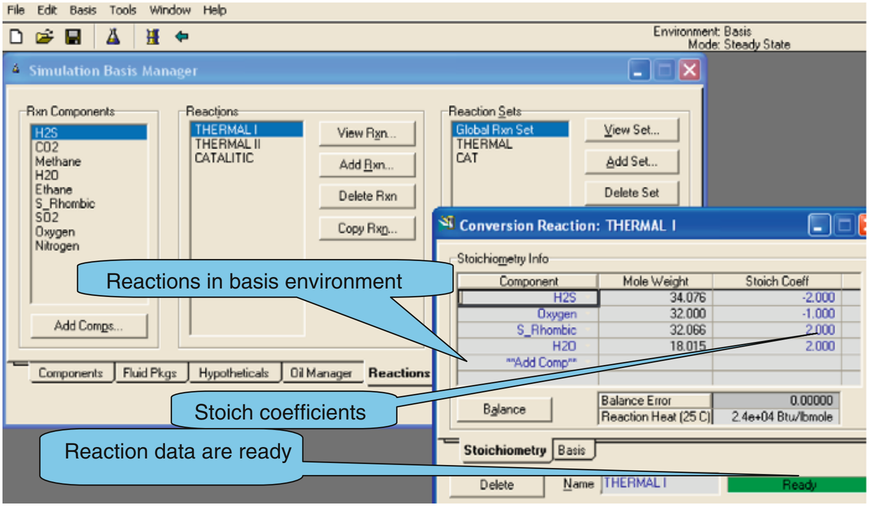
	Mole Fractions
Methane	0.000284
Ethane	0.000624
Propane	0.008618
i-Butane	0.005439
n-Butane	0.019285
H2O	0.000000
NBP[0]49*	0.036381
NBP[0]79*	0.043586
NBP[0]111*	0.042716

Total 1.00000

Figure C.9 Stream operating data and composition

- Can be any stream in a defined convergence loop
- Feedback controller used to specify a simulation variable result (Fig. C.12)

As soon as the stream colour changes, calculations are ready. Stream Results shown in Fig. C.13.



Component	Mole Weight	Stoich Coeff
H2S	34.076	-2.000
Oxygen	32.000	-1.000
S_Rhombic	32.066	2.000
H2O	18.015	2.000
Add Comp		

Balance Error 0.00000
Reaction Heat (25 C) 2.4e+04 Btu/lbmole

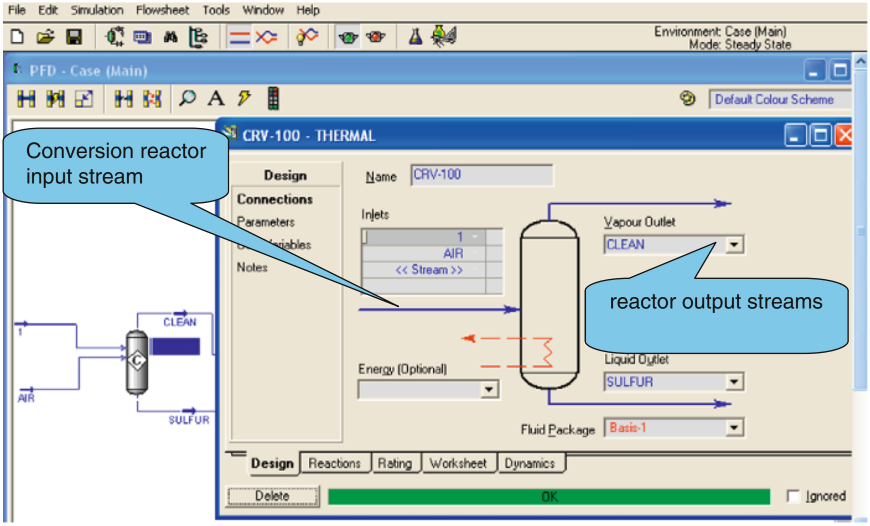
Name THERMAL I
Ready

Reactions in basis environment

Stoich coefficients

Reaction data are ready

Figure C.10 Reaction input data



Name CRV-100

Inlets: 1, AIR

Vapour Outlet CLEAN

Liquid Outlet SULFUR

Fluid Package Basis-1

OK

Conversion reactor input stream

reactor output streams

Figure C.11 Reactor design connection streams

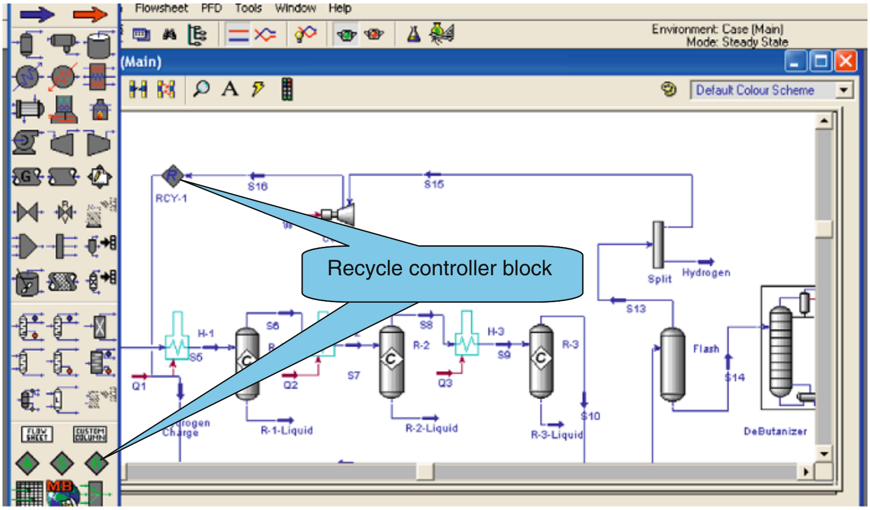
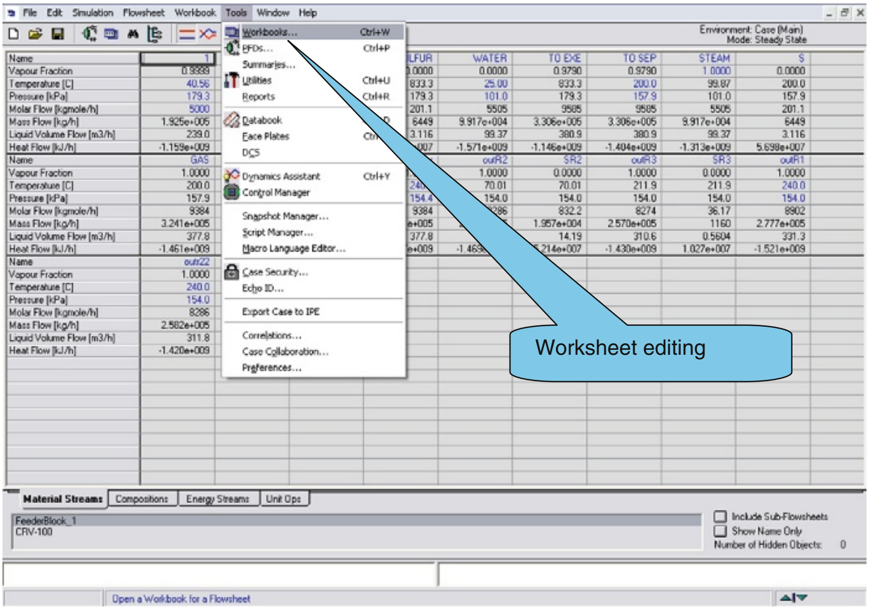


Figure C.12 Recycle stream controller



Environment: Case (Main)
Mode: Steady State

Name	1	LFUR	WATER	TO EXE	TO SEP	STEAM	S
Vapour Fraction	0.9999	0.0000	0.0000	0.9790	0.9790	1.0000	0.0000
Temperature [C]	40.56	833.3	25.00	833.3	200.0	99.87	200.0
Pressure [kPa]	179.3	179.3	101.0	179.3	157.9	101.0	157.9
Molar Flow [kgmole/h]	5000	201.1	5505	9585	9585	5505	201.1
Mass Flow [kg/h]	1.925e+005	6449	9.917e+004	3.306e+005	3.306e+005	9.917e+004	6449
Liquid Volume Flow [m3/h]	239.0	3.116	99.37	380.9	380.9	99.37	3.116
Heat Flow [kJ/h]	-1.159e+009	007	-1.571e+009	-1.146e+009	-1.404e+009	-1.313e+009	5.698e+007
Name	GAS		outR2	SR2	outR3	SR3	outR1
Vapour Fraction	1.0000		1.0000	0.0000	1.0000	0.0000	1.0000
Temperature [C]	200.0	240	70.01	70.01	211.9	211.9	240.0
Pressure [kPa]	157.9	154.4	154.0	154.0	154.0	154.0	154.0
Molar Flow [kgmole/h]	9384	9384	286	832.2	8274	36.17	8902
Mass Flow [kg/h]	3.241e+005	e+005		1.957e+004	2.570e+005	1160	2.777e+005
Liquid Volume Flow [m3/h]	377.8	377.8		14.19	310.6	0.5604	331.3
Heat Flow [kJ/h]	-1.461e+009	e+009	-1.469	214e+007	-1.430e+009	1.027e+007	-1.521e+009
Name	outr22						
Vapour Fraction	1.0000						
Temperature [C]	240.0						
Pressure [kPa]	154.0						
Molar Flow [kgmole/h]	8286						
Mass Flow [kg/h]	2.582e+005						
Liquid Volume Flow [m3/h]	311.8						
Heat Flow [kJ/h]	-1.420e+009						

FeederBlock_1
CRV-100

Number of Hidden Objects: 0

Figure C.13 Stream results summary

REFERENCE

UNISIM Design, Suite R370, (2007). Honeywell Process Solutions, Calgary, Alberta, Canada.

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Appendix D

D. Research Octane Number for Hydrocarbons (Antos *et al.*, 1995)

See Table D.1

Table D.1 Research octane numbers of pure hydrocarbons

Paraffins		Naphthenes	
n-Butane	94	Cyclopentane	>100
Isobutane	>100	Cyclohexane	83
n-Pentane	61.8	Methylcyclopentane	91.3
2-Methyl-1-butane	92.3	Methylcyclohexane	74.8
n-Hexane	24.8	1,3-Dimethylcyclopentane	80.6
2-Methyl-1-pentane	73.4	1,1,3-Trimethylcyclopentane	87.7
2,2-Dimethyl-1-butane	91.8	Ethylcyclohexane	45.6
n-Heptane	0	Isobutylcyclohexane	33.7
2-Methylhexane	52	**Aromatic**	
2,3-Dimethylpentane	91.1	Benzene	–
2,2,3-Trimethylbutane	>100	Toluene	>100
n-Octane	<0	*o*-Xylene	–
3,3-Dimethylhexane	75.5	*m*-Xylene	>100
2,2,4-Trimethylpentane	100	p-Xylene	>100
n-Nonane	<0	Ethylbenzene	>100
2,2,3,3-Tetramethylpentane	>100	*n*-Propylbenzene	>100
n-decane	<0	Isopropylbenzene	>100
Olefins		1-Methyl-3-ethylbenzene	>100
1-Hexene	76.4	*n*-butylbenzene	>100
1-Heptene	54.5	1-Methyl-3-isopropylbenzene	–
2-Methyl-2-hexene	90.4	1,2,3,4-Tetramethylbenzene	>100
2,3-Dimethyl-1-pentene	99.3		

Fundamentals of Petroleum Refining
DOI: 10.1016/B978-0-444-52785-1.00030-9

REFERENCE

Antos, G.J. *et al.* (1995). "Catalytic Naphtha Reforming." Marcel Dekker, New York, USA.

Notation

A	Aromatics content
$\overline{A}$	Aromatic content of a blend
A_c	Catalyst activity
A_M	Membrane surface area
AG	Acid gas
AGO	Atmospheric gas oil
AR	Atmospheric residue
ARDS	Atmospheric residue desulphurization
ATK	Aviation turbine kerosene
BAT	Best available techniques
BOD	Biological oxygen demand
BPCD	Barrels per calendar day based on 365 days per year
BPD	Barrels per day
BPSD	Barrels per stream day
BTX	Benzene, toluene and xylene
C_c	Coke content in the catalyst
C_D	Drag force coefficient
C_p	Heat capacity
$\mathrm{C}_{p,air}$	Heat capacity of air
$C_{p,cat}$	Heat capacity of catalyst
$C_{p,s}$	Heat capacity of steam
CCR	Conradson carbon residue
CDU	Crude distillation unit
COD	Chemical oxygen demand
CONV	Conversion of reaction
D_T	Absorber diameter
dBA	Decibels of sound pressure
DAF	Dissolved air floatation
DAO	Deasphalted oil
DCC	Deep catalytic cracking
DEA	Diethanol Amine
DHDS	Deep hydrodesulphurization
DME	Dimethyl ether
DNHDS	Deep non-hydrodesulphurization
DOC	Dissolved organic carbon
EBP	End boiling point
EOR	End of run
EOS	Equation of state
EP	Emission rate
EPA	Environmental Protection Agency

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DOI: 10.1016/B978-0-444-52785-1.00032-2

ESP	Electrostatic precipitator
EVOC	Emission rate of VOC
F	Performance factor
F_{LV}	Entrainment flooding capacity
F_{st}	Surface tension factor
FAE	Fuel air explosives
FCC	Fluid catalytic cracking
FGD	Flue gas desulphurization
FOEB	Fuel oil equivalent barrels
FT	Fischer–Tropsch
FTA	Fault tree analysis
gpm	Gallons per minute
G	Gibbs free energy
G'	Carrier gas flow rate in absorption
GC	Gas chromatograph
GOR	Gas to oil ratio
GTL	Gas to liquid
H	Enthalpy
H	Henry's constant
$\overline{H}$	Stack height
H_{G}	Height transfer units
HAP	Hazardous air pollutants
HAZOP	Hazard operability
HCGO	Heavy cycle gas oil
HCN	Heavy cycle naphtha
HDA	Aromatic hydrogenation
HDC	Hydrocracking
HDI	Hydro-isomerization
HDN	Hydro-denitrogenation
HDS	Hydrodesulphurization
HF	Hydrofluoric acid
HN	Heavy naphtha
HPLC	High performance liquid chromatograph
HSR	Heavy straight run
HSS	High selective switch
HT	Hydrotreating
HTN	Hydrotreated naphtha
HTSC	High temperature shift converter
HTU	Hydrothermal upgrading
I_{AP}	Aniline point index
I_{cp}	Cloud point index
I_{E}	Isobutene effluent volume %
I_{FP}	Flash point index
I_{PP}	Pour point index
I_{RVP}	Reid vapour pressure index

$I_{\mathrm{vis,v}}$	Viscosity index based on volume basis
$I_{\mathrm{vis,w}}$	Viscosity index based on weight basis
IBP	Initial boiling point
IGCC	Integrated gasification combined cycle
I/O	Isobutane/olefin ratio
k_{i}	Reaction rate constant
K	Watson characterization factor
K_{eq}	Equilibrium reaction constant
K_{P}	Equilibrium reaction constant for gas phase
L	Solvent gas flow rate in absorption
L_{eq}	Equivalent level of sound
L_{max}	Maximum level of sound
LBG	Low BTU gas
LCGO	Light cycle gas oil
LCN	Light cycle naphtha
LEL	Lower explosive limit
LFL	Lower flammability limit
LHSV	Liquid hourly space velocity
LN	Light naphtha
LNG	Liquefied natural gas
LP	Linear programming
LPG	Liquefied petroleum gas
LSFO	Low sulphur fuel oil
LTA	Lost time accident
LTSC	Low temperature shift converter
LV%	Liquid volume%
m_{air}	Mass flow rate of air to the catalyst regenerator
m_{cat}	Catalyst mass flow rate
m_{f}	Mass flow rate of the feed to the reactor
m_{i}	Mass flow rate of the products from the reactor
m_{scat}	Mass flow rate of the spent catalyst
M	Molecular weight
$\overline{M}$	MON average of a blend
M_{L}	Liquid molecular weight
M_{v}	Vapour molecular weight
MAWP	Maximum allowable working pressure
MDEA	Methyl die ethanolamine
MeABP	Mean average boiling point
MEA	Monoethanol amine
MEROX	Mercaptans oxidation
MMSCFD	10^6 ft^3/day
MO	Metal oxide
MON	Motor octane number
MS	Mass spectroscopy
MSDS	Material safety data sheet

MTBE	Methyl ter butyl ether
n	Refractive index
N	Naphthenes
NBP	Normal boiling point
NESHAP	National Emissions Standards for Hazardous Air Pollutants
Nf	Number of gas components in the flue gas
NG	Natural gas
Ni	Nickel
Np	Number of products
$\overline{O}$	Olefin content in a blend
OSHA	Occupational safety and health administration
P	Pressure
P_{M}	Gas permeability
P_{c}	Critical pressure
PDF	Process flow diagram
Petro FCC	Petrochemical fluid catalytic cracking
PHA	Process hazard analysis
P&ID	Piping and instrumentation diagram
PIONA	Parrafins, isoparaffins, olefins and aromatic
PNA	Polynuclear aromatics
PPE	Personal protective equipment
PPM	Parts per million
PSA	Pressure swing adsorption
PTB	Pounds per thousand barrels
Q_{cat}	Energy of catalyst
Q_{f}	Energy of oil feed to the reactor
Q_{rxn}	Energy of reaction
Q_{scat}	Energy of spent catalyst
Q_{sin}	Energy injected steam
Q_{sout}	Energy of steam out
r_{A}	Rate of reaction of component A
r_{yi}	Rate of reaction for lump i
R	Refractivity parameter
$\overline{R}$	RON average of a blend
RFCC	Residue fluid catalytic cracking
RME	Rapeseed methyl ester
RON	Research octane number
RSH	Mercaptans
RVP	Reid vapour pressure
$R(t)$	Reliability of a process
S	Sulphur
$\overline{S}$	Average gasoline sensitivity
S_{in}	Injected steam flow rate
S_{out}	Output steam flow rate
S_{P}	Tray spacing

SCFB	Standard cubic feet per barrel
SCR	Selective catalytic reduction
SDA	Solvent deasphalting
SG	Specific gravity
SHE	Safety, health and environment
SNCR	Selective non-catalytic reduction
SR	Semi-regenerative
SRU	Sulphur recovery unit
STP	Standard temperature and pressure
SV	Space velocity
$t_{1/2}$	Half life of the catalyst
t_c	Coking time
T_b	True boiling point
T_c	Critical temperature
T_f	Feed temperature
TBP	True boiling point
TC	Temperature controller
TCCU	Tail gas clean-up
TCD	Thermal conductivity detector
TNT	Tri nitro toluene
TOC	Total organic carbon
TSP	Total suspended particulates
TSS	Total suspended solids
UEL	Upper explosive limit
UFL	Upper flammability limit
V	Volume
V_{100}	Saybolt universal viscosity at 100 °F
V_{210}	Saybolt universal viscosity at 210 °F
Vac	Vacuum
VABP	Volume average boiling point
VG	Viscosity gravity constant
VGO	Vacuum gas oil
VOC	Volatile organic compound
VR	Vacuum residue
wt%	Weight percentage
WGS	Water gas shift
WWE	Waste water emission
x_a	Aromatics volume percentage in crude
x_n	Naphthenes volume percentage in crude
x_p	Parrafins volume percentage in crude
$y*$	Equilibrium gas composition
y_1	VGO weight fraction in 3-lump and 4-lump models
y_2	Gasoline weight fraction in 3-lump and 4-lump models
y_3	Gas and coke weight fraction in 3-lump and 4-lump models
Z	Compressibility factor

δ	Solubility parameter
ε_g	Hydrocarbon gases void fraction
ϕ	Catalyst activity
μ	Average failure rate
θ	Residence time
ρ_L	Liquid density
ρ_v	Vapour density
σ_y	Standard deviation in y-direction
σ_z	Standard deviation in z-direction
σ	Surface tension
$\upsilon100$	Kinematic viscosity (cSt) at 100 °F
$\upsilon210$	Kinematic viscosity (cSt) at 210 °F
ω	Acentric factor

INDEX

Note: Page numbers followed by "*f*" and "*t*" indicate figures and tables, respectively.