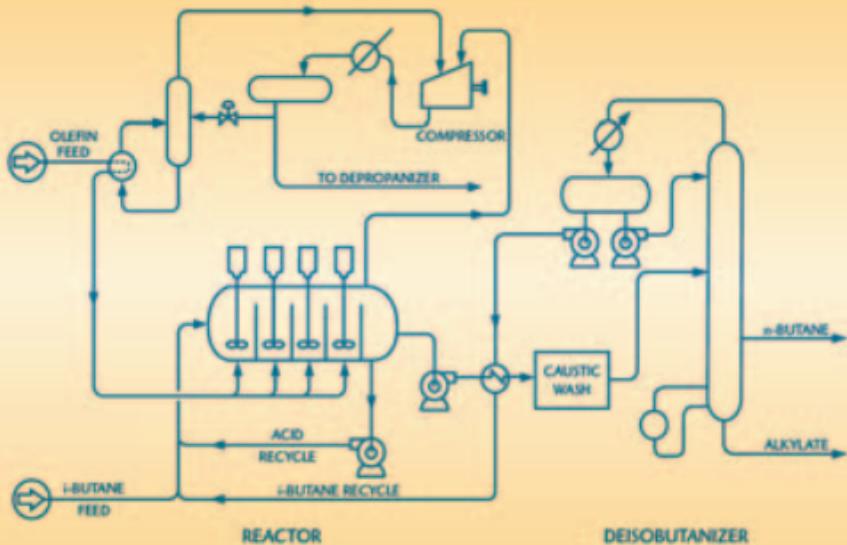


Petroleum Refining

*Technology and
Economics*

Fourth Edition



James H. Gary
Glenn E. Handwerk

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***Technology and
Economics***

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Preface

Today refiners are facing investments of billions of dollars in equipment to meet environmental requirements frequently set by political stipulation with little regard to true economic and environmental impacts. Guidelines set up by laws and regulations are changed frequently. Since the design and building of new processing units entail several years of lead time, refiners are reluctant to commit millions or billions of dollars to constructing equipment that may no longer meet requirements when the units come on stream. For the “short-term” period much effort is being devoted to the development of reformulated fuels that have a minimal impact on degradation of the environment. We say “short-term” because laws have already been passed stipulating that within the next two decades hydrocarbon fuel will not be acceptable and only totally nonpolluting fuels will be acceptable. At the present time the only nonpolluting fuels specified are solar and electric energy and hydrogen. This allows only a short time for the petroleum industry to recover the large investment required to meet the present legal requirements. It is apparent that the survivors of this period will be those companies utilizing the experience and skill of their engineers and scientists to the highest possible level of efficiency.

In writing this edition, we have taken the new environmental aspects of the industry into account, as well as the use of heavier crude oils and crude oils with higher sulfur and metal content. All these criteria affect the processing options and the processing equipment required in a modern refinery.

The basic aspects of current petroleum-refining technology and economics are presented in a systematic manner suitable for ready reference by technical managers, practicing engineers, university faculty members, and graduate or senior students in chemical engineering. In addition, the environmental aspects of refinery fuels and the place of reformulated fuels in refinery product distribution are covered.

The physical and chemical properties of petroleum and petroleum products are described, along with major refining processes. Data for determination of

typical product yields, investment, and operating costs for all major refining processes and for supporting processes are also given.

The investment, operating cost, and utility data given herein are typical average recent data. As such, this information is suitable for approximating the economics of various refining configurations. The information is not sufficiently accurate for definitive comparisons of competing processes.

The yield data for reaction processes have been extended to allow complete material balances to be made from physical properties. Insofar as possible, data for catalytic reactions represent average yields for competing proprietary catalysts and processes.

The material is organized to utilize the case-study method of learning. An example case-study problem begins in Chapter 4 (Crude Distillation) and concludes in Chapter 18 (Economic Evaluation). The appendices contain basic engineering data and a glossary of refining terms. Valuable literature references are noted throughout the book.

We have held responsible positions in refinery operation, design, and evaluation, and have taught practical approaches to many refinery problems. This publication relies heavily on our direct knowledge of refining in addition to the expertise shared with us by our numerous associates and peers.

Appreciation is expressed to the many people who contributed data and suggestions incorporated into this book.

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1

Introduction

Modern refinery operations are very complex and, to a person unfamiliar with the industry, it seems to be an impossible task to reduce the complexity to a coordinated group of understandable processes. It is the purpose of this book to present the refinery processes, as far as possible, in the same order in which the crude flows through the refinery in order to show the purposes and interrelationships of the processing units. The case-study method is best for quick understanding and we recommend that a crude oil be selected and yield and cost calculations be made as the refining processes are studied in order. An example problem is given in Chapter 17 for a refinery of low complexity and the example problem starting in Chapter 4 and ending in Chapter 18 presents a complex refinery typical of today's operations.

The typical fuels refinery has as a goal the conversion of as much of the barrel of crude oil into transportation fuels as is economically practical. Although refineries produce many profitable products, the high-volume profitable products are the transportation fuels gasoline, diesel and turbine (jet) fuels, and the light heating oils, No. 1 and No. 2. These transportation fuels have boiling points between 0 and 345°C (30 to 650°F). Light heating oils are not properly transportation fuels but the hydrocarbon components are interchangeable with those of diesel and jet fuels, only the additives are different. Although products such as lubricating oils, refrigeration and transformer oils, and petrochemical feedstocks are profitable, they amount to less than 5 percent of the total crude oil charged to U.S. refineries.

The process flow and products for a complete refinery of high complexity are shown in Figure 1.1. (See also Photo 1, Appendix E.) The processing equipment indicated is for processing crude oils of average gravities and sulfur contents. Crude oils with low API gravities (high specific gravities) and high sulfur contents require additional hydrotreating equipment.

The quality of crude oils processed by U.S. refineries is expected to worsen slowly in the future with the sulfur contents and densities to increase. The greater

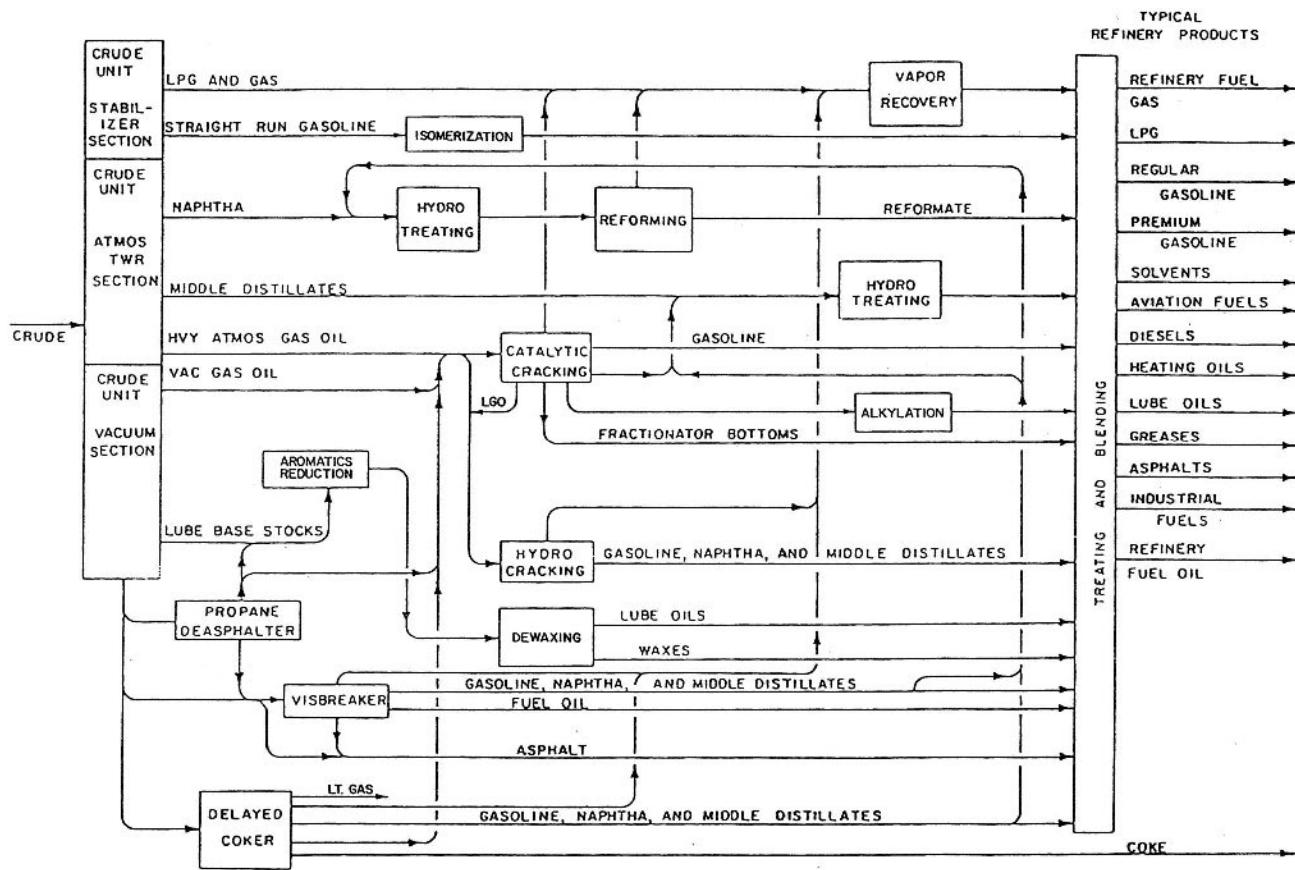


Figure 1.1 Refinery flow diagram.

densities will mean more of the crude oil will boil above 566°C (1050°F). Historically this high-boiling material or residua has been used as heavy fuel oil but the demand for these heavy fuel oils has been decreasing because of stricter environmental requirements. This will require refineries to process the entire barrel of crude rather than just the material boiling below 1050°F (566°C). Sulfur restrictions on fuels (coke and heavy fuel oils) will affect bottom-of-the-barrel processing as well. These factors will require extensive refinery additions and modernization and the shift in market requirements among gasolines and reformulated fuels for transportation will challenge catalyst suppliers and refinery engineers to develop innovative solutions to these problems.

The environmental impacts of fuel preparation and consumption will require that a significant shift take place in product distribution (i.e., less conventional gasoline and more reformulated and alternative fuels). This will have a major effect on refinery processing operations and will place a burden on refinery construction in addition to the need to provide increased capacity for high sulfur and heavier crude oils.

The language of the refining industry is unfamiliar to those not in it and to ease the entry into an unfamiliar world, feedstock and product specifications are discussed before the refinery processing units.

Appendix A contains a glossary of refining terms and will assist in understanding the descriptions. In many cases, however, there is no standard definition, and a term will have different meanings in different companies, and even in different refineries of the same company. It is always important, therefore, to define terms with respect to the individual writing or talking.

1.1 OVERALL REFINERY FLOW

Figure 1.1 shows the processing sequence in a modern refinery of high complexity, indicating major process flows between operations.

The crude oil is heated in a furnace and charged to an atmospheric distillation tower, where it is separated into butanes and lighter wet gas, unstabilized light naphtha, heavy naphtha, kerosine, atmospheric gas oil, and topped (reduced) crude (ARC). The topped crude is sent to the vacuum distillation tower and separated into vacuum gas oil stream and vacuum reduced crude bottoms (residua, resid, or VRC).

The reduced crude bottoms (VRC) from the vacuum tower is then thermally cracked in a delayed coker to produce wet gas, coker gasoline, coker gas oil, and coke. Without a coker, this heavy resid would be sold for heavy fuel oil or (if the crude oil is suitable) asphalt. Historically, these heavy bottoms have sold for about 70 percent of the price of crude oil.

The atmospheric and vacuum crude unit gas oils and coker gas oil are used as feedstocks for the catalytic cracking or hydrocracking units. These units crack the heavy molecules into lower molecular weight compounds boiling in the gasoline and distillate fuel ranges. The products from the hydrocracker are saturated. The unsaturated catalytic cracker products are saturated and improved in quality by hydrotreating or reforming.

The light naphtha streams from the crude tower, coker and cracking units are sent to an isomerization unit to convert straight-chain paraffins into isomers that have higher octane numbers.

The heavy naphtha streams from the crude tower, coker, and cracking units are fed to the catalytic reformer to improve their octane numbers. The products from the catalytic reformer are blended into regular and premium gasolines for sale.

The wet gas streams from the crude unit, coker, and cracking units are separated in the vapor recovery section (gas plant) into fuel gas, liquefied petroleum gas (LPG), unsaturated hydrocarbons (propylene, butylenes, and pentenes), normal butane, and isobutane. The fuel gas is burned as a fuel in refinery furnaces and the normal butane is blended into gasoline or LPG. The unsaturated hydrocarbons and isobutane are sent to the alkylation unit for processing.

The alkylation unit uses either sulfuric or hydrofluoric acid as catalyst to react olefins with isobutane to form isoparaffins boiling in the gasoline range. The product is called alkylate, and is a high-octane product blended into premium motor gasoline and aviation gasoline.

The middle distillates from the crude unit, coker, and cracking units are blended into diesel and jet fuels and furnace oils.

In some refineries, the heavy vacuum gas oil and reduced crude from paraffinic or naphthenic base crude oils are processed into lubricating oils. After removing the asphaltenes in a propane deasphalting unit, the reduced crude bottoms is processed in a blocked operation with the vacuum gas oils to produce lube-oil base stocks.

The vacuum gas oils and deasphalted stocks are first solvent-extracted to remove the aromatic compounds and then dewaxed to improve the pour point. They are then treated with special clays or high-severity hydrotreating to improve their color and stability before being blended into lubricating oils.

Each refinery has its own unique processing scheme which is determined by the process equipment available, crude oil characteristics, operating costs, and product demand. The optimum flow pattern for any refinery is dictated by economic considerations and no two refineries are identical in their operations.

2

Refinery Products

While the average consumer tends to think of petroleum products as consisting of a few items such as motor gasoline, jet fuel, home heating oils, kerosine, etc., a survey conducted by the American Petroleum Institute (API) of the petroleum refineries and petrochemical plants revealed over 2,000 products made to individual specifications [1]. Table 2.1 shows the number of individual products in 17 classes.

In general, the products which dictate refinery design are relatively few in number, and the basic refinery processes are based on the large-quantity products such as gasoline, diesel, jet fuel, and home heating oils. Storage and waste disposal are expensive, and it is necessary to sell or use all of the items produced from crude oil even if some of the materials, such as high-sulfur heavy fuel oil and fuel-grade coke, must be sold at prices less than the cost of fuel oil. Economic balances are required to determine whether certain crude oil fractions should be sold as is (i.e., straight-run) or further processed to produce products having greater value. Usually the lowest value of a hydrocarbon product is its heating value or fuel oil equivalent (FOE). This value is always established by location, demand, availability, combustion characteristics, sulfur content, and prices of competing fuels.

Knowledge of the physical and chemical properties of the petroleum products is necessary for an understanding of the need for the various refinery processes. To provide an orderly portrayal of the refinery products, they are described in the following paragraphs in order of increasing specific gravity and decreasing volatility and API gravity.

The petroleum industry uses a shorthand method of listing lower-boiling hydrocarbon compounds which characterize the materials by number of carbon atoms and unsaturated bonds in the molecule. For example, propane is shown as C_3 and propylene as $C_3=$. The corresponding hydrogen atoms are assumed to be present unless otherwise indicated. This notation will be used throughout this book.

Table 2.1 Products Made by the U.S. Petroleum Industry

Class	Number
Fuel gas	1
Liquefied gases	13
Gasolines	40
Motor	19
Aviation	9
Other (tractor, marine, etc.)	12
Gas turbine (jet) fuels	5
Kerosines	10
Middle distillates (diesel and light fuel oils)	27
Residual fuel oil	16
Lubricating oils	1156
White oils	100
Rust preventatives	65
Transformer and cable oils	12
Greases	271
Waxes	113
Asphalts	209
Cokes	4
Carbon blacks	5
Chemicals, solvents, miscellaneous	300
Total	2347

Source: Ref. 1.

2.1 LOW-BOILING PRODUCTS

The classification *low-boiling products* encompasses the compounds which are in the gas phase at ambient temperatures and pressures: methane, ethane, propane, butane, and the corresponding olefins.

Methane (C_1) is usually used as a refinery fuel, but can be used as a feedstock for hydrogen production by pyrolytic cracking and reaction with steam. Its quantity is generally expressed in terms of pounds or kilograms, standard cubic feet (scf) at 60°F and 14.7 psia, normal cubic meters (Nm^3) at 15.6°C and 1 bar (100 kPa), or in barrels fuel oil equivalent (FOE) based on a lower heating value (LHV) of 6.05×10^6 Btu (6.38×10^6 kJ). The physical properties of methane are given in Table 2.2.

Ethane (C_2) can be used as refinery fuel or as a feedstock to produce hydrogen or ethylene, which are used in petrochemical processes. Ethylene and hydrogen are sometimes recovered in the refinery and sold to petrochemical plants.

Table 2.2 Physical Properties of Paraffins

	C _n	Boiling point (°F)	Melting point (°F)	Specific gravity (60/60°F)	API gravity (°API)
Methane	1	−258.7	−296.5	0.30	340
Ethane	2	−128.5	−297.9	0.356	265.5
Propane	3	−43.7	−305.8	0.508	147.2
Butane					
Normal	4	31.1	−217.1	0.584	110.6
Iso	4	10.9	−225.3	0.563	119.8
Octane					
Normal	8	258.2	−70.2	0.707	68.7
2,2,4	8	210.6	−161.3	0.696	71.8
2,2,3,3	8	223.7	219.0	0.720	65.0
Decane, normal	10	345.5	−21.4	0.734	61.2
Cetane, normal	16	555.0	64.0	0.775	51.0
Eicosane, normal	20	650.0	98.0	0.782	49.4
Triacontane					
Normal	30	850.0	147.0	0.783	49.2
2,6,10,14,18,22	30	815.0	−31.0	0.823	40.4

Note: Generalizations:

1. Boiling point rises with increase in molecular weight.
2. Boiling point of a branched chain is lower than for a straight chain hydrocarbon of the same molecular weight.
3. Melting point increases with molecular weight.
4. Melting point of a branched chain is lower than for a straight-chain hydrocarbon of the same weight unless branching leads to symmetry.
5. Gravity increases with increase of molecular weight.
6. For more complete properties of paraffins, see Table B.2.

Propane (C₃) is frequently used as a refinery fuel but is also sold as a liquefied petroleum gas (LPG), whose properties are specified by the Gas Processors Association (GPA) [7]. Typical specifications include a maximum vapor pressure of 210 psig (1448 kPa) at 100°F (37.8°C) and 95% boiling point of −37°F (−38.3°C) or lower at 760 mmHg (1 bar) atmospheric pressure. In some locations, propylene is separated for sale to polypropylene manufacturers.

The butanes present in crude oils and produced by refinery processes are used as components of gasoline and in refinery processing as well as in LPG. Normal butane (nC₄) has a lower vapor pressure than isobutane (iC₄), and is usually preferred for blending into gasoline to regulate its vapor pressure and promote better starting in cold weather. Normal butane has a Reid vapor pressure

(RVP) of 52 psi (358 kPa) as compared with the 71 psi (490 kPa) RVP of isobutane, and more nC₄ can be added to gasoline without exceeding the RVP of the gasoline product. On a volume basis, gasoline has a higher sales value than that of LPG, thus, it is desirable from an economic viewpoint to blend as much normal butane as possible into gasoline. Normal butane is also used as a feedstock to isomerization units to form isobutane.

Regulations promulgated by the Environmental Protection Agency (EPA) to reduce hydrocarbon emissions during refueling operations and evaporation from hot engines after ignition turn-off have greatly reduced the allowable Reid vapor pressure of gasolines during summer months. This resulted in two major impacts on the industry. The first was the increased availability of n-butane during the summer months and the second was the necessity to provide another method of providing the pool octane lost by the removal of the excessive n-butane. The pool octane is the average octane of the total gasoline production of the refinery if the regular, mid-premium, and super-premium gasolines are blended together.

Table 2.3 Properties of Commercial Propane and Butane

Property	Commercial propane	Commercial butane
Vapor pressure, psig		
70°F (21.1°C)	124	31
100°F (38°C)	192	59
130°F (54°C)	286	97
Specific gravity of liquid, 60/60°F	0.509	0.582
Initial boiling point at 1 bar, °F (°C)	-51 (-47.4)	15
Dew point at 1 bar, °F (°C)	-46 (-44.6)	24
Sp. ht. liquid at 60°F, 15.6°C		
Btu/(lb) (°F)	0.588	0.549
kJ/(kg) (°C)	2.462	2.299
Limits of flammability, vol% gas in air		
Lower limit	2.4	1.9
Upper limit	9.6	8.6
Latent heat of vaporization at b.p.		
Btu/lb	185	165
kJ/kg	430.3	383.8
Gross heating values		
Btu/lb of liquid	21,550	21,170
Btu/ft ³ of gas	2,560	3,350
kJ/kg of liquid	50,125	49,241
kJ/m ³ of gas	9,538	12,482

Source: Ref. 7.

N-butane has a blending octane in the 90s and is a low-cost octane improver of gasoline.

Isobutane has its greatest value when used as a feedstock to alkylation units, where it is reacted with unsaturated materials (propenes, butenes, and pentenes) to form high-octane isoparaffin compounds in the gasoline boiling range. Although isobutane is present in crude oils, its principal sources of supply are from fluid catalytic cracking (FCC) and hydrocracking (HC) units in the refinery and from natural gas processing plants. Isobutane not used for alkylation unit feed can be sold as LPG or used as a feedstock for propylene (propene) manufacture. A significant amount of isobutane is converted to isobutylene which is reacted with methanol to produce methyl tertiary butyl ether (MTBE).

When butanes are sold as LPG, they conform to the GPA specifications for commercial butane. These include a vapor pressure of 70 psig (483 kPa) or less at 100°F (21°C) and a 95% boiling point of 36° (2.2°C) or lower at 760 mmHg atmospheric pressure. N-butane as LPG has the disadvantage of a fairly high boiling point [32°F (0°C) at 760 mmHg] and during the winter is not satisfactory for heating when stored outdoors in areas which frequently have temperatures below freezing. Isobutane has a boiling point of 11°F (−12°C) and is also unsatisfactory for use in LPG for heating in cold climates.

Butane–propane mixtures are also sold as LPG, and their properties and standard test procedures are also specified by the GPA.

Average properties of commercial propane and butane are given in Table 2.3.

2.2 GASOLINE

Although an API survey [1] reports that 40 types of gasolines are made by refineries, about 90% of the total gasoline produced in the United States is used as fuel in automobiles. Most refiners produce gasoline in two or three grades, unleaded regular, premium, and super-premium, and in addition supply a regular gasoline to meet the needs of farm equipment and pre-1972 automobiles. The principal difference between the regular and premium fuels is the antiknock performance. In 1999 the posted method octane number (PON) of unleaded regular gasolines (see Section 2.3) was about 87 and that of premium gasolines ranged from 89 to 93. The non-leaded regular gasolines averaged about 88 PON. For all gasolines, octane numbers average about two numbers lower for the higher elevations of the Rocky Mountain states. Posted octane numbers are arithmetic averages of the motor octane number (MON) and research octane number (RON) and average four to six numbers below the RON.

Gasolines are complex mixtures of hydrocarbons having typical boiling ranges from 100 to 400°F (38 to 205°C) as determined by the ASTM method.

Components are blended to promote high antiknock quality, ease of starting, quick warm-up, low tendency to vapor lock, and low engine deposits. Gruse and Stevens [5] give a very comprehensive account of properties of gasolines and the manner in which they are affected by the blending components. For the purposes of preliminary plant design, however, the components used in blending motor gasoline can be limited to light straight-run (LSR) gasoline or isomerate, catalytic reformate, catalytically cracked gasoline, hydrocracked gasoline, polymer gasoline, alkylate, n-butane, and such additives as MTBE (methyl tertiary butyl ether), ETBE (ethyl tertiary butyl ether), TAME (tertiary amyl methyl ether) and ethanol. Other additives, for example, antioxidants, metal deactivators, and antistall agents, are not considered individually at this time, but are included with the cost of the antiknock chemicals added. The quantity of antiknock agents added, and their costs, must be determined by making octane blending calculations.

Light straight-run (LSR) gasoline consists of the C₅-190°F (C₅-88°C) fraction of the naphtha cuts from the atmospheric crude still. (C₅-190°F fraction means that pentanes are included in the cut but that C₄ and lower-boiling compounds are excluded and the TBP end point is approximately 190°F.) Some refiners cut at 180 (83) or 200°F (93°C) instead of 190°F, but, in any case, this is the fraction that cannot be significantly upgraded in octane by catalytic reforming. As a result, it is processed separately from the heavier straight-run gasoline fractions and requires only caustic washing, light hydrotreating, or, if higher octanes are needed, isomerization to produce a gasoline blending stock. For maximum octane with no lead addition, some refiners have installed isomerization units to process the LSR fraction and achieve PON octane improvements of 13 to 20 octane numbers over that of the LSR.

Catalytic reformate is the C₅⁺ gasoline product of the catalytic reformer. Heavy straight-run (HSR) and coker gasolines are used as feed to the catalytic reformer, and when the octane needs require, FCC and hydrocracked gasolines of the same boiling range may also be processed by this unit to increase octane levels. The processing conditions of the catalytic reformer are controlled to give the desired product antiknock properties in the range of 90 to 104 RON (85 to 98 PON) clear (lead-free).

The FCC and HC gasolines are generally used directly as gasoline blending stocks, but in some cases are separated into light and heavy fractions with the heavy fractions upgraded by catalytic reforming before being blended into motor gasoline. This has been true since motor gasoline is unleaded and the clear gasoline pool octane is now several octane numbers higher than when lead was permitted. It is usual for the heavy hydrocrackate to be sent to the reformer for octane improvement.

The reformer increases the octane by converting low-octane paraffins to high-octane aromatics. Some aromatics have high rates of reaction with ozone to form visual pollutants in the air and some are claimed to be potentially carcinogenic.

genic by the EPA. Restrictions on aromatic contents of motor fuels will have increasing impacts on refinery processing as more severe restrictions are applied. This will restrict the severity of catalytic reforming and will require refiners to use other ways to increase octane numbers of the gasoline pool by incorporating more oxygenates in the blend.

Polymer gasoline is manufactured by polymerizing olefinic hydrocarbons to produce higher molecular weight olefins in the gasoline boiling range. Refinery technology favors alkylation processes rather than polymerization for two reasons: one is that larger quantities of higher octane product can be made from the light olefins available, and the other is that the alkylation product is paraffinic rather than olefinic, and olefins are highly photoreactive and contribute to visual air pollution and ozone production.

Alkylate gasoline is the product of the reaction of isobutane with propylene, butylene, or pentylene to produce branched-chain hydrocarbons in the gasoline boiling range. Alkylation of a given quantity of olefins produces twice the volume of high octane motor fuel as can be produced by polymerization. In addition, the blending octane (PON) of alkylate is higher and the sensitivity (RON – MON) is significantly lower than that of polymer gasoline.

Normal butane is blended into gasoline to give the desired vapor pressure. The vapor pressure [expressed as the Reid vapor pressure (RVP)] of gasoline is a compromise between a high RVP to improve economics and engine starting characteristics and a low RVP to prevent vapor lock and reduce evaporation losses. As such, it changes with the season of the year and varies between 7.2 psi (49.6 kPa) in the summer and 13.5 psi (93.1 kPa) in the winter. Butane has a high blending octane number and is a very desirable component of gasoline; refiners put as much in their gasolines as vapor pressure limitations permit. Isobutane can be used for this purpose but it is not as desirable because its higher vapor pressure permits a lesser amount to be incorporated into gasoline than n-butane.

Concern over the effects of hydrocarbon fuels usage on the environment has caused changes in environmental regulations which impact gasoline and diesel fuel compositions. The main restrictions on diesel fuels limit sulfur and total aromatics contents and gasoline restrictions include not only sulfur and total aromatics contents but also specific compound limits (e.g., benzene), limits on certain types of compounds (e.g., olefins), maximum Reid vapor pressures, and also minimum oxygen contents for areas with carbon monoxide problems. This has led to the concept of "reformulated gasolines." A reformulated gasoline specification is designed to produce a fuel for spark ignition engines which is at least as clean burning as high methanol content fuels. As more is learned about the relationship between fuels and the environment, fuel specifications are undergoing change. Here, main sources of items of concern are discussed along with relative impacts on the environment. For current specifications of fuels see ASTM specifications for the specific fuel desired.

Table 2.4 Sources of Sulfur in Gasoline Pool

	Composition wt%	Contribution to pool, %
LSR Naphtha	0.014	1.7
C ₅ -270°F (132°C) FCC Gasoline	0.07	11.2
Heavy FCC Gasoline	0.83	86.1
Lt. Coker Gasoline	0.12	1.0

Source: Ref. 8.

Field tests indicate that it is desirable to have gasoline sulfur contents of less than 300 ppm (0.03 wt%). As shown in Table 2.4, the fluid catalytic cracker (FCC) naphtha is the main source of sulfur in the refinery gasoline pool. For a given refinery crude oil charge, to meet the <300 ppm sulfur specification, with no octane penalty, it is necessary to hydrotreat the FCC feedstock to reduce the sulfur level sufficiently to produce FCC naphthas with acceptable sulfur contents. The alternative is to hydrotreat the FCC naphtha, but this saturates the olefins in the naphtha and results in a blending octane reduction of two to three numbers.

Some aromatics and most olefins react with components of the atmosphere to produce visual pollutants. The activities of these gasoline components are expressed in terms of reactivity with (OH) radicals in the atmosphere. The sources and reactivities of some of these gasoline components are shown in Tables 2.5 and 2.6. Specifically, xylenes and olefins are the most reactive and it may be necessary to place limits on these materials.

Table 2.5 Aromatics and Olefins in Gasoline

Blendstock	Percent of pool	Percent aromatics	Percent olefins
Reformate	27.2	63	1
LSR naphtha	3.1	10	2
Isomerate	3.7	1	0
FCC naphtha	38.0	30	29
Lt. coker naphtha	0.7	5	35
Lt. HC naphtha	2.4	3	0
Alkylate	12.3	0.4	0.5
Polymer	0.4	0.5	96
n-butane	3.1	0	2.6

Source: Ref. 8.

Table 2.6 Reactivity and RVP of Gasoline Components

	Reactivity ^a	RVP	
		psi	kPa
n-butane	2.7	60	414
i-pentane	3.6	21	145
n-pentane	5.0	16	110
i-hexane	5.0	7	48
n-hexane	5.6	5	34
Benzene	1.3	3	21
Toluene	6.4	0.5	3
m-xylene	23.0	0.3	2
Butene-1	30.0	65	448
Butene-2	65.0	50	200
Pentene-1	30.0	16	110
2-Methyl, 2-butene	85.0	15	103
2-Methyl, 1-butene	70.0	19	131

^a Reactivity with —OH free radical in atmosphere.

Source: Ref. 9.

Producing motor fuels to reduce environmental impact will require refinery equipment additions as well as changes in catalysts and processing techniques.

Since the 1940s, motor gasoline has been the principal product of refineries and, in 1998, gasoline production was the largest of any of the basic industries in the United States. The 400 million tons of gasoline produced exceeded the output of steel, lumber, and other high-volume products [10]. Of this production, over 90% was used in trucks and automobiles.

The aviation gasoline market is relatively small and accounts for less than 3% of the gasoline market. For this reason, it is usually not considered in the preliminary refinery design.

2.3 GASOLINE SPECIFICATIONS

Although there are several important properties of gasoline, the three that have the greatest effects on engine performance are the Reid vapor pressure, boiling range, and antiknock characteristics.

The Reid vapor pressure (RVP) and boiling range of gasoline governs ease of starting, engine warm-up, rate of acceleration, loss by crankcase dilution, mileage economy, and tendency toward vapor lock. Engine warm-up time is affected by the percent distilled at 158°F (70°C) and the 90% ASTM distillation temperature. Warm-up is expressed in terms of the distance operated to develop full power without excessive use of the choke. A two- to four-mile (3- to 7-km) warm-up is considered satisfactory and the relationship between outside temperature and percent distilled to give acceptable warm-up properties is:

% dist. at 158°F (70°C)	3	11	19	28	38	53
Min. ambient temp.						
°F	80	60	40	20	0	20
°C	26.7	15.6	4.4	-6.7	-18	-29

Crankcase dilution is controlled by the 90% ASTM distillation temperature and is also a function of outside temperature. To keep crankcase dilution within acceptable limits, the volatility should be:

Min. ambient temp.						
°F	80	60	40	20	0	-20
°C	26.7	15.6	4.4	-6.7	-18	-29
90% ASTM dist.						
°F	370	350	340	325	310	300
°C	188	177	171	163	154	149

Tendency to vapor lock is directly related to the RVP of the gasoline. In order to control vapor, the vapor pressure of the gasoline should not exceed the following limits:

Ambient temp.	Max. allowable RVP			
	°F	°C	psia	kPa
60	15.6	12.7	87.6	
70	21.1	11.0	75.8	
80	26.7	9.4	64.8	
90	32.2	8.0	55.2	

The Reid vapor pressure is approximately the vapor pressure of the gasoline at 100°F (38°C) in absolute units (ASTM designation D-323).

Altitude affects several properties of gasoline, the most important of which are losses by evaporation and octane requirement. Octane number requirement is greatly affected by altitude and, for a constant spark advance, is about three units lower for each 1000 ft (305 m) of elevation. In practice, however, the spark is advanced at higher elevations to improve engine performance and the net effect is to reduce the PON of the gasoline marketed by about two numbers for a 5000-ft (1524-m) increase in elevation. Octane requirements for the same model of engine will vary by 7 to 12 RON because of differences in tuneup, engine deposits, and clearances. Table 2.7 lists some typical effects of variables on engine octane requirements.

There are several types of octane numbers for spark ignition engines with the two determined by laboratory tests considered most common: those determined by the "motor method" (MON) and those determined by the "research method" (RON). Both methods use the same basic type of test engine but operate under different conditions. The RON (ASTM D-908) represents the performance during city driving when acceleration is relatively frequent, and the MON (ASTM D-357) is a guide to engine performance on the highway or under heavy load conditions. The difference between the research and motor octane is an indicator of the sensitivity of the performance of the fuel to the two types of driving conditions and is known as the "sensitivity" of the fuel. Obviously, the driver would like for the fuel to perform equally well both in the city and on the highway, therefore low sensitivity fuels are better. Since the posting of octane numbers on the service station pump has been required in the United States, the posted octane number (PON) is the one most well-known by the typical driver. This is the arithmetic average of the research and motor octane numbers [(RON + MON)/2].

Table 2.7 Effects of Variables on Octane Requirements

Variable	Effect on octane requirements
Altitude	-3 RON per 1000 ft (305 m) increase in altitude
Humidity	-0.5 RON per 10% increase in rel. humidity at 70°F (21.1°C)
Engine speed	-1 RON per 300 rpm increase
Air temperature	+1 RON per 20°F (11.1°C) rise
Spark advance	+1.5 RON per 1° advance
Coolant temperature	+1 RON per 10°F (5.6°C) increase
Combustion chamber deposits	+1 to 2 RON per 1000 miles (1609 km) up to 6000 miles (9650 km)

2.4 DISTILLATE FUELS

Distillate fuels can be divided into three types: jet or turbine fuels, diesel fuels, and heating oils. These products are blended from a variety of refinery streams to meet the desired specifications.

The consumption of heating oils has ranked high in the refinery production goals, but as a percentage of refinery products has been decreasing because of increases in gasoline, diesel, and jet fuels in recent years. Increasingly severe environmental restrictions on fuel emissions have caused some users of heating oils to convert to natural gas and LPG. Expansion of air and truck travel has increased diesel and jet fuel demands.

2.5 JET AND TURBINE FUELS

Jet fuel is blended for use by both commercial aviation and military aircraft. It is also known as turbine fuel and there are several commercial and military jet fuel specifications. For most refineries the primary source of jet fuel blending stocks is the straight-run kerosine fraction from the atmospheric crude unit because stringent total aromatic and naphthalene content and smoke point specifications limit the amount of cracked stocks which can be included. For refineries with a hydrocracker, kerosine boiling range hydrocarbons from this unit can also meet jet fuel specifications and is a major contributor to jet fuel production. Usually jet fuels sell at higher prices than diesel fuels and No. 1 and No. 2 heating oils, and it is more profitable for the refiner to blend the kerosine fractions from the atmospheric crude unit and the hydrocracker into jet fuel rather than other products.

Commercial jet fuel is a material in the kerosine boiling range and must be clean burning. The ASTM specifications for jet and turbine fuels are given in Table 2.8. Two of the critical specifications relate to its clean burning requirements and limit the total aromatics as well as the content of double ring aromatic compounds. These are the smoke point, expressed in mm of flame height at which smoking is detected, and the volume percent total aromatics and naphthalenes. Specifications limit total aromatic concentration to 20% and the naphthalene content to 3% or 3.0% depending upon the specific specifications. Hydrocracking saturates many of the double ring aromatics in cracked products and raises the smoke point. The freeze point specification is very low [−40 to −58°F max. (−40 to −50°C max.)] and hydrocracking is also used to isomerize paraffins and lower the freeze point. Hydrocracking normally produces a very low (14 to 16 mm) smoke point jet fuel when the cracking is done in the presence of a small amount of hydrogen sulfide or ammonia.

Jet fuel is blended from low sulfur or desulfurized kerosine, hydrotreated

Table 2.8 Characteristics of Aircraft Turbine Fuels (ASTM D-1655 and DERD 2494)

Property	Jet A	JP-5	DERD 2494	JP-8
Aromatics, vol%, max.	20	25	22.0	22.0
Combustion prop.				
Smoke point, mm, min, or	25	19	—	25
Smoke point, mm, min, and	18	—	19	20
Naphthalenes, vol%, max.	3.0	—	3.0	3.0
Distillation, D-86, °F (°C)				
10% recovered °F (°C), max.	400 (205)	400 (205)	401 (205)	401 (205)
50% recovered °F (°C), max.	report	report	report	report
FBP, °F (°C), max.	572 (300)	554 (290)	572 (300)	572 (300)
Flashpoint, °F (°C), min.	100 (38)	140 (60)	100 (38)	100 (38)
Freeze point, °F (°C), max.	-40 (-40)	-51 (-46)	-52.6 (-47)	-52.6 (-47)
Sulfur, wt%, max.	0.30	0.4	0.3	0.3

light coker gas oil, and hydrocracked blending stocks. The smoke point and percent aromatics specifications limit the amount of cracked stocks which can be blended into jet fuels.

The two basic types of jet fuels are naphtha and kerosine. Naphtha jet fuel is produced primarily for the military and is a wide-boiling-range stock which extends through the gasoline and kerosine boiling ranges. The naphtha-type jet fuel is more volatile and has more safety problems in handling, but in case of a national emergency, there would be a tremendous demand for jet fuels and to meet the requirements both naphtha and kerosine production would be needed. The military is studying alternatives and the JP-8 jet fuel is being phased in. The jet fuels are blended from the various components to arrive at the lowest-cost blend that meets specifications.

Safety considerations limit commercial jet fuels to the narrower-boiling-range product [350–550°F (177–288°C)] which is sold as Jet A, Jet A-1, JP-5, or JP-50. The principal differences among these are freezing points, which range from -40 to -58°F (-40 to -50°C) maximum. In addition to freezing point, the limiting specifications are flash point [110 to 150°F (43 to 66°C)], distillation, smoke point, and aromatics content.

2.6 AUTOMOTIVE DIESEL FUELS

Volatility, ignition quality (expressed as cetane number or cetane index), viscosity, sulfur content, percent aromatics, and cloud point are the important properties

of automotive diesel fuels. No. 1 diesel fuel (sometimes called super-diesel) is generally made from virgin or hydrocracked stocks having cetane numbers above 45. It has a boiling range from 360 to 600°F (182 to 316°C) and is used in high-speed engines in automobiles, trucks, and buses.

No. 2 diesel fuel is very similar to No. 2 fuel oil, and has a wider boiling range than No. 1. It usually contains cracked stocks and may be blended from naphtha, kerosine, and light cracked oils from the coker and the fluid catalytic cracking unit. Limiting specifications are flash point [125°F (52°C)], sulfur content (0.05% max.), distillation range, cetane number or cetane index (40 min.), percent aromatics, and cloud point.

The ignition properties of diesel fuels are expressed in terms of cetane number or cetane index. These are very similar to the octane number (except the opposite) and the cetane number expresses the volume percent of cetane ($C_{16}H_{34}$, high-ignition quality) in a mixture with alpha-methyl-naphthalene ($C_{11}H_{10}$, low-ignition quality). The fuel is used to operate a standard diesel test engine according to ASTM test method D-613. Since many refineries do not have cetane test engines, a mathematical expression developed to estimate the cetane number is used. The number derived is called the cetane index and is calculated from the mid-boiling point and gravity of the sample. This equation uses the same parameters as the Watson or UOP correlation factor (K) and U.S. Bureau of Mines Correlation Index (CI) and is actually an expression of the hydrogen/carbon ratio of the hydrocarbon components in the sample; the higher the H/C ratio, the better the burning characteristics (i.e., the higher the smoke point and the higher the cetane index).

To improve air quality, more severe restrictions are placed on the sulfur and aromatic contents of diesel fuels. As the cetane index is an indicator of the H/C ratio, it is also an indirect indicator of the aromatic content of the diesel fuel. Therefore, frequently a minimum cetane index specification is used as an alternative to maximum aromatics content. Lowering sulfur and aromatics contents specifications also lowers the particulate emissions from diesel engines.

2.7 RAILROAD DIESEL FUELS

Railroad diesel engine fuel [4] is one of the significant markets for diesel fuels. Railroad diesel fuels are similar to the heavier automotive diesel fuels but have higher boiling ranges [up to 750°F (400°C) end point] and lower cetane numbers (30 min.). No. 4 diesel and No. 4 fuel oil have very similar specifications.

2.8 HEATING OILS

Although the consumption of petroleum products for space heating ranks very high, the consumption varies widely according to locality and climate. In recent years the proportional demand for heating oils has decreased as LPG usage has increased. The ASTM specifications for heating oils are given in Table 2.9. The principal distillate fuel oils consist of No. 1 and No. 2 fuel oils. No. 1 fuel oil is very similar to kerosine, but generally has a higher pour point and end point. Limiting specifications are distillation, pour point, flash point, and sulfur content.

No. 2 fuel oil is very similar to No. 2 diesel fuel, contains cracked stock, and is blended from naphtha, kerosine, diesel, and cracked gas oils. Limiting specifications are sulfur content, pour point, distillation, and flash point.

Table 2.9 Heating Oil Specifications (ASTM D-396)

	No. 1	No. 2	No. 4	No. 6
Flashpoint, °F (°C), min.	100 (38)	100 (38)	130 (55)	140 (60)
Pour point, °F (°C), max.	9 (-18)	28 (-6)	28 (-6)	—
Distillation temp., °F (°C)				
10% recovered, max.	419 (215)	—	—	—
90% recovered, min.	—	540 (282)	—	—
Max.	550 (288)	640 (338)	—	—
Viscosity, mm ² /s				
at 104°F (40°C)				
Min.	1.3	1.9	>5.5	—
Max.	2.1	3.4	24.0	—
at 212° F (100°C)				
Min.	—	—	—	15.0
Max.	—	—	—	50.0
Density, kg/m ³ 60°F (15°C)				
Max. (°API min.)	850 (35)	876 (30)	—	—
Ramsbottom carbon residue on	0.15	0.35	—	—
10% btms, wt%, max.				
Ash, wt%, max.	—	—	0.10	—
Sulfur, wt%, max.	0.50	0.50	—	—
Water and sediment, vol%,	0.05	0.05	0.50	2.00
max.				

2.9 RESIDUAL FUEL OILS

Most of the residual fuel oil used in the United States is imported. It is composed of the heaviest parts of the crude and is generally the fractionating tower bottoms from vacuum distillation. It sells for a very low price (historically about 70% of the price of crude from which it is produced) and is considered a by-product. Critical specifications are viscosity and sulfur content. Sulfur content specifications are generally set by the locality in which it is burned. Currently only low-sulfur fuel oils can be burned in some areas and this trend will continue to expand. Heavy fuel oils with very low sulfur contents are much in demand and sell at prices near those of the crude oils from which they are derived.

NOTES

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2. W. F. Bland and R. L. Davidson, Eds., *Petroleum Processing Handbook* (McGraw-Hill Book Company, New York, 1967), pp. 1–11.
3. Ibid., pp. 11–12.
4. Ibid., pp. 11–39.
5. W. A. Gruse and D. R. Stevens, *Chemical Technology of Petroleum*, 3rd Ed. (McGraw-Hill Book Company, New York, 1960), pp. 424–472.
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8. M. E. Reno, U. S. Bozzano, and W. C. Tieman, UOP 1990 Technology Conference (UOP, Des Plaines, IL, 1990).
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3

Refinery Feedstocks

The basic raw material for refineries is petroleum or crude oil, even though in some areas synthetic crude oils from other sources (Gilsonite, tar sands, etc.) and natural gas liquids are included in the refinery feedstocks. The chemical compositions of crude oils are surprisingly uniform even though their physical characteristics vary widely. The elementary composition of crude oil usually falls within the following ranges.

Element	Percent by weight
Carbon	84–87
Hydrogen	11–14
Sulfur	0–3
Nitrogen	0–0.6

In the United States, crude oils are classified as paraffin base, naphthene base, asphalt base, or mixed base. There are some crude oils in the Far East which have up to 80% aromatic content, and these are known as aromatic-base oils. The U.S. Bureau of Mines [1,2] has developed a system which classifies the crude according to two key fractions obtained in distillation: No. 1 from 482 to 527°F (250 to 275°C) at atmospheric pressure and No. 2 from 527 to 572°F (275 to 300°C) at 40 mmHg pressure. The gravity of these two fractions is used to classify crude oils into types as shown below.

	Key fractions, °API	
	No. 1	No. 2
Paraffin	40	30
Paraffin, intermediate	40	20–30
Intermediate, paraffin	33–40	30
Intermediate	33–40	20–30
Intermediate, naphthene	33–40	20
Naphthene, intermediate	33	20–30
Naphthene	<33	<20

The paraffinic and asphaltic classifications in common use are based on the properties of the residuum left from nondestructive distillation and are more descriptive to the refiner because they convey the nature of the products to be expected and the processing necessary.

3.1 CRUDE OIL PROPERTIES

Crude petroleum is very complex and, except for the low-boiling components, no attempt is made by the refiner to analyze for the pure components contained in the crude oil. Relatively simple analytical tests are run on the crude and the results of these are used with empirical correlations to evaluate the crude oils as feedstocks for the particular refinery. Each crude is compared with the other feedstocks available and, based upon the operating cost and product realization, is assigned a value. The more useful properties are discussed.

API Gravity

The density of petroleum oils is expressed in the United States in terms of API gravity rather than specific gravity; it is related to specific gravity in such a fashion that an increase in API gravity corresponds to a decrease in specific gravity. The units of API gravity are °API and can be calculated from specific gravity by the following:

$$\text{°API} = \frac{141.5}{\text{specific gravity}} - 131.5 \quad (1)$$

In equation (1), specific gravity and API gravity refer to the weight per unit volume at 60°F as compared to water at 60°F. Crude oil gravity may range

from less than 10°API to over 50°API but most crudes fall in the 20 to 45°API range. API gravity always refers to the liquid sample at 60°F (15.6°C). API gravities are not linear and, therefore, cannot be averaged. For example, a gallon of 30°API gravity hydrocarbons when mixed with a gallon of 40°API hydrocarbons will not yield two gallons of 35°API hydrocarbons, but will give two gallons of hydrocarbons with an API gravity different from 35°API. Specific gravities can be averaged.

Sulfur Content, wt%

Sulfur content and API gravity are two properties which have had the greatest influence on the value of crude oil, although nitrogen and metals contents are increasing in importance. The sulfur content is expressed as percent sulfur by weight and varies from less than 0.1% to greater than 5%. Crudes with greater than 0.5% sulfur generally require more extensive processing than those with lower sulfur content. Although the term "sour" crude initially had reference to those crudes containing dissolved hydrogen sulfide independent of total sulfur content, it has come to mean any crude oil with a sulfur content high enough to require special processing. There is no sharp dividing line between sour and sweet crudes, but 0.5% sulfur content is frequently used as the criterion.

Pour Point, °F (°C)

The pour point of the crude oil, in °F or °C, is a rough indicator of the relative paraffinicity and aromaticity of the crude. The lower the pour point, the lower the paraffin content and the greater the content of aromatics.

Carbon Residue, wt%

Carbon residue is determined by distillation to a coke residue in the absence of air. The carbon residue is roughly related to the asphalt content of the crude and to the quantity of the lubricating oil fraction that can be recovered. In most cases the lower the carbon residue, the more valuable the crude. This is expressed in terms of the weight percent carbon residue by either the Ramsbottom (RCR) or Conradson (CCR) ASTM test procedures (D-524 and D-189).

Salt Content, lb/1000 bbl

If the salt content of the crude, when expressed as NaCl, is greater than 10 lb/1000 bbl, it is generally necessary to desalt the crude before processing. If the salt is not removed, severe corrosion problems may be encountered. If residua are processed catalytically, desalting is desirable at even lower salt contents of

the crude. Although it is not possible to have an accurate conversion unit between lb/1000 bbl and ppm by weight because of the different densities of crude oils, 1 lb/1000 bbl is approximately 3 ppm.

Characterization Factors

There are several correlations between yield and the aromaticity and paraffinicuity of crude oils, but the two most widely used are the UOP or Watson "characterization factor" (K_w) and the U.S. Bureau of Mines "correlation index" (CI).

$$K_w = \frac{T_B^{1/3}}{G} \quad (2)$$

$$CI = \frac{87,552}{T_B} + 473.7G - 456.8 \quad (3)$$

where

T_B = mean average boiling point, °R

G = specific gravity at 60°F.

The Watson characterization factor ranges from less than 10 for highly aromatic materials to almost 15 for highly paraffinic compounds. Crude oils show a narrower range of K_w and vary from 10.5 for a highly naphthenic crude to 12.9 for a paraffinic base crude.

The correlation index is useful in evaluating individual fractions from crude oils. The CI scale is based upon straight-chain paraffins having a CI value of 0 and benzene having a CI value of 100. The CI values are not quantitative, but the lower the CI value, the greater the concentrations of paraffin hydrocarbons in the fraction; and the higher the CI value, the greater the concentrations of naphthenes and aromatics [3].

Nitrogen Content, wt%

A high nitrogen content is undesirable in crude oils because organic nitrogen compounds cause severe poisoning of catalysts used in processing and cause corrosion problems such as hydrogen blistering. Crudes containing nitrogen in amounts above 0.25% by weight require special processing to remove the nitrogen.

Distillation Range

The boiling range of the crude gives an indication of the quantities of the various products present. The most useful type of distillation is known as a true boiling

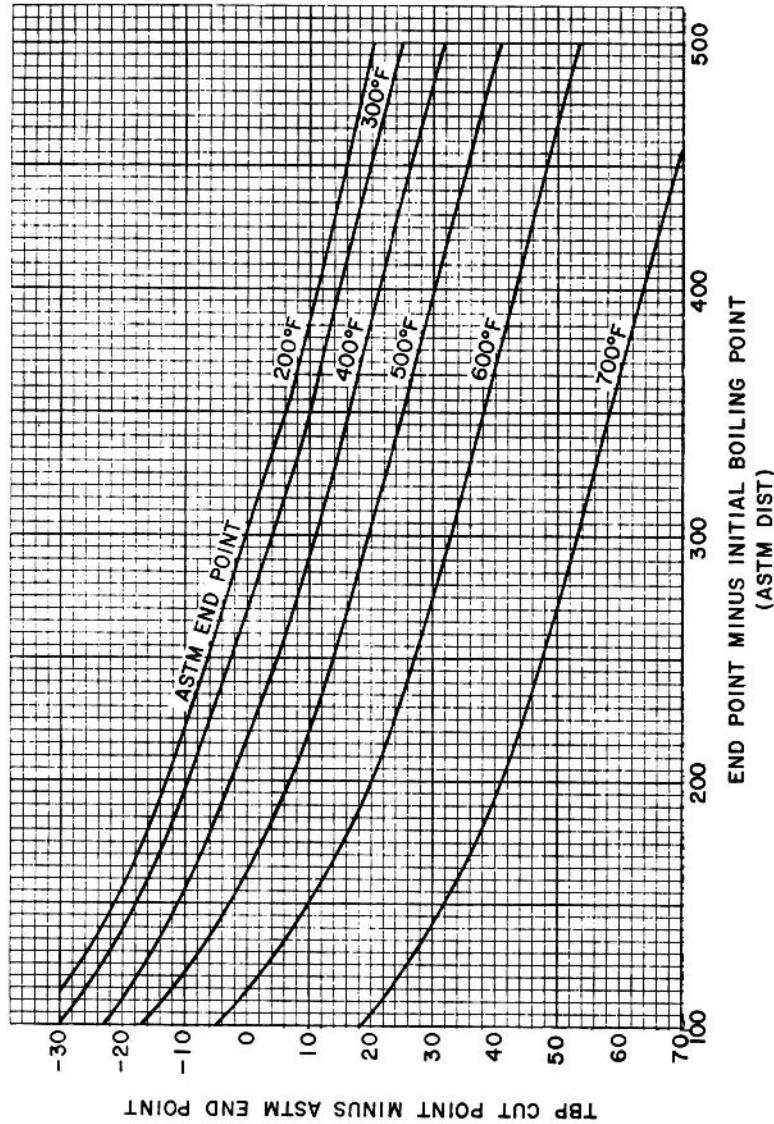


Figure 3.1 TBP cut point versus ASTM end point.

point (TBP) distillation and generally refers to a distillation performed in equipment that accomplishes a reasonable degree of fractionation. There is no specific test procedure called a TBP distillation, but the U.S. Bureau of Mines Hempel and ASTM D-285 distillations are the tests most commonly used. Neither of these specify either the number of theoretical plates or the reflux ratio used and, as a result, there is a trend toward using the results of a 15:5 distillation (D-2892) rather than the TBP. The 15:5 distillation is carried out using 15 theoretical plates at a reflux ratio of 5:1.

The crude distillation range also has to be correlated with ASTM distillations because product specifications are generally based on the simple ASTM distillation tests D-86 and D-1160. The TBP cut point for various fractions can be approximated by use of Figure 3.1. A more detailed procedure for correlation of ASTM and TBP distillations is given in the *API Technical Data Book—Petroleum Refining* published by the American Petroleum Institute, Washington, DC.

Metals Content, ppm

The metals content of crude oils can vary from a few parts per million to more than 1000 ppm and, in spite of their relatively low concentrations, are of considerable importance [4]. Minute quantities of some of these metals (nickel, vanadium, and copper) can severely affect the activities of catalysts and result in a lower-value product distribution. Vanadium concentrations above 2 ppm in fuel oils can lead to severe corrosion to turbine blades and deterioration of refractory furnace linings and stacks [2].

Distillation concentrates the metallic constituents of crude in the residues, but some of the organometallic compounds are actually volatilized at refinery distillation temperatures and appear in the higher-boiling distillates [5].

The metallic content may be reduced by solvent extraction with propane or similar solvents as the organometallic compounds are precipitated with the asphaltenes and resins.

3.2 COMPOSITION OF PETROLEUM

Crude oils and high-boiling crude oil fractions are composed of many members of a relatively few homologous series of hydrocarbons [6]. The composition of the total mixture, in terms of elementary composition, does not vary a great deal, but small differences in composition can greatly affect the physical properties and the processing required to produce salable products. Petroleum is essentially a mixture of hydrocarbons, and even the non-hydrocarbon elements are generally present as components of complex molecules predominantly hydrocarbon in character, but containing small quantities of oxygen, sulfur, nitrogen, vanadium,

nickel, and chromium [4]. The hydrocarbons present in crude petroleum are classified into three general types: paraffins, naphthenes, and aromatics. In addition, there is a fourth type, olefins, that is formed during processing by the dehydrogenation of paraffins and naphthenes.

Paraffins

The paraffin series of hydrocarbons is characterized by the rule that the carbon atoms are connected by a single bond and the other bonds are saturated with hydrogen atoms. The general formula for paraffins is C_nH_{2n+2} .

The simplest paraffin is methane, CH_4 , followed by the homologous series of ethane, propane, normal and isobutane, normal, iso-, and neopentane, etc. (Fig. 3.2). When the number of carbon atoms in the molecule is greater than three, several hydrocarbons may exist which contain the same number of carbon and hydrogen atoms but have different structures. This is because carbon is capable not only of chain formation, but also of forming single- or double-branched chains which give rise to isomers that have significantly different properties. For example, the motor octane number of n-octane is -17 and that of iso-octane (2,2,4-trimethyl pentane) is 100.

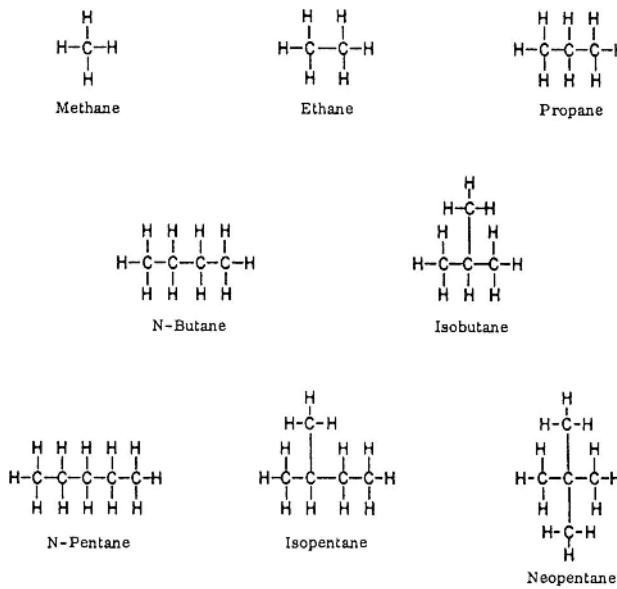


Figure 3.2 Paraffins in crude oil.

The number of possible isomers increases in geometric progression as the number of carbon atoms increases. There are two paraffin isomers of butane, three of pentane, 17 structural isomers of octane and, by the time the number of carbon atoms has increased to 18, there are 60,533 isomers of cetane. Crude oil contains molecules with up to 70 carbon atoms, and the number of possible paraffinic hydrocarbons is very high.

Olefins

Olefins do not naturally occur in crude oils but are formed during the processing. They are very similar in structure to paraffins but at least two of the carbon atoms are joined by double bonds. The general formula is C_nH_{2n} . Olefins are generally undesirable in finished products because the double bonds are reactive and the compounds are more easily oxidized and polymerized to form gums and varnishes. In gasoline boiling-range fractions, some olefins are desirable because

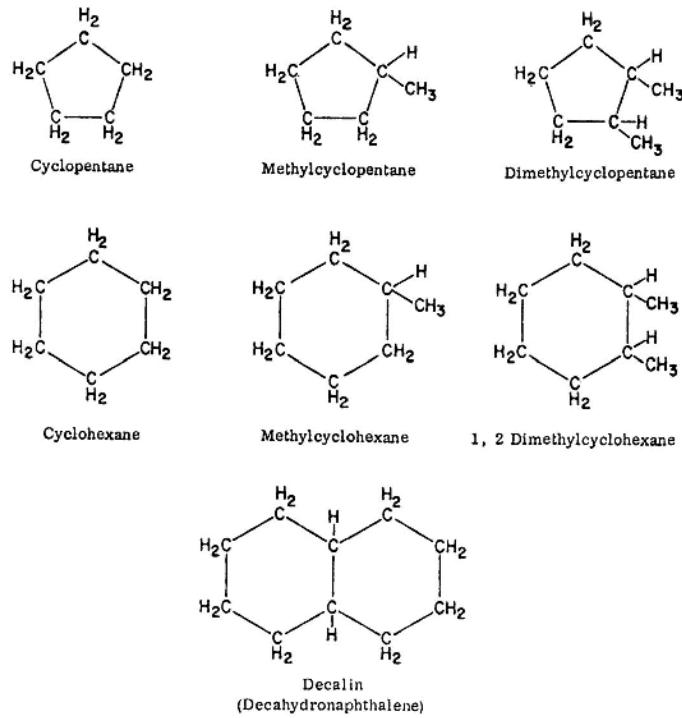


Figure 3.3 Naphthenes in crude oil.

olefins have higher research octane numbers than paraffin compounds with the same number of carbon atoms. Olefins containing five carbon atoms have high reaction rates with compounds in the atmosphere that form pollutants and, even though they have high research octane numbers, are considered generally undesirable.

Some diolefins (containing two double bonds) are also formed during processing, but they react very rapidly with olefins to form high-molecular-weight polymers consisting of many simple unsaturated molecules joined together. Diolefins are very undesirable in products because they are so reactive they polymerize and form filter and equipment plugging compounds.

Naphthenes (Cycloparaffins)

Cycloparaffin hydrocarbons in which all of the available bonds of the carbon atoms are saturated with hydrogen are called naphthenes. There are many types

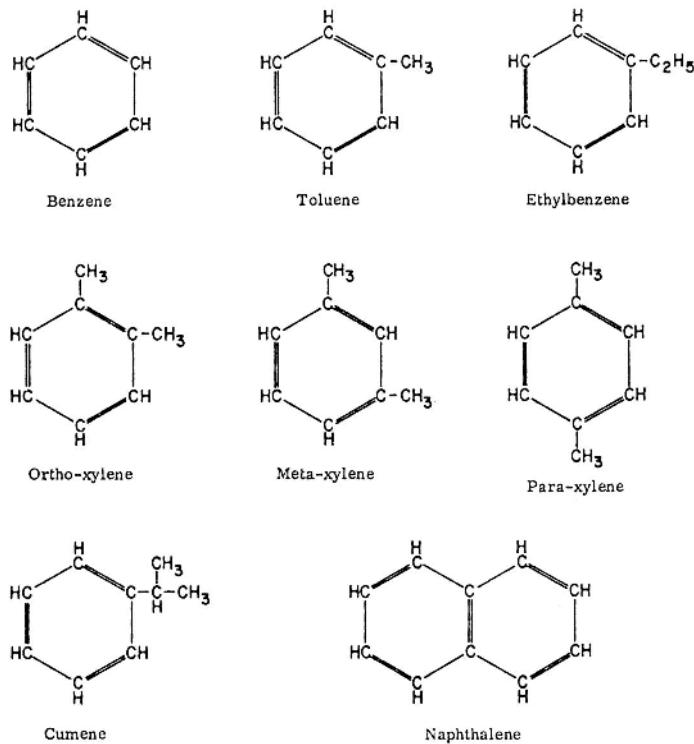


Figure 3.4 Aromatic hydrocarbons in crude oil.

of naphthenes present in crude oil, but, except for the lower-molecular-weight compounds such as cyclopentane and cyclohexane, are generally not handled as individual compounds. They are classified according to boiling range and their properties determined with the help of correlation factors such as the K_w factor or CI. Some typical naphthenic compounds are shown in Figure 3.3.

Aromatics

The aromatic series of hydrocarbons is chemically and physically very different from the paraffins and cycloparaffins (naphthenes). Aromatic hydrocarbons contain a benzene ring which is unsaturated but very stable and frequently behaves as a saturated compound. Some typical aromatic compounds are shown in Figure 3.4.

The cyclic hydrocarbons, both naphthenic and aromatic, can add paraffin side chains in place of some of the hydrogen attached to the ring carbons and form a mixed structure. These mixed types have many of the chemical and physical characteristics of both of the parent compounds, but generally are classified according to the parent cyclic compound.

3.3 CRUDES SUITABLE FOR ASPHALT MANUFACTURE

It is not possible to predict with 100% accuracy whether or not a particular crude will produce specification asphalts without actually separating the asphalts from the crude and running the tests. There are, however, certain characteristics of crude oils that indicate if they are possible sources of asphalt. If the crude oil contains a residue [750°F (399°C)] mean average boiling point having a Watson characterization factor of less than 11.8 and the gravity is below 35°API, it is usually suitable for asphalt manufacture [7]. If, however, the difference between the characterization factors for the 750°F and 550°F fraction is greater than 0.15, the residue may contain too much wax to meet most asphalt specifications.

3.4 CRUDE DISTILLATION CURVES

When a refining company evaluates its own crude oils to determine the most desirable processing sequence to obtain the required products, its own laboratories will provide data concerning the distillation and processing of the oil and its fractions [8]. In many cases, information not readily available is desired concerning the processing qualities of crude oils. In such instances, true boiling point (TBP) and gravity-midpercent curves can be developed from U.S. Bureau of Mines crude petroleum analysis data sheets (Fig. 3.5).

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 53016

IDENTIFICATION

Hastings Field

Texas
Brazoria County

GENERAL CHARACTERISTICS

Gravity, specific, 0.867	Gravity, ° API, 31.7	Pour point, ° F., below 5
Sulfur, percent, 0.15		Color, brownish green
Viscosity, Saybolt Universal at 100°		Nitrogen, percent,

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 751 mm. Hg
First drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_{20}° at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.8	0.8	0.673	78.8					
2	167	1.0	1.8	.685	75.1	15				
3	212	3.0	4.8	.725	63.7	24	1.39574	127.7		
4	257	3.4	8.2	.755	55.9	29	1.41756	128.6		
5	302	3.1	11.3	.777	50.6	32	1.42985	135.4		
6	347	3.9	15.2	.798	45.8	35	1.44192	137.8		
7	392	4.9	20.1	.817	41.7	38	1.45217	139.9		
8	437	6.8	26.9	.833	38.4	40	1.46057	140.3		
9	482	8.0	34.9	.848	35.4	41	1.46875	148.0		
10	527	10.9	45.8	.864	32.3	44	1.47679	149.8		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	7.3	53.1	0.873	30.6	45	1.48274	155.2	42	Below 5
12	437	7.8	60.9	.879	29.5	44	1.48474	156.2	50	do
13	482	6.2	67.1	.889	27.7	45	1.49058	152.7	71	do
14	527	5.7	72.8	.901	25.6	48			125	10
15	572	6.9	79.7	.916	28.0	52			280	20
Residuum		20.3	100.0	.945	18.2					

Carbon residue, Conradson: Residuum, 4.7 percent; crude, 1.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	4.8	0.708	68.4	
Total gasoline and naphtha	20.1	0.771	52.0	
Kerosine distillate	—	—	—	
Gas oil	36.9	0.858	33.4	
Nonviscous lubricating distillate	10.2	.879-.895	29.5-26.6	50-100
Medium lubricating distillate	5.8	.895-.908	26.6-24.3	100-200
Viscous lubricating distillate	6.7	.908-.924	24.3-21.6	Above 200
Residuum	20.3	0.945	18.2	
Distillation loss	0			

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Figure 3.5 U.S. Bureau of Mines crude petroleum analysis.

The U.S. Bureau of Mines has carried out Hempel distillations on thousands of crude oil samples from wells in all major producing fields. Although the degree of fractionation in a Hempel assay is less than that in a 15:5 distillation, the results are sufficiently similar that they can be used without correction. If desired, correction factors developed by Nelson [9] can be applied.

The major deficiency in a Bureau of Mines assay is the lack of information concerning the low-boiling components. The materials not condensed by water-cooled condensers are reported as "distillation loss." An estimate of the composition of the butane and lighter components is frequently added to the low-boiling end of the TBP curve to compensate for the loss during distillation.

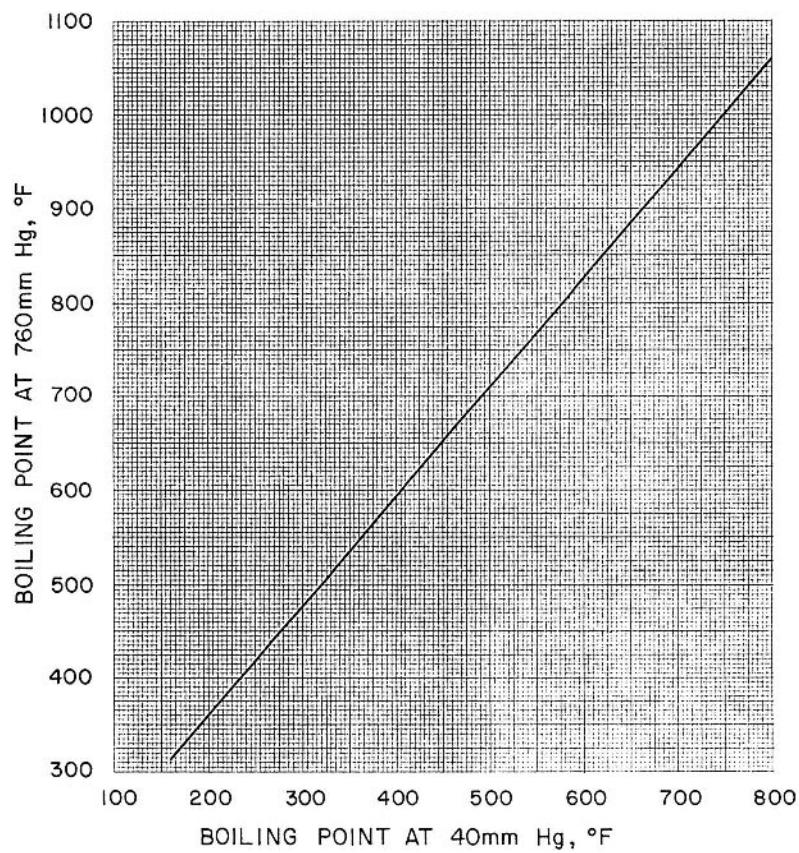


Figure 3.6 Boiling point at 760 mmHg versus boiling point at 40 mmHg.

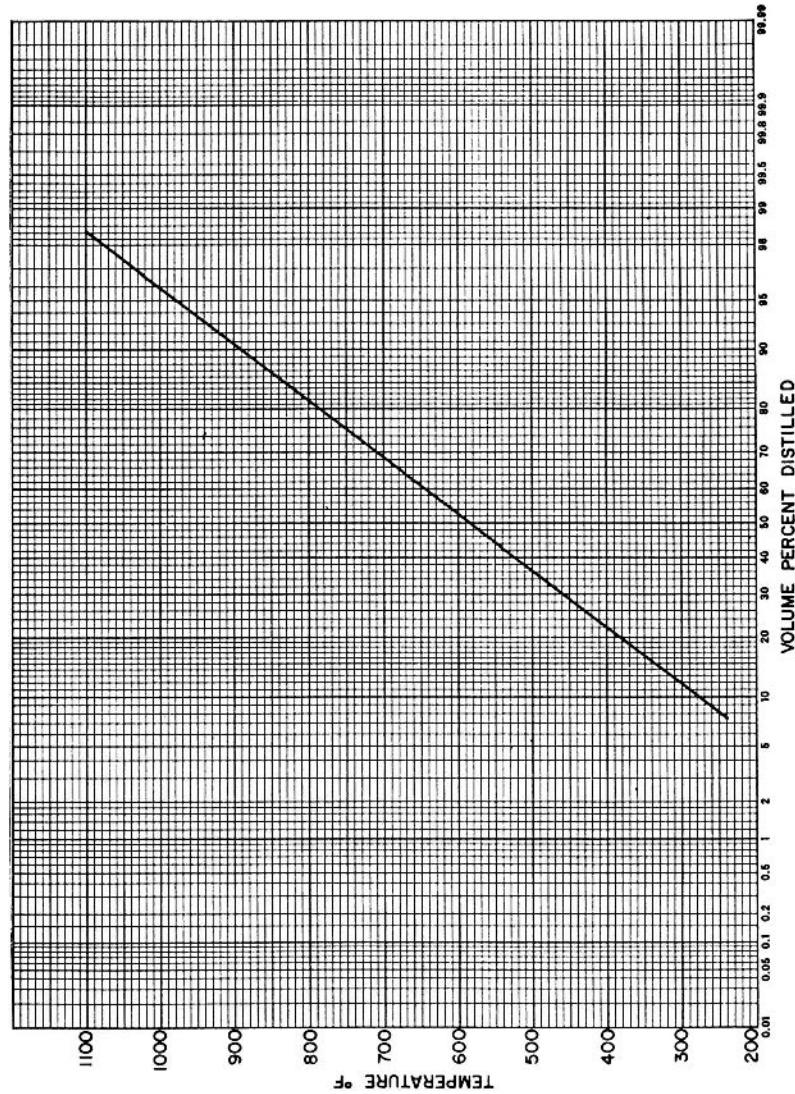


Figure 3.7 Crude distillation curve.

The Bureau of Mines analysis is reported in two parts: the first is the portion of the distillation performed at atmospheric pressure and up to 527°F (275°C) end point, the second at 40 mmHg total pressure to 572°F (300°C) end point. The portion of the distillation at reduced pressure is necessary to prevent excessive pot temperatures, which cause cracking of the crude oil.

The distillation temperatures reported in the analysis must be corrected to 760 mmHg pressure. Generally, those reported in the atmospheric distillation section need not be corrected, but if carried out at high elevations it may also

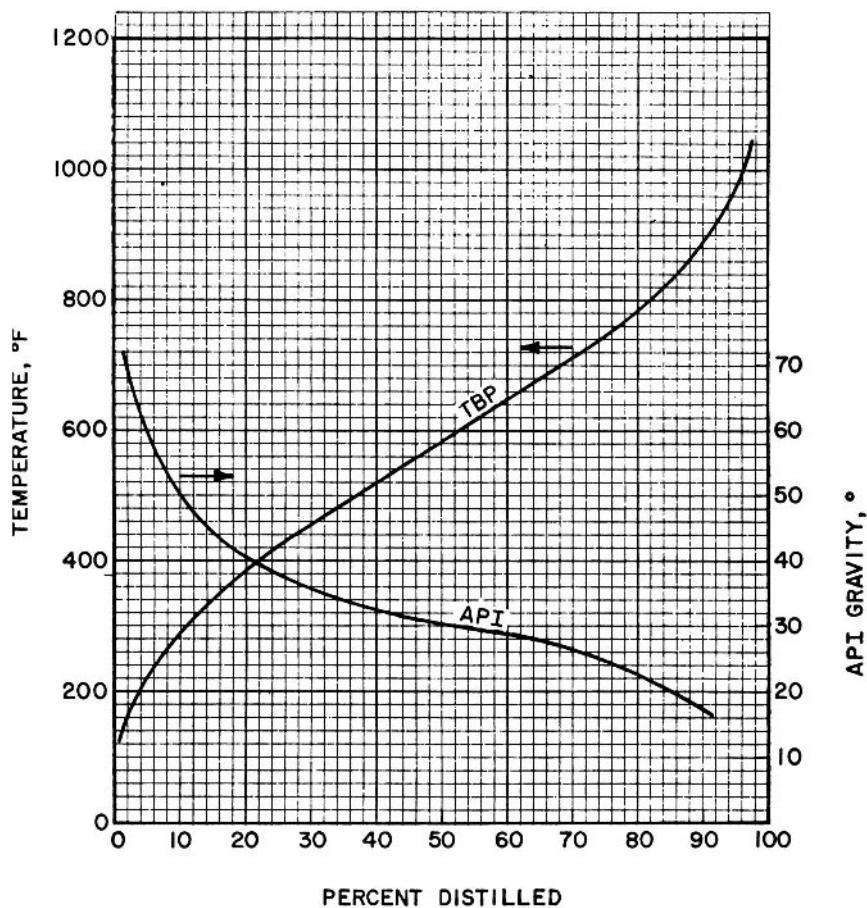


Figure 3.8 TBP and gravity-midpercent curves. Hastings Field, Texas crude: gravity, 31.7°API; sulfur, 0.15 wt%.

be necessary to correct these. The distillation temperatures at 40 mmHg pressure can be converted to 760 mmHg by use of charts developed by Esso Research and Engineering Company [6]. Figure 3.6 shows the relationships between boiling temperatures at 40 mmHg and 760 mmHg pressure.

The 572°F (300°C) end point at 40 mmHg pressure corresponds to 790°F (421°C) at 760 mmHg. Refinery crude oil distillation practices take overhead streams with end points from 950 to 1050°F (510 to 566°C) at 760 mmHg. Estimates of the shape of the TBP curve above 790°F (421°C) can be obtained by plotting the distillation temperature versus percentage distilled on probability graph paper and extrapolating to 1100°F (593°C) [11]. (See Fig. 3.7.) The data points above 790°F (421°C) can be transferred to the TBP curve.

The gravity mid-percent curve is plotted on the same chart with the TBP curve. The gravity should be plotted on the average volume percent of the fraction, as the gravity is the average of the gravities from the first to the last drops in the fraction. For narrow cuts, a straight-line relationship can be assumed and the gravity used as that of the mid-percent of the fraction.

Smooth curves are drawn for both the TBP and gravity mid-percent curves. Figure 3.8 illustrates these curves for the crude oil reported in Figure 3.5.

PROBLEMS

1. Develop a TBP and gravity-midpercent curve for one of the crude oils given in Appendix D.
2. Using the TBP and gravity curves from problem 1, calculate the Watson characterization factors for the fractions having mean average boiling points of 550°F (288°C) and 750°F (399°C). Is it probable this crude oil will produce a satisfactory quality asphalt?
3. Using the U.S. Bureau of Mines method for classifying crude oils from the gravities of the 482 to 527°F (250 to 275°C) and 527 to 572°F (275 to 300°C) fractions, classify the crude oil used in problem 1 according to type.

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4

Crude Distillation

The crude stills are the first major processing units in the refinery. They are used to separate the crude oils by distillation into fractions according to boiling point so that each of the processing units following will have feedstocks that meet their particular specifications. Higher efficiencies and lower costs are achieved if the crude oil separation is accomplished in two steps: first by fractionating the total crude oil at essentially atmospheric pressure; then by feeding the high-boiling bottoms fraction (topped or atmospheric reduced crude) from the atmospheric still to a second fractionator operated at a high vacuum. (See Photo 2, Appendix E.)

The vacuum still is employed to separate the heavier portion of the crude oil into fractions because the high temperatures necessary to vaporize the topped crude at atmospheric pressure cause thermal cracking to occur, with the resulting loss to dry gas, discoloration of the product, and equipment fouling due to coke formation.

Typical fraction cut points and boiling ranges for atmospheric and vacuum still fractions are given in Tables 4.1 and 4.2.

Relationships among the volume-average, molal-average, and mean-average boiling points of the crude oil fractions are shown in Figure 4.1a and b.

Nitrogen and sulfur contents of petroleum fractions as functions of original crude oil contents are given in Figures 4.2–4.5.

4.1 DESALTING CRUDE OILS

If the salt content of the crude oil is greater than 10 lb/1000 bbl (expressed as NaCl), the crude requires desalting to minimize fouling and corrosion caused by salt deposition on heat transfer surfaces and acids formed by decomposition of

Note: Throughout this text the symbol M is used to represent 1000 in accordance with standard U.S. engineering practice. For example, MBPSD means 1000 BPSD and MMBtu means 1,000,000 Btu.

Table 4.1 Boiling Ranges of Typical Crude Oil Fractions

Fraction	Boiling ranges, °F	
	ASM	TBP
Butanes and lighter		
Light straight-run naphtha (LSR)	90–220	90–190
Heavy straight-run naphtha (HSR)	180–400	190–380
Kerosine	330–540	380–520
Light gas oil (LGO)	420–640	520–610
Atmospheric gas oil (AGO)	550–830	610–800
Vacuum gas oil (VGO)	750–1050	800–1050
Vacuum reduced crude (VRC)	1050+	1050+

Table 4.2 TBP Cut Points for Various Crude Oil Fractions

Cut	IBP (°F)	EP (°F)	Processing use
LSR gasoline cut	90	180	Min. light gasoline
	90	190	Normal LSR cut
	80	220	Max. LSR cut
HSR gasoline (naphtha)	180	380	Max. reforming cut
	190	330	Max. jet fuel opr.
	220	330	Min. reforming cut
Kerosine	330	520	Max. kerosine cut
	330	480	Max. jet-50 cut
	380	520	Max. gasoline operation
Light gas oil	420	610 ^a	Max. diesel fuel
	480	610 ^a	Max. jet fuel
	520	610 ^a	Max. kerosine
Heavy gas oil (HGO)	610	800	Catalytic cracker or hydrocracker feed
Vacuum gas oil	800	1050	Desphalting or catalytic cracker feed
	800	950	Catalytic cracker or hydrocracker feed

^a For maximum No. 2 diesel fuel production, end points as high as 650°F (343°C) can be used.

Note: In some specific locations, economics can dictate that all material between 330°F IBP and 800°F EP (166 to 427°C) be utilized as feed to a hydrocracker.

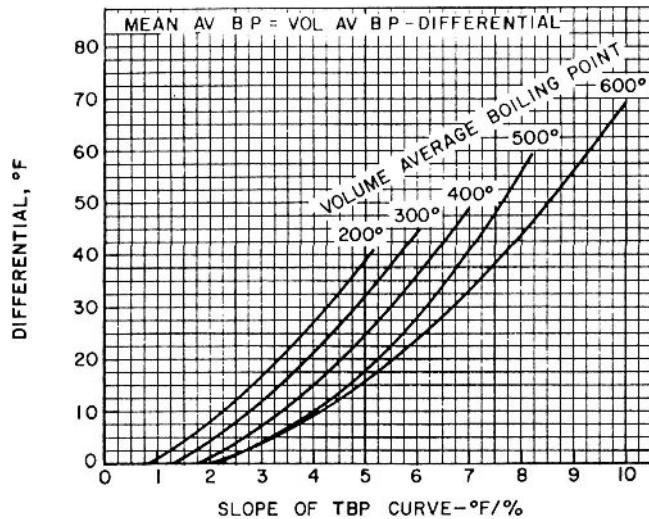


Figure 4.1a Mean average boiling point of petroleum fractions.

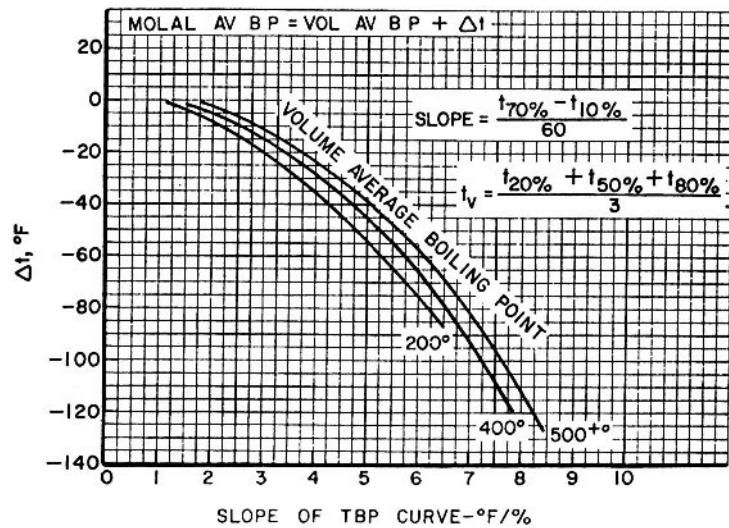


Figure 4.1b Molal average boiling point of petroleum fractions.

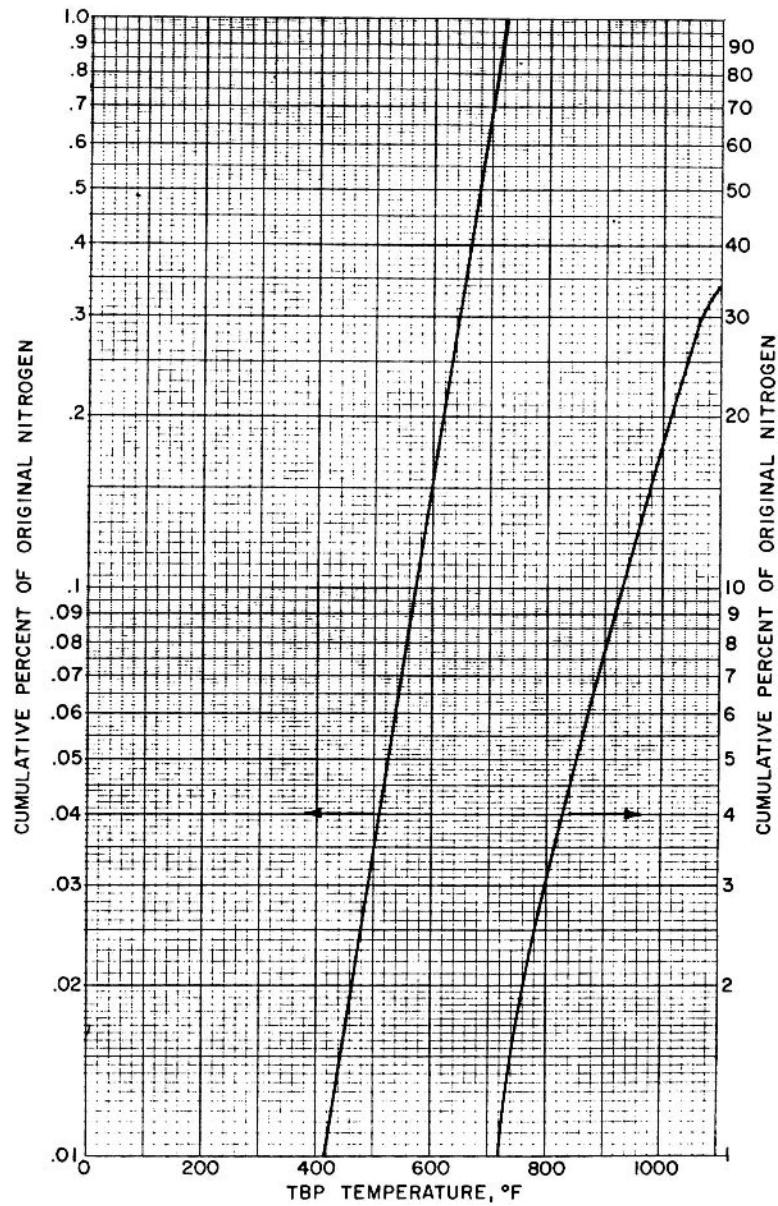
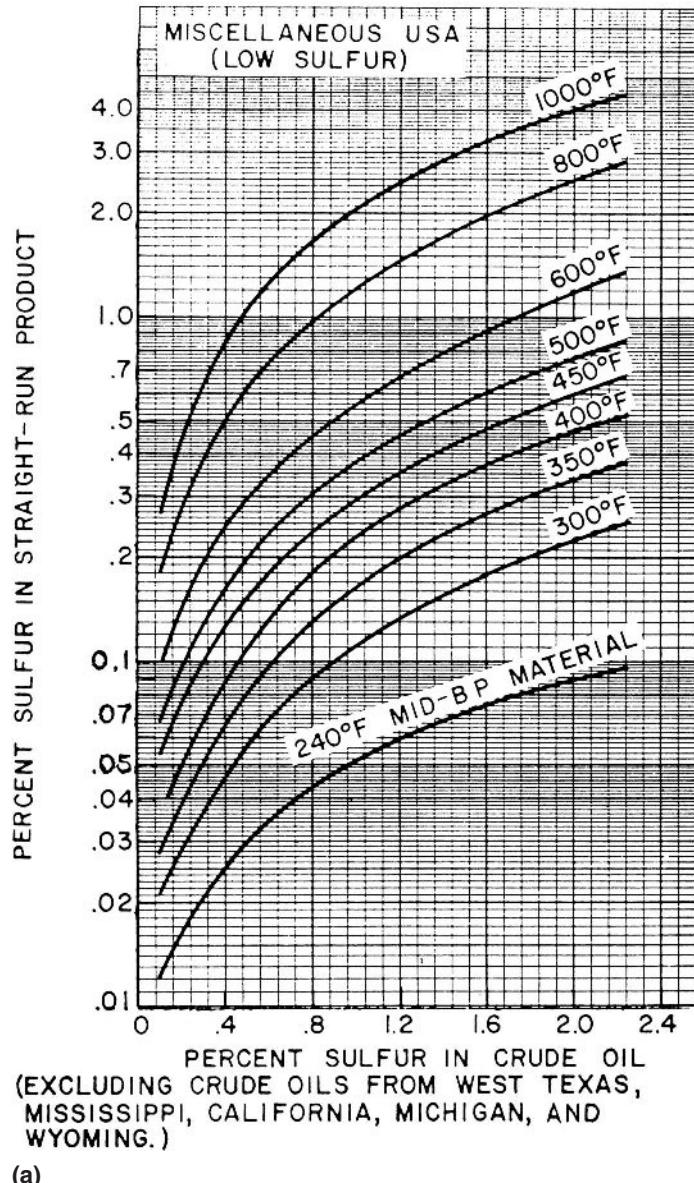


Figure 4.2 Nitrogen distributions in crude oil fractions.



(a)

Figure 4.3a Sulfur content of products from miscellaneous U.S. crude oils. (From Ref. 5.)

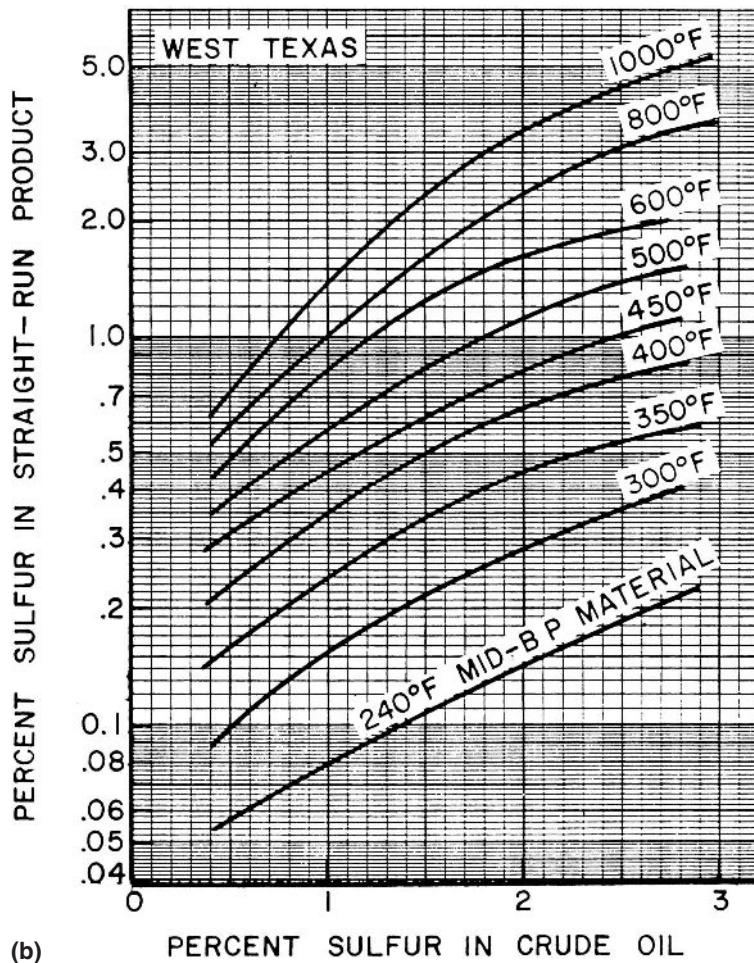


Figure 4.3b Sulfur content of products from West Texas crude oils. (From Ref. 5.)

the chloride salts. In addition, some metals in inorganic compounds dissolved in water emulsified with the crude oil, which can cause catalyst deactivation in catalytic processing units, are partially rejected in the desalting process.

The trend toward running heavier crude oils has increased the importance of efficient desalting of crudes. Until recently, the criterion for desalting crude oils was 10 lb salt/1000 bbl (expressed as NaCl) or more, but now many companies desalt all crude oils. Reduced equipment fouling and corrosion and longer catalyst life provide justification for this additional treatment. Two-stage de-

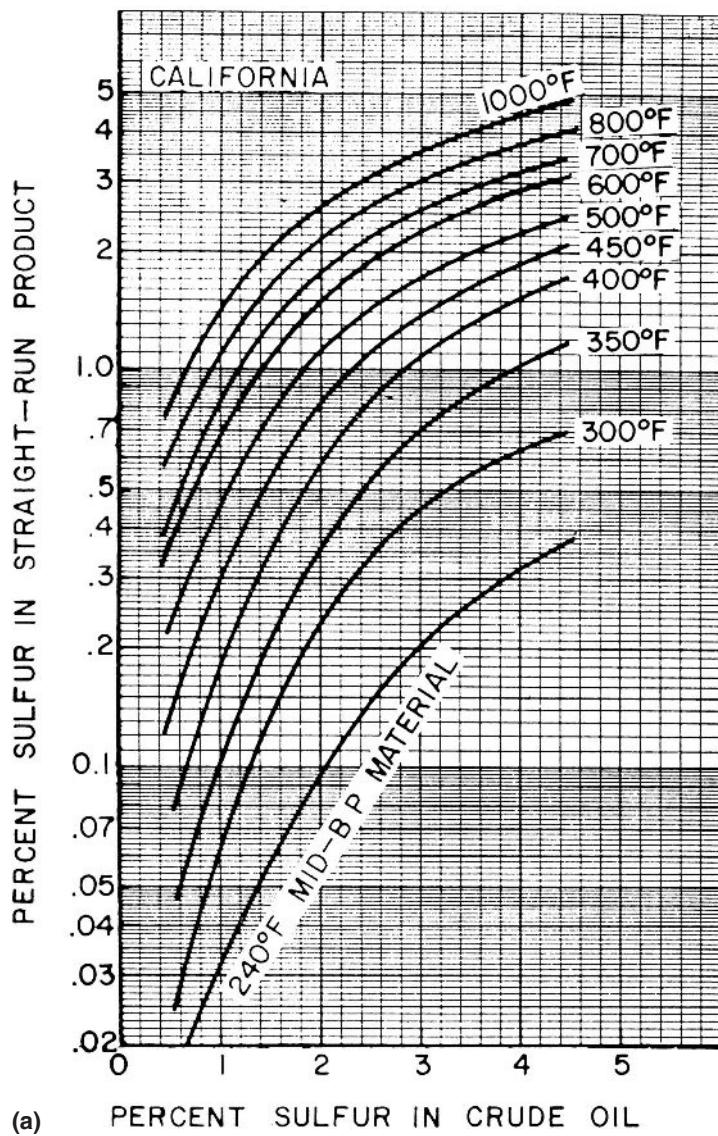


Figure 4.4a Sulfur content of products from California crude oils. (From Ref. 5.)

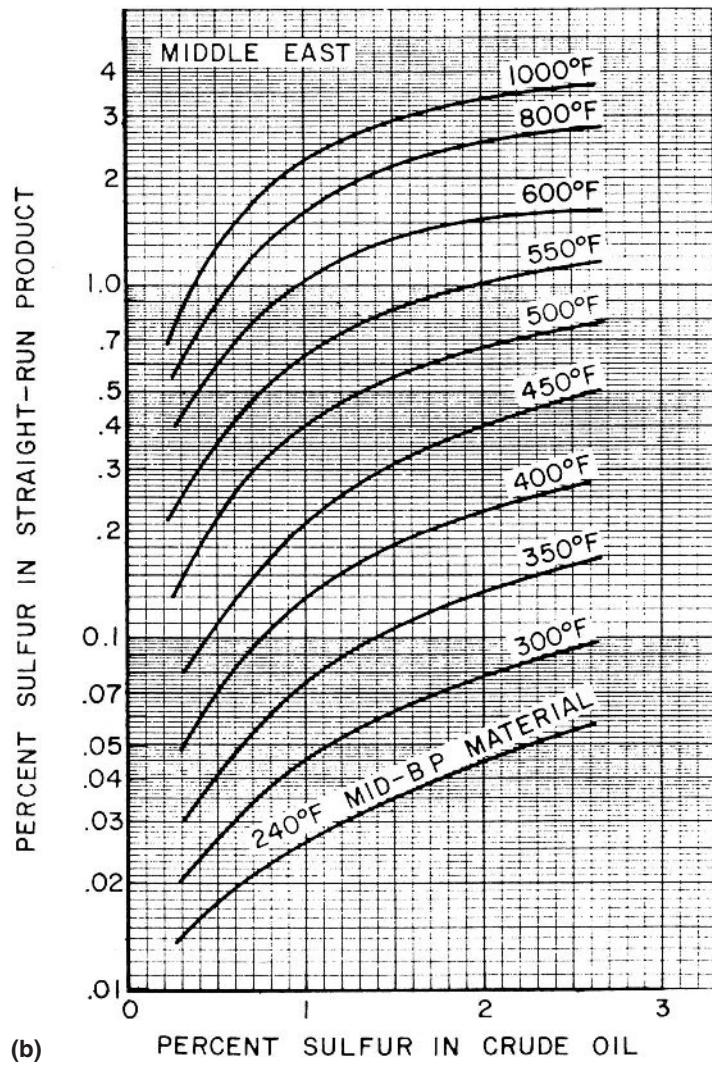


Figure 4.4b Sulfur content of products from Middle East crude oils. (From Ref. 5.)

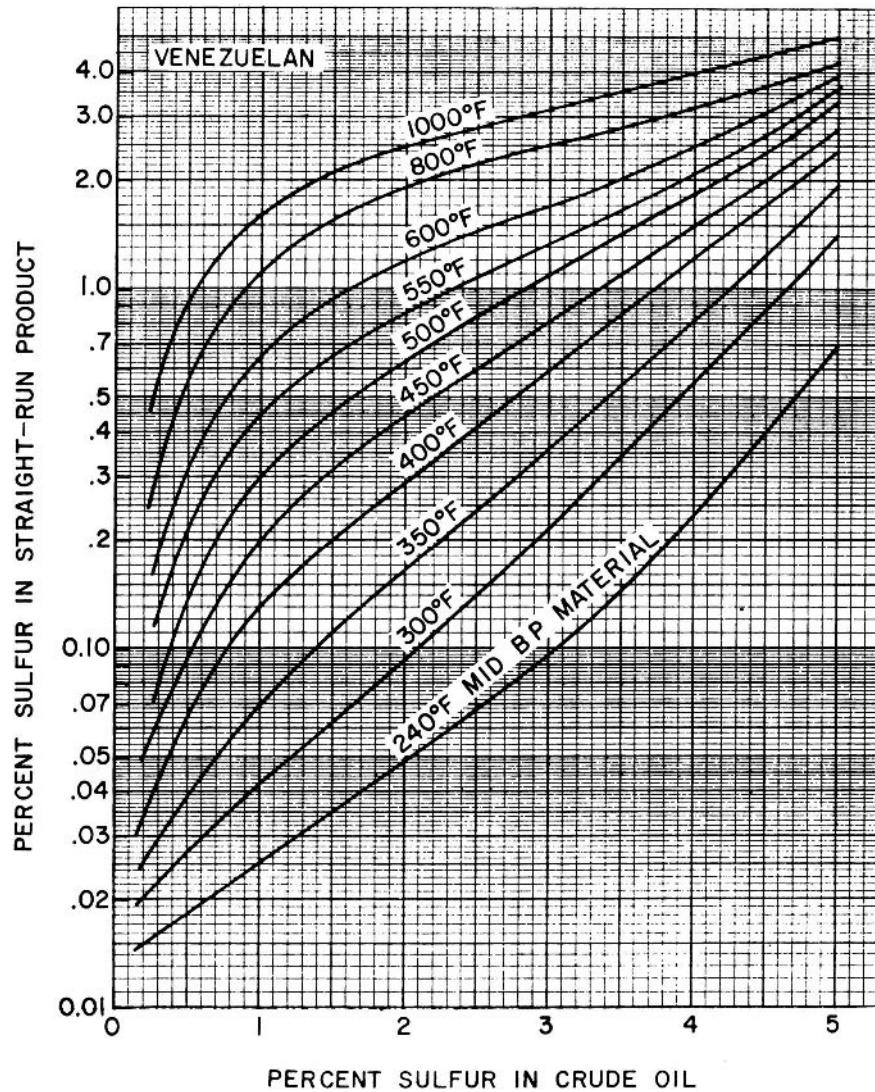


Figure 4.5 Sulfur content of products from Venezuelan crude oils. (From Ref. 5.)

salting is used if the crude oil salt content is more than 20 lb/1000 bbl and, in the cases where residua are catalytically processed, there are some crudes for which three-stage desalting is used.

The salt in the crude is in the form of dissolved or suspended salt crystals in water emulsified with the crude oil. The basic principle is to wash the salt from the crude oil with water. Problems occur in obtaining efficient and economical water/oil mixing, water-wetting of suspended solids, and separation of the wash water from the oil. The pH, gravity, and viscosity of the crude oil, as well as the volume of wash water used per volume of crude, affect the separation ease and efficiency.

A secondary but important function of the desalting process is the removal of suspended solids from the crude oil. These are usually very fine sand, clay, and soil particles; iron oxide and iron sulfide particles from pipelines, tanks, or tankers; and other contaminants picked up in transit or production. Total suspended solids removal should be 60% or better [1] with 80% removal of particles greater than 0.8 micron in size.

Desalting is carried out by mixing the crude oil with from 3 to 10 vol% water at temperatures from 200 to 300°F (90 to 150°C). Both the ratio of the water to oil and the temperature of operation are functions of the density of the oil. Typical operating conditions are [1]:

°API	Water wash, vol%	Temp. °F (°C)
>40	3–4	240–260 (115–125)
30–40	4–7	260–280 (125–140)
<30	7–10	280–330 (140–150)

The salts are dissolved in the wash water and the oil and water phases separated in a settling vessel either by adding chemicals to assist in breaking the emulsion or by developing a high-potential electrical field across the settling vessel to coalesce the droplets of salty water more rapidly (Fig. 4.6). Either AC or DC fields may be used and potentials from 12,000 to 35,000 volts are used to promote coalescence. For single-stage desalting units 90 to 95% efficiencies are obtained and two-stage processes achieve 99% or better efficiency.

One process uses both AC and DC fields to provide high dewatering efficiency. An AC field is applied near the oil–water interface and a DC field in the oil phase above the interface. Efficiencies of up to 99% water removal in a single stage are claimed for the dual field process. About 90% of desalters use AC field separation only.

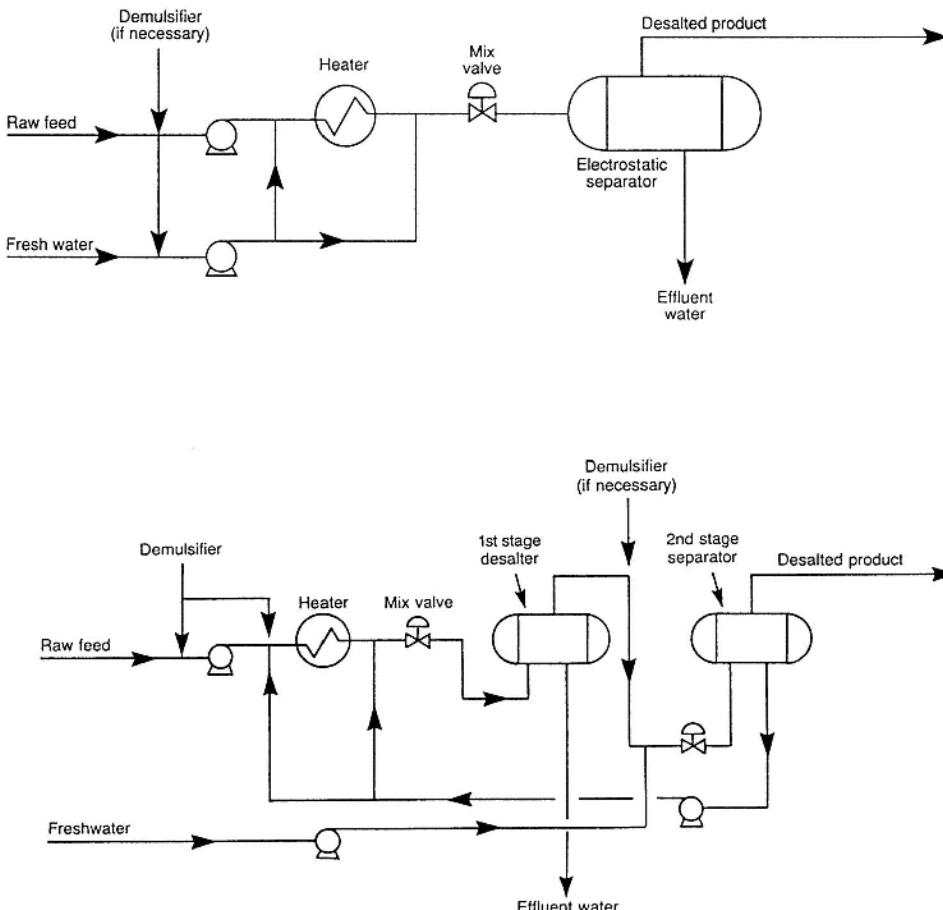


Figure 4.6 Single- and two-stage electrostatic desalting systems. (Flowsheets courtesy of Petrolite Corporation.)

The dual field electrostatic process provides efficient water separation at temperatures lower than the other processes and, as a result, higher energy efficiencies are obtained.

Heavy naphthenic crudes form more stable emulsions than most other crude oils and desalts usually operate at lower efficiencies when handling them. The crude oil densities are close to the density of water and temperature above 280°F (138°C) are needed. It is sometimes necessary to adjust the pH of the brine to obtain pH values of 7 or less in the water. If the pH of the brine exceeds 7,

emulsions can be formed because of the sodium naphthenate and sodium sulfide present. For most crude oils it is desirable to keep the pH below 8.0. Better dehydration is obtained in electrical desalters when they are operated in the pH range of 6 to 8 with the best dehydration obtained at a pH near 6. The pH value is controlled by using another water source or by the addition of acid to the inlet or recycled water.

Make-up water averages 4 to 5% on crude oil charge and is added to the second stage of a two-stage desalter. For very heavy crude oils (<15° API),

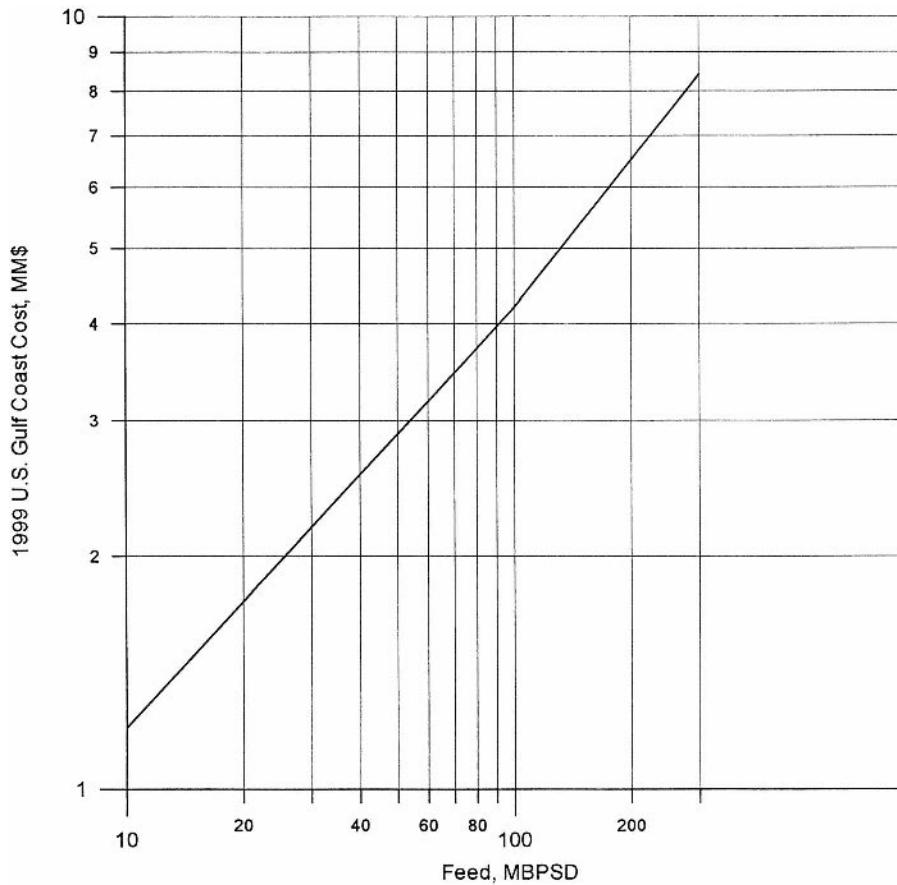


Figure 4.7 Crude oil desalting units investment cost: 1999 U.S. Gulf Coast. (See Table 4.3.)

addition of gas oil as a diluent to the second stage is recommended to provide better separation efficiencies.

Frequently, the wash water used is obtained from the vacuum crude unit barometric condensers or other refinery sources containing phenols. The phenols are preferentially soluble in the crude oil thus reducing the phenol content of the water sent to the refinery waste water handling system.

Suspended solids are one of the major causes of water-in-oil emulsions. Wetting agents are frequently added to improve the water wetting of solids and reduce oil carry-under in desalters. Oxyalkylated alkylphenols and sulfates are the most frequently used wetting agents.

The following analytical methods are used to determine the salt content of crude oils:

1. HACH titration with mercuric nitrate after water extraction of the salt
2. Potentiometric titration after water extraction
3. Mohr titration with silver nitrate after water extraction
4. Potentiometric titration in a mixed solvent
5. Conductivity

Although the conductivity method is the one most widely used for process control, it is probably the least accurate of these methods. Whenever used it should be standardized for each type of crude oil processed.

Table 4.3 Desalter Unit Cost Data

Costs included

1. Conventional electrostatic desalting unit
2. Water injection
3. Caustic injection
4. Water preheating and cooling

Costs not included

1. Waste water treating and disposal
2. Cooling water and power supply

Utility data (per bbl feed)

Power, kWh	0.01–0.02
Water injection, gal (m^3)	1–3 (0.004–0.012)
Demulsifier chemical, lb (kg) ^a	0.005–0.01 (0.002–0.005)
Caustic, lb (kg)	0.001–0.003 (0.005–0.0014)

^a 1999 price approximately \$1.50/lb.

Note: See Fig. 4.6.

Installed costs of desalting units are shown in Figure 4.7, and utility and chemical requirements are given by Table 4.3.

4.2 ATMOSPHERIC TOPPING UNIT

After desalting, the crude oil is pumped through a series of heat exchangers and its temperature raised to about 550°F (288°C) by heat exchange with product and reflux streams [1,2]. It is then further heated to about 750°F (399°C) in a furnace (i.e., direct-fired heater or “pipe-still”) and charged to the flash zone of the atmospheric fractionators. The furnace discharge temperature is sufficiently high [650 to 750°F (343 to 399°C)] to cause vaporization of all products withdrawn above the flash zone plus about 10 to 20% of the bottoms product. This 10 to 20% “over-flash” allows some fractionation to occur on the trays just above the flash zone by providing internal reflux in excess of the sidestream withdrawals.

Reflux is provided by condensing the tower overhead vapors and returning a portion of the liquid to the top of the tower, and by pump-around and pumpback streams lower in the tower. Each of the sidestream products removed from the tower decreases the amount of reflux below the point of drawoff. Maximum reflux and fractionation is obtained by removing all heat at the top of the tower, but this results in an inverted cone-type liquid loading which requires a very large diameter at the top of the tower. To reduce the top diameter of the tower and even the liquid loading over the length of the tower, intermediate heat-removal streams are used to generate reflux below the sidestream removal points. To accomplish this, liquid is removed from the tower, cooled by a heat exchanger, and returned to the tower or, alternatively, a portion of the cooled sidestream may be returned to the tower. This cold stream condenses more of the vapors coming up the lower and thereby increases the reflux below that point.

The energy efficiency of the distillation operation is also improved by using pump-around reflux. If sufficient reflux were produced in the overhead condenser to provide for all sidestream drawoffs as well as the required reflux, all of the heat energy would be exchanged at the bubble-point temperature of the overhead stream. By using pump-around reflux at lower points in the column, the heat transfer temperatures are higher and a higher fraction of the heat energy can be recovered by preheating the feed.

Although crude towers do not normally use reboilers, several trays are generally incorporated below the flash zone and steam is introduced below the bottom tray to strip any remaining gas oil from the liquid in the flash zone and to produce a high-flash-point bottoms. The steam reduces the partial pressure of the hydrocarbons and thus lowers the required vaporization temperature.

The atmospheric fractionator normally contains 30 to 50 fractionation trays. Separation of the complex mixtures in crude oils is relatively easy and generally five to eight trays are needed for each sidestream product plus the same number above and below the feed plate. Thus, a crude oil atmospheric fractionation tower with four liquid sidestream drawoffs will require from 30 to 42 trays.

The liquid sidestream withdrawn from the tower will contain low-boiling components which lower the flashpoint, because the lighter products pass through the heavier products and are in equilibrium with them on every tray. These ‘light ends’ are stripped from each sidestream in a separate small stripping tower containing four to ten trays with steam introduced under the bottom tray. The steam and stripped light ends are vented back into the vapor zone of the atmospheric fractionator above the corresponding side-draw tray (Fig. 4.8).

The overhead condenser on the atmospheric tower condenses the pentane-and-heavier fraction of the vapors that passes out of the top of the tower. This is the light gasoline portion of the overhead, containing some propane and butanes and essentially all of the higher-boiling components in the tower overhead vapor. Some of this condensate is returned to the top of the tower as reflux, and the remainder is sent to the stabilization section of the refinery gas plant where the butanes and propane are separated from the C₅-180°F (C₅-82°C) LSR gasoline.

Installed costs of atmospheric crude distillation units are shown in Figure 4.9, and utility requirements are given by Table 4.4.

4.3 VACUUM DISTILLATION

The furnace outlet temperatures required for atmospheric pressure distillation of the heavier fractions of crude oil are so high that thermal cracking would occur, with the resultant loss of product and equipment fouling. These materials are therefore distilled under vacuum because the boiling temperature decreases with a lowering of the pressure. Distillation is carried out with absolute pressures in the tower flash zone area of 25 to 40 mmHg (Fig. 4.9). To improve vaporization, the effective pressure is lowered even further (to 10 mmHg or less) by the addition of steam to the furnace inlet and at the bottom of the vacuum tower. Addition of steam to the furnace inlet increases the furnace tube velocity and minimizes coke formation in the furnace as well as decreasing the total hydrocarbon partial pressure in the vacuum tower. The amount of stripping steam used is a function of the boiling range of the feed and the fraction vaporized, but generally ranges from 10 to 50 lb/bbl feed [3,6],

Furnace outlet temperatures are also a function of the boiling range of the feed and the fraction vaporized as well as of the feed coking characteristics. High tube velocities and steam addition minimize coke formation, and furnace outlet

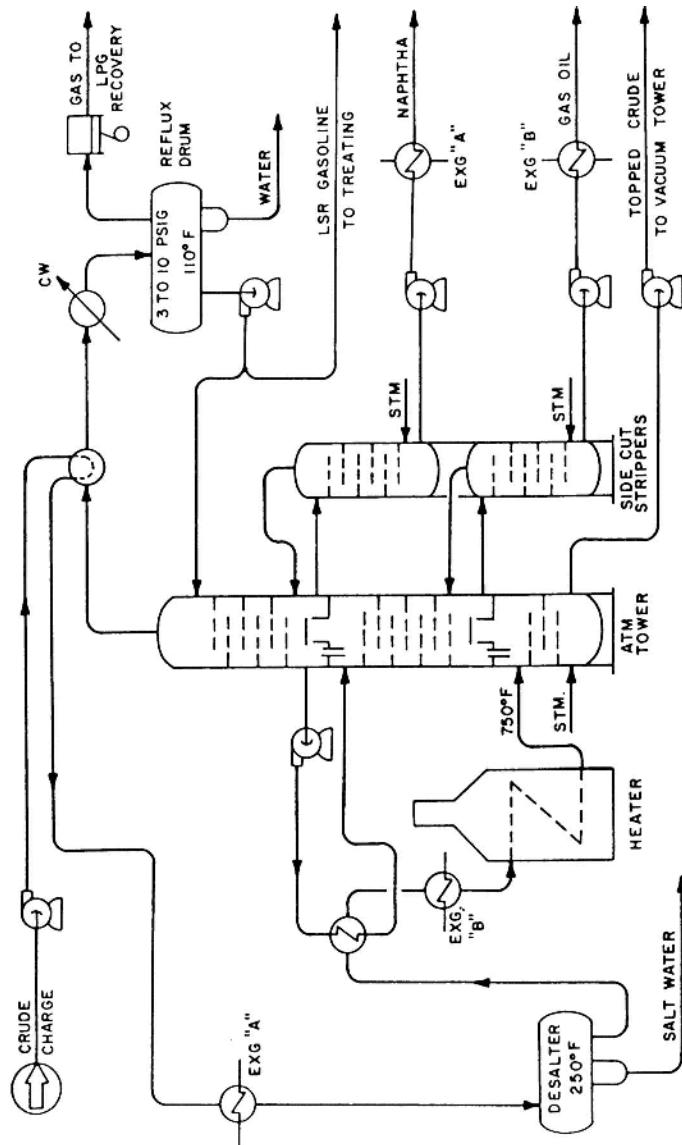


Figure 4.8 Crude distillation. For simplicity, only two side strippers are shown. Usually at least four are provided to produce extra cuts such as kerosine and diesel.

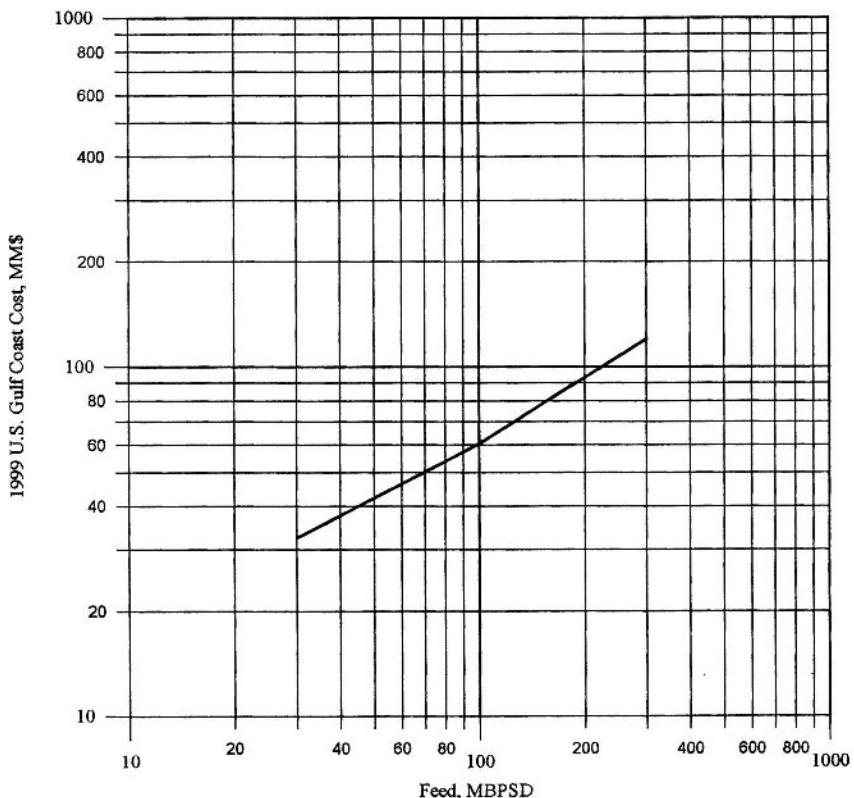


Figure 4.9 Atmospheric crude distillation units investment cost; 1999 U.S. Gulf Coast. (See Table 4.4.)

temperatures in the range of 730 to 850°F (388 to 454°C) are generally used [7].

Typically the highest furnace outlet temperatures are for “dry” operation of the vacuum unit; that is, no steam is added either to the furnace inlet or to the vacuum column. The lowest furnace outlet temperatures are for “wet” operation when steam is added to both the furnace inlet and to the bottom of the vacuum tower. Intermediate temperatures are used for “damp” operation of the vacuum unit when steam is added to the furnace inlet only. For most crude oils the furnaces can be operated from three to five years between turnarounds.

The effective pressure (total absolute pressure–partial pressure of the steam) at the flash zone determines the fraction of the feed vaporized for a given furnace outlet temperature, so it is essential to design the fractionation tower,

Table 4.4 Atmospheric Crude Distillation Unit Cost Data

Costs included	
1. Side cuts with strippers	
2. All battery limits (BL) process facilities	
3. Sufficient heat exchange to cool top products and side cuts to ambient temperature	
4. Central control system	
<i>Costs not included</i>	
1. Cooling water, steam, and power supply	
2. Desalting	
3. Cooling on reduced crude (bottoms)	
4. Sour water treating and disposal	
5. Feed and product storage	
6. Naphtha stabilization	
7. Light ends recovery	
<i>Utility data (per bbl feed)</i>	
Steam [300 psig (2068 kPa)], lb (kg)	10.0 (4.5)
Power, kWh	0.9
Cooling water circulation, gal (m^3) ^a	150 (0.58)
Fuel, MMbtu (kJ) ^b	0.05 (52,750)

^a 30°F (17°C) rise; about 50% of this duty can be used for BFW preheat.

^b LHV basis, heater efficiency taken into account. (All fuel data in this text are on this same basis.)

Note: See Fig. 4.9.

overhead lines, and condenser to minimize the pressure drop between the vacuum-inducing device and the flash zone. A few millimeters decrease in pressure drop will save many dollars in operating costs.

The lower operating pressures cause significant increases in the volume of vapor per barrel vaporized and, as a result, the vacuum distillation columns are much larger in diameter than atmospheric towers. It is not unusual to have vacuum towers up to 40 feet in diameter.

The desired operating pressure is maintained by the use of steam ejectors and barometric condensers or vacuum pumps and surface condensers. The size and number of ejectors and condensers used is determined by the vacuum needed and the quality of vapors handled. For a flash zone pressure of 25 mmHg, three ejector stages are usually required. The first stage condenses the steam and compresses the noncondensable gases, while the second and third stages remove the noncondensable gases from the condensers. The vacuum produced is limited to the vapor pressure of the water used in the condensers. If colder water is

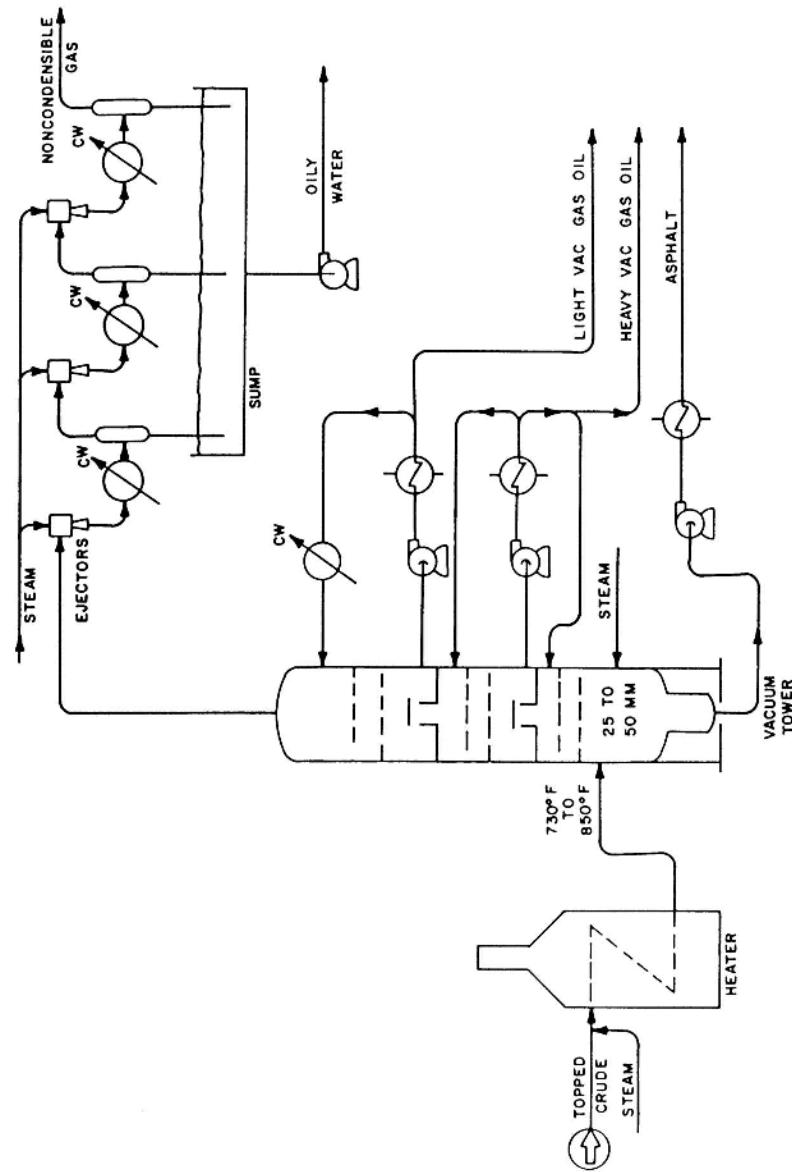


Figure 4.10 Vacuum distillation.

supplied to the condensers, a lower absolute pressure can be obtained in the vacuum tower.

Although more costly than barometric condensers, a recent trend is the use of vacuum pumps and surface condensers in order to reduce the contamination of water with oil.

A schematic of a crude oil vacuum distillation unit is shown in Figure 4.10, and installed costs are shown in Figure 4.11, and utility requirements are given by Table 4.5.

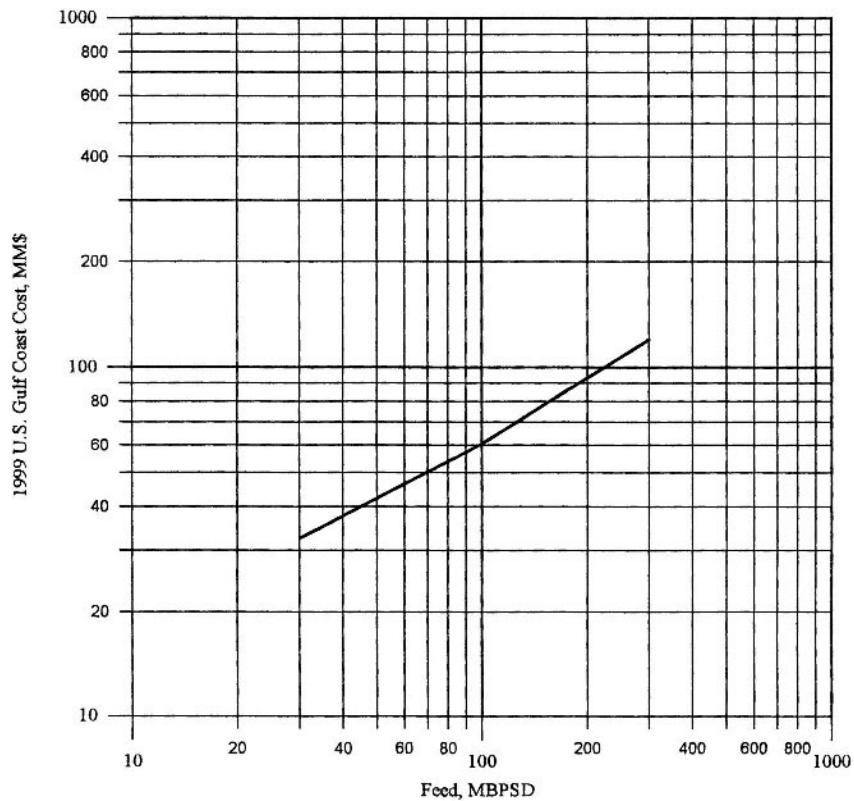


Figure 4.11 Vacuum distillation units investment cost: 1999 U.S. Gulf Coast. (See Table 4.5.)

Table 4.5 Vacuum Distillation Unit Cost Data

Costs included	
1. All facilities required for producing a clean vacuum gas oil (single cut)	
2. Three-stage jet system for operation of flash zone at 30 to 40 torr	
3. Coolers and exchangers to reduce VGO to ambient temperature	
<i>Costs not included</i>	
1. Cooling water, steam, power supply	
2. Bottoms cooling below 400°F (204°C)	
3. Feed preheat up to 670°F (354°C), \pm 10 (assumes feed is direct from atm crude unit)	
4. Sour water treating and disposal	
5. Feed and product storage	
6. Multiple “cuts” or lube oil production	
<i>Utility data (per bbl feed)</i>	
Steam [300 psig (2068 kPa)], lb (kg)	10.0 (4.5)
Power, kWh	0.3
Cooling water circulation, gal (m^3) ^a	150 (0.57)
Fuel, MMBtu (kJ) ^b	0.03 (31,650)

^a 30°F (16.7°C) rise.^b LHV basis, heater efficiency taken into account.

Note: See Figs. 4.10 and 4.11.

4.4 AUXILIARY EQUIPMENT

In many cases, a flash drum is installed between the feed-preheat heat exchangers and the atmospheric pipe-still furnace. The lower boiling fractions which are vaporized by heat supplied in the preheat exchangers are separated in the flash drum and flow directly to the flash zone of the fractionator. The liquid is pumped through the furnace to the tower flash zone. This results in a smaller and lower-cost furnace and lower furnace outlet temperatures for the same quantity of overhead streams produced.

A stabilizer is incorporated in the crude distillation section of some refineries instead of being placed with the refinery gas plant. The liquid condensed from the overhead vapor stream of the atmospheric pipe-still contains propane and butanes which make the vapor pressure much higher than is acceptable for gasoline blending. To remove these, the condensed liquid in excess of reflux requirements is charged to a stabilizing tower where the vapor pressure is adjusted by

removing the propane and butanes from the LSR gasoline stream. Later, in the product-blending section of the refinery, n-butane is added to the gasoline stream to provide the desired Reid vapor pressure.

4.5 CRUDE DISTILLATION UNIT PRODUCTS

In the order of increasing boiling points, the main products from a typical crude distillation unit are as follows.

Fuel gas. The fuel gas consists mainly of methane and ethane. In some refineries, propane in excess of LPG requirements is also included in the fuel gas stream. This stream is also referred to as “dry gas.”

Wet gas. The wet gas stream contains propane and butanes as well as methane and ethane. The propane and butanes are separated to be used for LPG and, in the case of butanes, for gasoline blending and alkylation unit feed.

LSR naphtha. The stabilized LSR naphtha (or LSR gasoline) stream is desulfurized and used in gasoline blending or processed in an isomerization unit to improve octane before blending into gasoline.

HSR naphtha or HSR gasoline. The naphtha cuts are generally used as catalytic reformer feed to produce high-octane reformate for gasoline blending and aromatics.

Gas oils. The light, atmospheric, and vacuum gas oils are processed in a hydrocracker or catalytic cracker to produce gasoline, jet, and diesel fuels. The heavier vacuum gas oils can also be used as feedstocks for lubricating oil processing units.

Residuum. The vacuum still bottoms can be processed in a visbreaker, coker, or deasphalting unit to produce heavy fuel oil or cracking and/or lube base stocks. For asphalt crudes, the residuum can be processed further to produce road and/or roofing asphalts.

4.6 CASE-STUDY PROBLEM: CRUDE UNITS

To illustrate the operation of a fuels refinery and the procedures for making a preliminary economic evaluation, a material balance will be made on each processing unit in a refinery and operating and construction costs will be estimated. The material balance for each unit is located at the end of the chapter that discusses that particular unit, and the evaluation of operating and construction costs is located at the end of Chapter 17 (Cost Estimation). An overall economic evaluation is given at the end of Chapter 18 (Economic Evaluation).

The example problem is worked using units of measurement common to U.S. refineries. Using both U.S. and international units of measurement makes

it more difficult to follow the problem and the international set of units is not standard in refinery operations throughout the world even though research and most technical publications require their use.

In order to determine the economics of processing a given crude oil or of constructing a complete refinery or individual processing units, it is necessary to make case studies for each practical processing plan and to select the one giving the best economic return. This is a very time-consuming process and can be very costly. The use of computer programs to optimize processing schemes is widespread throughout the refining industry. For the purpose of illustrating calculation methods, the process flow will not be optimized in this problem, but all units will be utilized (i.e., delayed coker, fluid catalytic cracker, and hydro-cracker) even though certain ones cannot be economically justified under the assumed conditions.

In addition to the basic data contained in this book, it is necessary to use industry publications such as the *Oil and Gas Journal*, *Chemical Week*, *Oil Daily*, and *Chemical Marketing* (formerly *Oil, Paint, and Drug Reporter*) for current prices of raw materials and products. *Chemical Week*, for example, has an annual issue on plant sites which lists utility costs, wages, taxes, etc., by location within the United States.

In many processing units, there is a change in volume between the feed and the products, so it is not possible to make a volume balance around the unit. For this reason, it is essential that a weight balance be made. Even though in practice, the weights of individual streams are valid to only three significant figures, for purposes of calculation it is necessary to carry them out to at least the closest 100 pounds. For this example, they will be carried to the nearest pound.

In order to make the balance close on each unit, it is necessary to determine one product stream by difference. Generally, the stream having the least effect is determined by difference and, in most cases, this works out to be the heaviest product.

Conversion factors (e.g., lb/hr per BPD) and properties of pure compounds are tabulated in Appendix B. Properties of products and intermediate streams are given in the chapters on products and the individual process units.

Statement of the Problem

Develop preliminary estimates of product yields, capital investment, operating costs, and economics of building a grassroots refinery on the West Coast to process 100,000 BPCD of North Slope Alaska crude oil.

The major income products will be motor gasoline, jet fuel, and diesel fuel and the refinery will be operated to maximize gasoline yields within economic limits. The gasoline split will be 50/50 87 PON regular and 93 PON premium [PON = (RON + MON)/2]. Analysis of the crude oil is given in Table 4.6. It

Table 4.6 Petroleum Analysis, North Slope Alaska Crude

Gravity, °API, 26.4
 Sulfur, wt%, 0.99
 Viscosity, SUS at 70°F (21°C), 182.5 sec
 at 100°F (38°C), 94.1 sec
 Conradson carbon: crude, 5.99%; 1050+°F VRC, 14.2%

TBP Distillation

TBP cut (°F)	vol% on crude		Sp. gr. (60/60°F)	°API	Sulfur (wt %)	N (wppm)	Ni (wppm)	V (wppm)
	Frac.	Sum						
C ₂	0.1	0.1	0.374	—				
C ₃	0.3	0.4	0.509	—				
iC ₄	0.2	0.6	0.564	—				
nC ₄	0.6	1.2	0.584	—				
iC ₅	0.5	1.7	0.625	—				
nC ₅	0.7	2.4	0.631	—				
97–178	1.7	4.1	0.697	71.6				
178–214	2.1	6.2	0.740	59.7				
214–242	2.0	8.2	0.759	55.0				
242–270	2.0	10.2	0.764	53.8				
270–296	2.0	12.2	0.781	49.6				
296–313	1.0	13.2	0.781	49.6				
313–342	2.0	15.2	0.791	47.3				
342–366	1.9	17.1	0.797	46.0				
366–395	2.0	19.1	0.806	44.0				
395–415	2.0	21.1	0.831	38.8				
415–438	2.0	23.1	0.832	38.6				
438–461	2.0	25.1	0.839	37.2				
461–479	2.0	27.1	0.848	35.4				
479–501	2.0	29.1	0.856	33.9				
501–518	2.0	31.1	0.860	33.1				
518–538	2.0	33.1	0.864	32.2				
538–557	2.0	35.1	0.867	31.8				
557–578	2.0	37.1	0.868	31.6				
578–594	2.1	39.2	0.872	30.7				
594–610	2.0	41.2	0.878	29.6				
610–632	2.0	43.2	0.887	28.0				
632–650	1.8	45.0	0.893	26.9				
650–1,000	31.8	76.8	0.933	20.3	1.0	1390		
1000+	23.2	100.0	0.995	10.7	2.4	4920	56	97

Source: Ref. 7.

is estimated that this crude oil will be available FOB the refinery at \$20.00/bbl. Product prices will be based on the average posted prices for 1999 less the following:

1. \$0.005/gal on all liquid products except fuel oil
2. \$0.05/bbl on fuel oil
3. \$0.50/ton on coke

Utility prices will be those reported in the 1999 Plant Sites issue of *Chemical Week* (October 1999) for the area in which the refinery will be built. Federal and state income taxes will be 45% (38% U.S. and 7% Calif.) and land cost will be 5% of the cost of the process units, storage, steam systems, cooling water systems, and offsites.

General Procedure

1. From the crude distillation data given in Table 4.6, plot TBP and gravity-midpercent curves. These are shown in Figure 4.12.
2. From Table 4.2, select TBP cut-points of products to be made from atmospheric and vacuum pipe stills.
3. From TBP and gravity curves, determine percentages and gravities of fractions.
4. Using Tables B.1 and B.2, convert volumes to weights.
5. Determine weight of 1050+ °F (566°C) bottoms stream by difference. If the volume of 1050+ stream is taken from the TBP curve, then gravity is calculated from weight and volume. In this case, since the gravity on 1050+ °F stream was determined in the laboratory and the gravity is very sensitive to small changes in weight, it was decided to use the laboratory gravity and calculate the volume. This gives a total volume recovery of 100.6%. This is reasonable because there is a negative volume change on mixing of petroleum fractions, and it is possible on some crudes to obtain liquid products [more properly liquid-equivalent products because C₄ and lighter products are not liquids at 60°F (16°C) and 1 atm pressure] having a total volume of up to 103% on crude. The material balance and utility requirements for the crude units are given in Table 4.7.
6. For crude oils containing significant amounts of sulfur or nitrogen, it is also necessary to make sulfur and/or nitrogen balances around each unit. The North Slope crude has a sufficiently high quality of sulfur to require a sulfur balance, but since there is no nitrogen shown in the analysis, a nitrogen balance is not made. It is assumed that the North Slope crude is similar to those represented in Figure 4.3.

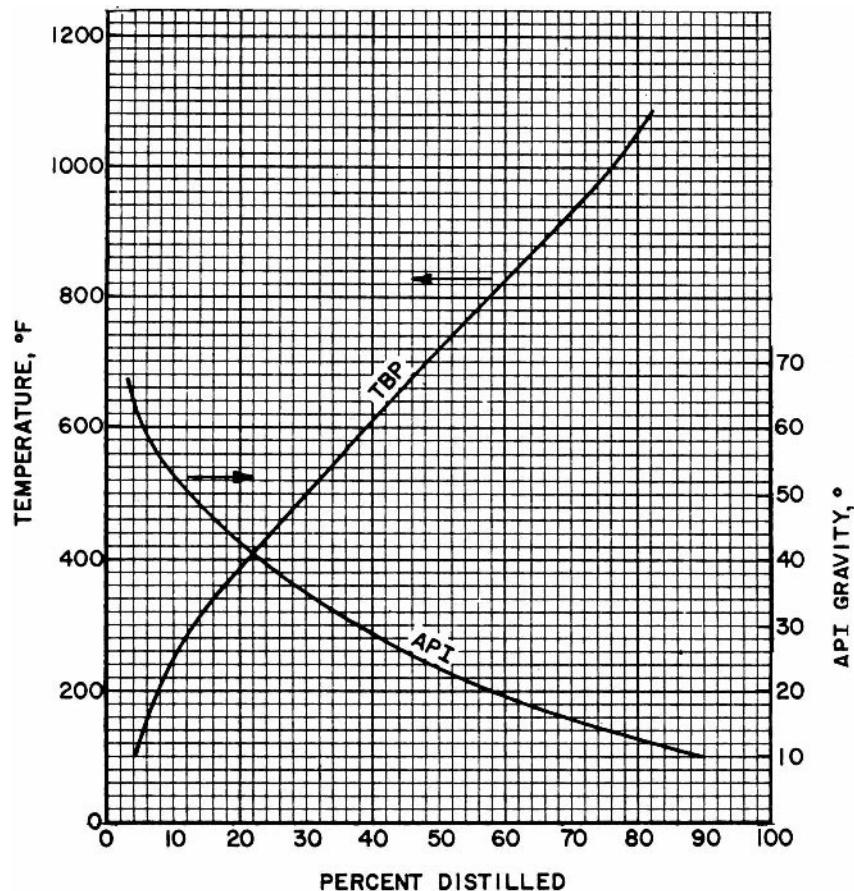


Figure 4.12 TBP and gravity-midpercent curves, Alaska North Slope crude: gravity, 26.4 API; sulfur, 0.99 wt%. (From Ref. 8.)

PROBLEMS

1. Using one of the crude oils in Appendix D, make TBP and gravity midpercent curves. From these curves and the crude oil fraction specifications in Tables 4.1 or 4.2, make a complete material balance around an atmospheric crude still. Assume a 100,000 BPCD crude oil feed rate to the atmospheric crude still. Make the balances to the nearest pound.

2. For the crude oil used in problem 1, make sulfur and nitrogen weight balances for the feed and products to the nearest pound.
3. Using the high-boiling fraction from problem 1 as feed to a vacuum pipe still, make an overall weight balance and nitrogen and sulfur balances. Assume the reduced crude bottoms stream from the vacuum pipe still has an initial TBP boiling point of 1050°F (566°C).
4. Estimate the calendar day utility and chemical requirements for the crude oil desalter, atmospheric pipe still, and vacuum pipe still of problems 1 and 3.
5. Calculate the Watson characterization factors and U.S. Bureau of Mines Correlation Indices for the crude oil and product streams from problems 1 and 3.
6. Estimate the carbon content of the reduced crude bottoms product of problem 3. Express as weight percent Conradson carbon.
7. Using information in Table 4.2, tell where each product stream from the crude stills will be utilized (unit feed or product).
8. a. Calculate the Btu required per hour to heat 100,000 BPSD of the assigned crude oil from 60°F (15.6°C) to 806°F (430°C) in the atmospheric distillation unit furnace.
b. Assuming a furnace efficiency of 73%, how many barrels of 13.0° API residual fuel oil will be burned per barrel of crude oil charged?
9. Calculate the atmospheric distillation unit furnace exit temperature needed to vaporize 30% of the assigned crude oil in the tower flash zone.
10. a. Determine the API gravity, characterization factor and temperature of the topped crude leaving the bottom of the tower in problem 9.
b. If the topped crude used as the hot fluid in a train of feed preheater heat exchangers is exited at 100°F (38°C), what was the temperature to which the crude oil feed to the furnace was heated? [Assume crude inlet temperature is 60°F (15.6°C).]
11. If the crude oil leaving the preheater heat exchanger train in problem 10 was partially vaporized in a flash drum and the liquid from the flash drum heated to 752°F (400°C) in the furnace, calculate the percent on original crude oil feed of the topped crude exiting from the bottom of the atmospheric crude tower.
12. If the assigned crude oil has an atmospheric crude unit furnace outlet temperature of 752°F (400°C) and a flash zone pressure of 1 atmosphere gauge (101 kPa), calculate the flash zone temperature and the volume percent vaporized.
13. The crude oil in problem 11 can be heated to 527°F (275°C) in a preheater train and flashed in a flash drum before the liquid fraction

Table 4.7 Crude Units Material Balance: 100,000 BPCD Alaska North Slope Crude Oil Basis

Component	Vol%	BPCD	°API	(lb/h)/BPD	lb/h	wt% S	wt% S	lb/h S
Atmospheric distillation unit								
<i>Feed</i>								
Crude	100.0	100,000	26.4	13.1	1,307,464	100.0	0.99	12,944
<i>Products</i>								
C ₂ –	0.1	72	5.18	3.72	0.03			
C ₃	0.3	317	7.39	2,341	0.18			
iC ₄	0.2	159	8.20	1,302	0.10			
nC ₄	0.6	629	8.51	5,353	0.41			
C ₅ –180°F	4.3	4,277	63.0	10,61	45,394	3.47	0.00	1
180–350	11.7	11,685	9.9	11.38	132,988	10.17	0.01	13
350–400	4.3	4,332	42.5	11.85	52,534	3.93	0.11	56
400–525	12.2	12,200	36.5	12.21	148,906	11.39	0.24	357
525–650	12.5	12,500	38.0	12.77	159,653	12.21	0.52	830
650+	57.0	54,147	15.5	14.03	759,799	58.11	1.54	11,686
Total		100,317			1,307,464	100.0		12,944

Crude Distillation

65

Vacuum distillation unit						
<i>Feed</i>	57.0	54,147	15.5	14.03	759,799	58.11
650°F+						11,686
<i>Products</i>						
650–850°F	20.5	20,500	22.2	13.42	275,119	36.2
850–1050	15.6	15,644	15.5	14.03	219,518	28.9
1050+	18.0	18,003	8.7	14.73	265,162	34.9
Total		54,177			759,799	100.0
Utility requirements (per day)						
Desalter			Atm. PS		Vac. PS	Total
Steam (300 psig), Mlb			1,000		541	1,541
Power, MrWh		1	90		16	107
CW circ., Mgal			15,000		8,122	23,122
Fuel, MMBtu			5,000		1,624	6,624
Water inj., Mgal			200		200	
Demul. Chem., lb			500		500	
Caustic, Mlb			100		100	

is heated to 752°F (400°C) in the crude unit furnace. If the fractionating tower flash zone pressure is 1 atmosphere (101 kPa), what is the total volume percent of the crude oil vaporized in the flash drum and the fractionating tower?

NOTES

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5

Coking and Thermal Processes

The “bottom of the barrel” has become more of a problem for refiners because heavier crudes are being processed and the market for heavy residual fuel oils has been decreasing. Historically, the heavy residual fuel oils have been burned to produce electric power and to supply the energy needs of heavy industry, but more severe environmental restrictions have caused many of these users to switch to natural gas. Thus when more heavy residuals are in the crude there is more difficulty in economically disposing of them. Coking units convert heavy feedstocks into a solid coke and lower boiling hydrocarbon products which are suitable as feedstocks to other refinery units for conversion into higher value transportation fuels.

From a chemical reaction viewpoint, coking can be considered as a severe thermal cracking process in which one of the end products is carbon (i.e., coke). Actually the coke formed contains some volatile matter or high-boiling hydrocarbons. To eliminate essentially all volatile matter from petroleum coke it must be calcined at approximately 2000 to 2300°F (1095 to 1260°C). Minor amounts of hydrogen remain in the coke even after calcining, which gives rise to the theory held by some authors that the coke is actually a polymer.

Coking was used primarily to pretreat vacuum residuals to prepare coker gas oil streams suitable for feed to a catalytic cracker. This reduced coke formation on the cracker catalyst and thereby allowed increased cracker throughputs. This also reduced the net refinery yield of low-priced residual fuel. Added benefit was obtained by reducing the metals content of the catalytic cracker feed stocks.

In recent years coking has also been used to prepare hydrocracker feedstocks and to produce a high quality “needle coke” from stocks such as heavy catalytic gas oils and decanted oils from the fluid catalytic cracking unit [19,20]. Coal tar pitch is also processed in delayed coking units [16].

Delayed coking is described in Sections 5.2 to 5.7. This is the most widely used coking process. Fluid coking and Flexicoking are described in Sections 5.7 to 5.10. These fluid bed processes have been under development by Exxon over

the past 40 years and are now commercially operated in several refineries around the world [17,20].

5.1 TYPES, PROPERTIES, AND USES OF PETROLEUM COKE

There are several types of petroleum coke produced depending upon the process used, operating conditions, and feedstock properties. All cokes, as produced from the coker, are called “green” cokes and contain some high-molecular-weight hydrocarbons (have some hydrogen in the molecules) left from incomplete carbonization reactions. These incompletely carbonized molecules are referred to as volatile materials in the coke (expressed on a moisture-free basis). Fuel grade cokes are sold as green coke, but coke used to make anodes for aluminum production or electrodes for steel production must be calcined at temperatures from

Table 5.1 Petroleum Coke Characteristics

Process	Coke type	Characteristics
Delayed	Sponge	Spongelike appearance Higher surface area Lower contaminants level Higher volatile content Higher HGI ^a (~100 [22]) Typical size of 0–6 in. (0–15 cm)
	Shot	Spherical appearance Lower surface area Lower volatiles Lower HGI ^a (<50) Tends to agglomerate
	Needle	Needlelike appearance Low volatiles High carbon content
Fluid	Fluid	Low volatiles Higher contaminants level Low HGI ^a (<40) Black sandlike particles
Flexicoker	Flexicoke	Highest metals level 80% <200 mesh

^a Hardgrove grindability index.

Source: Ref. 5.

1800 to 2400°F (980 to 1315°C) to complete the carbonization reactions and reduce the volatiles to a very low level.

Much of delayed coker coke is produced as hard, porous, irregular-shaped lumps ranging in size from 20 inches (50 cm) down to fine dust. This type of coke is called sponge coke because it looks like a black sponge.

A second form of petroleum coke being produced in increasing quantities is needle coke. Needle coke derives its name from its microscopic elongated crystalline structure. Needle coke is produced from highly aromatic feedstocks (FCC cycle oils, etc.) when a coking unit is operated at high pressures [100 psig (690 kPa)] and high recycle ratios (1:1). Needle coke is preferred over sponge coke for use in electrode manufacture because of its lower electrical resistivity and lower coefficient of thermal expansion.

Occasionally a third type of coke is produced unintentionally. This coke is called shot coke because of the clusters of shot-sized pellets which characterize it. Its production usually occurs during operational upsets or when processing very heavy residuals such as those from some Canadian, Californian, and Venezuelan crudes. These shot clusters can grow large enough to plug the coke drum outlet (>12 in. or 30 cm). It is also produced from some high sulfur residuals [13]. Shot coke is undesirable because it does not have the high surface area of sponge coke nor the useful properties, characteristic of needle coke, for electrode manufacture.

Table 5.2 Typical Coke End Uses

Application	Coke type	State	End use
Carbon source	Needle	Calcined	Electrodes Synthetic graphite
	Sponge	Calcined	Aluminum anodes TiO_2 pigments Carbon raiser
	Sponge	Green	Silicon carbide Foundries Coke ovens
	Sponge	Green lump	Space heating in Europe/Japan
	Sponge	Green	Industrial boilers
	Shot	Green	Utilities
Fuel use	Fluid	Green	Cogeneration
	Flexicoke	Green	Lime Cement

Source: Ref. 5.

The main uses of petroleum coke are as follows:

1. Fuel
2. Manufacture of anodes for electrolytic cell reduction of alumina
3. Direct use as chemical carbon source for manufacture of elemental phosphorus, calcium carbide, and silicon carbide
4. Manufacture of electrodes for use in electric furnace production of elemental phosphorus, titanium dioxide, calcium carbide, and silicon carbide
5. Manufacture of graphite

Petroleum coke characteristics and end uses by source and type are given in Tables 5.1 and 5.2.

It is important to note that petroleum coke does not have sufficient strength to be used in blast furnaces for the production of pig iron nor is it generally acceptable for use as foundry coke. Coal-derived coke is used for these purposes. Typical analyses of petroleum cokes and specifications for anode and electrode grades are summarized in Table 5.3.

Table 5.3 Typical Coke Specifications

	Sponge anodes	Needle electrodes
Calcined coke		
Moisture, wt%	<0.5	<0.5
Volatile matter, wt%	0.5	
Sulfur, wt%	<3.0	<1.5
Metals, ppm		
V	<350	
Ni	<300	
Si	<150	
Fe	<270	
Density, g/cc		
–200 Mesh RD	2.04–2.08	>2.12
VBD	>0.80	
CTE, 1/°C × 10 ⁻⁷	<40	<4.0
	As produced (wt%)	After calcining (wt%)
Water	2–4	—
Volatile matter	7–10	2–3
Fixed carbon	85–91	95+
Ash	0.5–1.0	1–2

The sulfur content of petroleum coke varies with the sulfur content of the coker feedstock. It is usually in the range of 0.3 to 1.5 wt%. It can sometimes, however, be as high as 8%. The sulfur content is not significantly reduced by calcining.

5.2 PROCESS DESCRIPTION—DELAYED COKING

This discussion relates to conventional delayed coking as shown in the flow diagram in Figure 5.1. See also Photo 3, Appendix E.

The delayed coking process was developed to minimize refinery yields of residual fuel oil by severe thermal cracking of stocks such as vacuum residuals, aromatic gas oils, and thermal tars. In early refineries, severe thermal cracking of such stocks resulted in unwanted deposition of coke in the heaters. By gradual evolution of the art it was found that heaters could be designed to raise residual stock temperatures above the coking point without significant coke formation in the heaters. This required high velocities (minimum retention time) in the heaters. Providing an insulated surge drum on the heater effluent allowed sufficient time

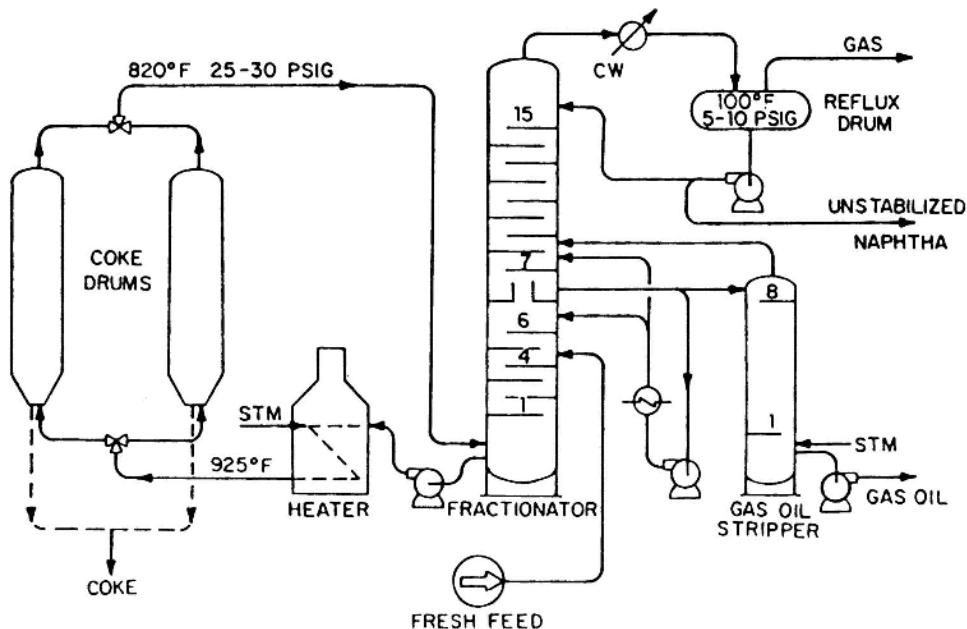


Figure 5.1 Delayed coking unit.

for the coking to take place before subsequent processing, hence the term “delayed coking.”

Typically furnace outlet temperatures range from 900–930°F (482–500°C). The higher the outlet temperature, the greater the tendency to produce shot coke and the shorter the time before the furnace tubes have to be decoked. Usually furnace tubes have to be decoked every three to five months.

Hot fresh liquid feed is charged to the fractionator two to four trays above the bottom vapor zone. This accomplishes the following:

1. The hot vapors from the coke drum are quenched by the cooler feed liquid thus preventing any significant amount of coke formation in the fractionator and simultaneously condensing a portion of the heavy ends which are recycled.
2. Any remaining material lighter than the desired coke drum feed is stripped (vaporized) from the fresh liquid feed.
3. The fresh feed liquid is further preheated making the process more energy efficient.

Vapors from the top of the coke drum return to the base of the fractionator. These vapors consist of steam and the products of the thermal cracking reaction: gas, naphtha, and gas oils. The vapors flow up through the quench trays previously described. 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 in order 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.

Major design criteria for coking units are described in the literature [12,18].

Coke Removal—Delayed Coking

When the coke drum in service is filled to a safe margin from the top, the heater effluent is switched to the empty coke drum and the full drum is isolated, steamed to remove hydrocarbon vapors, cooled by filling with water, opened, drained, and the coke removed.

The decoking operation is accomplished in some plants by a mechanical drill or reamer [7], however most plants use a hydraulic system. The hydraulic system is simply a number of high pressure [2,000 to 4,500 psig (13,800 to 31,000 kPa)] water jets which are lowered into the coke bed on a rotating drill stem. A small diameter hole [18 to 24 in. (45 to 60 cm) in diameter] called a “rat hole” is first cut all the way through the bed from top to bottom using a special jet. This is done to allow the main drill stem to enter and permit movement of coke and water through the bed.

The main bulk of coke is then cut from the drum, usually beginning at the bottom. Some operators prefer to begin at the top of drum to avoid the chance of dropping large pieces of coke which can trap the drill stem or cause problems in subsequent coke handling facilities. Today some operators use a technique referred to as “chipping” the coke out of the drum. In this technique, the cutting bit is repeatedly transferred back and forth from top to bottom as the hydraulic bit rotates, and the coke is cut from the center to the wall. This reduces cutting time, produces fewer fines, and eliminates the problem of the bit being trapped.

The coke which falls from the drum is often collected directly in railroad cars. Alternatively, it is sluiced or pumped as a water slurry to a stockpile or conveyed by belt.

5.3 OPERATION—DELAYED COKING

As indicated in the paragraph describing coke removal, the coke drums are filled and emptied on a time cycle. The fractionation facilities are operated continuously. Usually just two coke drums are provided but units having four drums are not uncommon. The following time schedule is the maximum used:

Operation	Hours
Fill drum with coke	24
Switch and steam out	3
Cool	3
Drain	2
Unhead and decoke	5

Operation	Hours
Head up and test	2
Heat up	7
Spare time	2
Total	48

Coker operators typically will increase capacity by operating with shorter cycle times. Usual design factors will allow a 20% increase in capacity by shortening coking cycles from 24 to 20 hours [6], and moderate debottlenecking projects will allow coking cycles as low as 9 to 12 hours. Shorter cycle times usually mean a lower yield of liquid products because of higher drum and fractionating tower pressures which may be needed to prevent too high vapor velocities and fractionator and compressor overloading. Shorter cycle times can result in a shorter drum life because of additional drum stresses due to more rapid temperature cycles. In one case shortening the coking cycle from 21 hours to 18 hours reduced the remaining drum life by about 25% [6].

The main independent operating variables in delayed coking (Table 5.4)

Table 5.4 Relation of Operating Variables in Delayed Coking

	Independent variables							
	Heater outlet temp.		Fractionator pressure		Hat temp. ^a		Feed carbon residue ^b	
	+	-	+	-	+	-	+	-
Gas yield	+	-	+	-	-	+	+	-
Naphtha yield	+	-	+	-	-	+	+	-
Coke yield	+	-	+	-	-	+	+	-
Gas oil yield	-	+	-	+	+	-	-	+
Gas oil EP	c	c	-	+	+	-	c	c
Gas oil metals content	c	c	-	+	+	-	c	c
Coke metals content	c	c	+	-	-	+	c	c
Recycle quantity	c	c	+	-	-	+	c	c

^a Hat temperature is the temperature of the vapors rising to the gas oil drawoff tray in the fractionator.

^b Carbon residue is that determined by Conradson residue test procedure (ASTM).

^c For these items, the heater outlet temperature and the carbon residue, per se, do not have a significant independent effect.

Table 5.5 Coke Yields When Conradson Carbon Is Known

Coke wt%	=	$1.6 \times (\text{wt\% Conradson carbon}^a)$
Gas (C_4^-) wt%	=	$7.8 + 0.144 (\text{wt\% Conradson carbon}^a)$
Gaso. wt%	=	$11.29 + 0.343 (\text{wt\% Conradson carbon}^a)$
Gas oil wt%	=	$100 - \text{wt\% coke} - \text{wt\% gas} - \text{wt\% gaso.}$
Gaso. vol%	=	$(131.5 + {}^\circ\text{API}) 186.5 (\text{gaso. wt\%})^b$
Gas oil vol%	=	$(131.5 + {}^\circ\text{API}) 155.5 (\text{gas oil wt\%})^b$

^a Use actual Conradson carbon when available.^b All °API are those for net fresh feed to coker.*Note:* These yield correlations are based on the following conditions:

1. Coke drum pressure 35 to 45 psig.
2. Feed is "straight-run" residual.
3. Gas oil end point 875 to 925°F.
4. Gasoline end point 400°F.

Table 5.6 Coke Yields, East Texas Crude Residuals

Coke wt%	=	$45.76 - 1.78 \times {}^\circ\text{API}$
Gas (C_4^-) wt%	=	$11.92 - 0.16 \times {}^\circ\text{API}$
Naphtha wt%	=	$20.5 - 0.36 \times {}^\circ\text{API}$
Gas oil wt%	=	$21.82 + 2.30 \times {}^\circ\text{API}$
Naphtha vol%	=	$(131.5 + {}^\circ\text{API}) 186.5 (\text{gaso. wt\%})$
Gas oil vol%	=	$(131.5 + {}^\circ\text{API}) 155.5 (\text{gas oil wt\%})$

Table 5.7 Coke Yields, Wilmington Crude Residuals

Coke wt%	=	$39.68 - 1.60 \times {}^\circ\text{API}$
Gas (C_4^-) wt%	=	$11.27 - 0.14 \times {}^\circ\text{API}$
Naphtha wt%	=	$20.5 - 0.36 \times {}^\circ\text{API}$
Gas oil wt%	=	$28.55 + 2.10 \times {}^\circ\text{API}$
Naphtha vol%	=	$(131.5 + {}^\circ\text{API}) 186.5 (\text{gaso. wt\%})$
Gas oil vol%	=	$(155.5 + {}^\circ\text{API}) 155.5 (\text{gas oil wt\%})$

are the heater outlet temperature, the fractionator pressure, the temperature of the vapors rising to the gas oil drawoff tray, and the "free" carbon content of the feed as determined by the Conradson or Ramsbottom carbon tests. As would be expected, high heater outlet temperatures increase the cracking and coking reactions, thus increasing yields of gas, naphtha, and coke and decreasing the yield of gas oil. An increase in fractionator pressure has the same effect as an increase in the heater outlet temperature. This is due to the fact that more recycle is condensed in the fractionator and returned to the heater and coke drums. The temperature of the vapors rising to the gas oil drawoff tray is controlled to produce the desired gas oil end point. If this temperature is increased more heavies will be drawn off in the gas oil leaving less material to be recycled to the furnace.

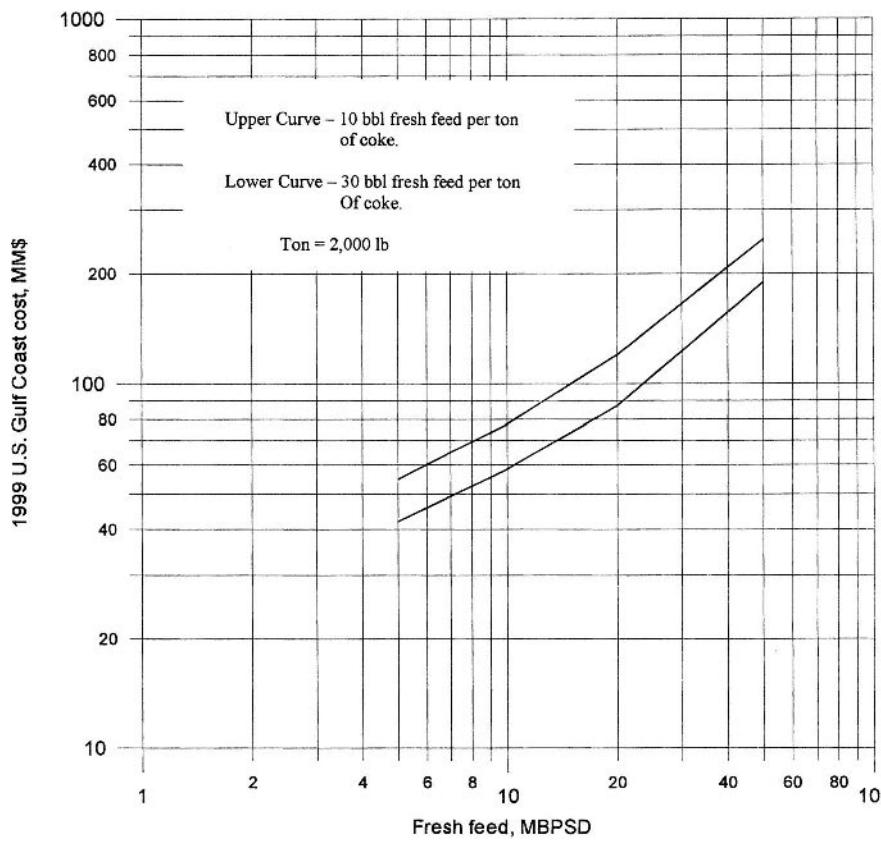


Figure 5.2 Delayed coking units investment cost—1999 U.S. Gulf Coast. (See Table 5.10.)

Table 5.8 Typical Gas Composition for Delayed Coking (Sulfur-Free Basis)

Component	mol%
Methane	51.4
Ethene	1.5
Ethane	15.9
Propene	3.1
Propane	8.2
Butenm	2.4
i-Butane	1.0
n-Butane	2.6
H ₂	13.7
CO ₂	0.2
Total	100.0

Note: MW = 22.12.

The naphtha or gasoline fraction may be split into light and heavy cuts. After hydrotreating for sulfur removal and olefin saturation, the light cut is either isomerized to improve octane or blended directly into finished gasoline. The heavy cut is hydrotreated and reformed. A typical split of coker naphtha is as follows:

Light naphtha = 35.1 vol%, 65°API

Heavy naphtha = 64.9 vol%, 50°API

Table 5.9 Sulfur and Nitrogen Distribution for Delayed Coking (Basis: Sulfur and Nitrogen in Feed to Coker)

	Sulfur (%)	Nitrogen (%)
Gas	30	—
Light naphtha	1.7	
Heavy naphtha	3.3	1
LCGO	15.4	2
HCGO	19.6	22
Coke	30	75
Total	100	100

The gas-oil fraction is usually split into a light and heavy cut before further processing. The light fraction may be hydrotreated and subsequently fed to a FCC. The heavy fraction may be used as heavy fuel or sent to the vacuum distillation unit. An approximate split of the coker gas oil can be estimated from the following:

$$\text{Light gas oil (LCGO)} = 67.3 \text{ vol\%, } 30^\circ\text{API}$$

$$\text{Heavy gas oil (HCGO)} = 32.7 \text{ vol\%, } \sim 13^\circ\text{API}$$

These yield data have been developed from correlations of actual plant operating data and pilot plant data. Values calculated from these equations are sufficiently accurate for primary economic evaluation studies (see Table 5.5 for

Table 5.10 Delayed Coking Unit Cost Data

Costs included

1. Coker fractionator to produce naphtha, light gas oil, and heavy gas oil
2. Hydraulic decoking equipment
3. Coke dewatering, crushing to <2 in. and separation of material < $\frac{1}{4}$ in. from that > $\frac{1}{4}$ in.
4. Three days covered storage for coke
5. Coke drums designed for 50 to 60 psig (345 to 415 kPa)
6. Blowdown condensation and purification of waste water
7. Sufficient heat exchange to cool products to ambient temperatures

Costs not included

1. Light ends recovery facilities
2. Light ends sulfur removal
3. Product sweetening
4. Cooling water, steam, and power supply
5. Off gas compression

Utility data

Steam, lb/ton coke	700
Power, kWh/ton coke ^a	30
Cooling water, gal/bbl feed ($30^\circ\text{F } \Delta T$)	70
Fuel, MMBtu/bbl feed ^b	0.14

^a Includes electric motor drive for hydraulic decoking pump.

^b Based on 600°F (1110°C) fresh feed. LHV basis, heater efficiency taken into account.

Note: See Fig. 5.2.

calculating yields when the Conradson carbon Figure is known); however, for the actual design of a specific coking unit the yields should be determined by the pilot plant operation. In all cases, the weight and volume percents given are based on the net fresh feed to the coking unit and are limited to feedstocks having gravities of less than 18°API. The yields shown will vary significantly if the coker feed is derived from material other than straight-run crude residuals. The numerical values in the equations do not represent a high degree of accuracy but are included for the purpose of establishing a complete weight balance.

Typical gas compositions and sulfur and nitrogen distributions in products produced by delayed coking of reduced crudes are given in Tables 5.6 and 5.7. The 1999 installed costs for delayed cokers in the Gulf Coast section of the United States are given by Figure 5.2. Tables 5.8 and 5.9 give data for typical gas composition and sulfur and nitrogen distribution for delayed coking, respectively. Table 5.10 gives utility requirements for delayed coker operation.

5.4 PROCESS DESCRIPTION—FLEXICOKING

The Flexicoking process is shown in Figure 5.3 [1].

Feed can be any heavy oil such as vacuum resid, coal tar, shale oil, or tar sand bitumen. The feed is preheated to about 600 to 700°F (315 to 370°C) and sprayed into the reactor where it contacts a hot fluidized bed of coke. This hot coke is recycled to the reactor from the coke heater at a rate which is sufficient to maintain the reactor fluid bed temperature between 950 and 1000°F (510 to 540°C). The coke recycle from the coke heater thus provides sensible heat and heat of vaporization for the feed and the endothermic heat for the cracking reactions.

The cracked vapor products pass through cyclone separators in the top of the reactor to separate most of the entrained coke particles (cyclone separators are efficient down to particle sizes about 7 microns, but the efficiency falls off rapidly as the particles become smaller) and are then quenched in the scrubber vessel located at the top of the reactor. Some of the high-boiling [925+°F (495+°C)] cracked vapors are condensed in the scrubber and recycled to the reactor. The balance of the cracked vapors flow to the coker fractionator where the various cuts are separated. Wash oil circulated over baffles in the scrubber provides quench cooling and also serves to reduce further the amount of entrained fine coke particles.

The coke produced by cracking is deposited as thin films on the surface of the existing coke particles in the reactor fluidized bed. The coke is stripped with steam in a baffled section at the bottom of the reactor to prevent reaction products, other than coke, from being entrained with the coke leaving the reactor.

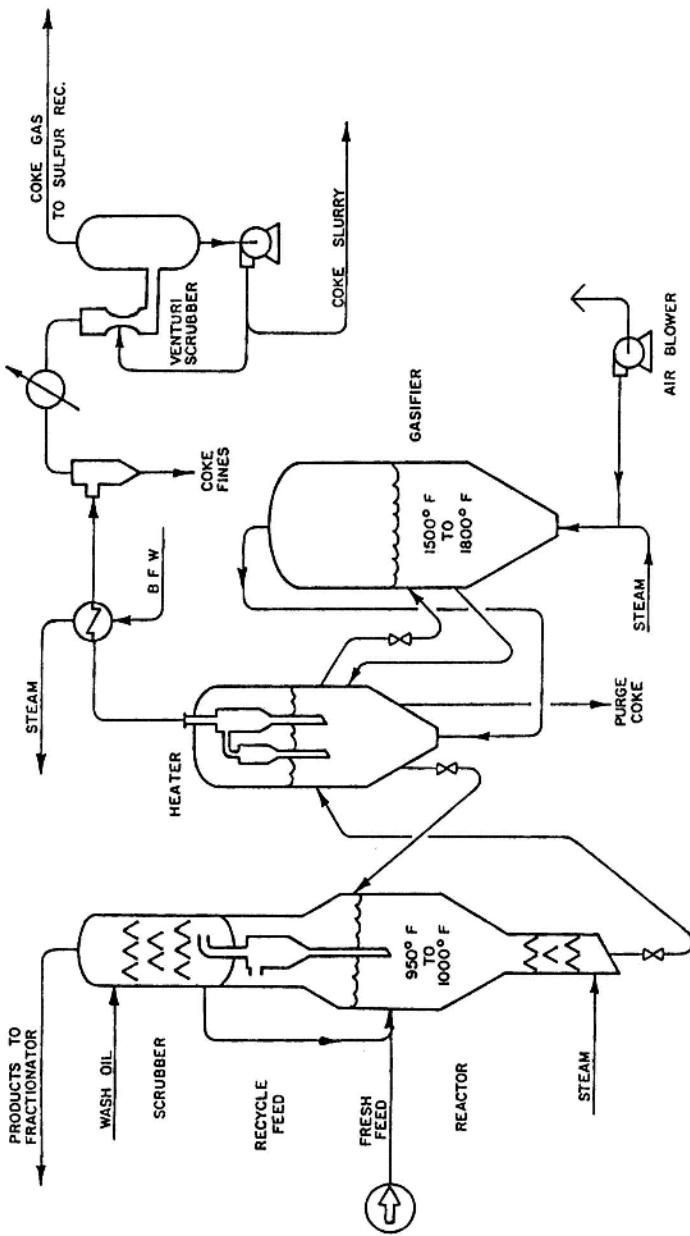


Figure 5.3 Simplified flow diagram for a Flexicoker.

Coke flows from the reactor to the heater where it is reheated to about 1100°F (593°C). The coke heater is also a fluidized bed and its primary function is to transfer heat from the gasifier to the reactor.

Coke flows from the coke heater to a third fluidized bed in the gasifier where it is reacted with air and steam to produce a fuel gas product consisting of CO, H₂, CO₂, and N₂. Sulfur in the coke is converted primarily to H₂S, plus a small amount of COS, and nitrogen in the coke is converted to NH₃ and N₂. This gas flows from the top of the gasifier to the bottom of the heater where it serves to fluidize the heater bed and provide the heat needed in the reactor. The reactor heat requirement is supplied by recirculating hot coke from the gasifier to the heater.

The system can be designed and operated to gasify about 60 to 97% of the coke product in the reactor. The overall coke inventory in the system is maintained by withdrawing a stream of purge coke from the heater.

The coke gas leaving the heater is cooled in a waste heat steam generator before passing through external cyclones and a venturi-type wet scrubber. The coke fines collected in the venturi scrubber plus the purge coke from the heater represent the net coke yield and contain essentially all of the metal and ash components of the reactor feed stock.

After removal of entrained coke fines the coke gas is treated for removal of hydrogen sulfide in a Stretford unit and then used for refinery fuel. The treated fuel gas has a much lower heating value than natural gas (100 to 130 Btu/scf vs. 900 to 1000 Btu/scf) and therefore modifications of boilers and furnaces may be required for efficient combustion of this gas.

5.5 PROCESS DESCRIPTION—FLUID COKING

Fluid coking is a simplified version of flexicoking. In the fluid coking process only enough of the coke is burned to satisfy the heat requirements of the reactor and the feed preheat. Typically, this is about 20 to 25% of the coke produced in the reactor. The balance of the coke is withdrawn from the burner vessel and is not gasified as it is in a flexicoker. Therefore, only two fluid beds are used in a fluid coker—a reactor and a burner which replaces the heater.

The primary advantage of the Flexicoker (Fig. 5.3) over the more simple fluid coker is that most of the heating value of the coke product is made available as low sulfur gas which can be burned without an SO₂ removal system on the resulting stack gas, whereas such a system would be necessary if coke which contains 3 to 8 wt% sulfur is burned directly in a boiler. In addition, the coke gas can be used to displace liquid and gaseous hydrocarbon fuels in the refinery process heaters and does not have to be used exclusively in boilers as is the case with fluid coke.

5.6 YIELDS FROM FLEXICOKING AND FLUID COKING

As with delayed coking, the yields from the fluidized-bed coking processes can be accurately predicted only from pilot plant data for specific feeds. Typical yields for many various feeds are available from the licensor. One set of yields is shown in Table 5.11

If specific yield data are not available, it can be assumed for preliminary estimates that the products from Flexicoking and fluid coking are the same as those from delayed coking except for the amount of reactor coke product which is burned or gasified. Thus the coke yield from a fluid coking unit would be about 75 to 80% of the coke yield from a delayed coker, and the yield of coke from a Flexicoker would be in the range of 2 to 40 wt% of the delayed coker yield.

The coke which is gasified in a Flexicoker produces coke gas of the following approximate composition after H₂S removal:

Table 5.11 Comparison of Coking Yields

<i>Feed</i>			
Arabian Medium 1050°F+ Vacuum Resid	Delayed coking	Fluid coking	Flexicoking
Gravity, °API		4.9	
Sulfur, wt%		5.4	
Nitrogen, wt%		0.26	
Conradson carbon, wt%		23.3	
Nickel, wt ppm		32	
Vanadium, wt ppm		86	
Iron, wt ppm		30	
<i>Yields</i>			
Recycle cut point, °F VT	900	975	975
Yields on Fresh Feed, wt%			
Gas	9.3	11.8	11.8
Light naphtha	2.0	1.9	1.9
Heavy naphtha	8.0	7.8	7.8
Gas oil	46.7	50.4	50.4
Gross coke	34.0	28.1	28.1
Total	100.0	100.0	100.0
Net coke	34.0	22.4	2.3
C ₅ ⁺ Liquid	56.7	60.1	60.1

Component	Mol%
H ₂	15
CO	20
CH ₄	2
CO ₂	10
N ₂	53
Total	100

This composition is on a dry basis. The coke gas as actually produced from the H₂S removal step is water saturated, which means it contains typically 5 to 6 mol% water vapor.

Assuming that the coke is about 98 wt% carbon on a sulfur-free and ash-free basis, the calculated amount of coke gas produced having the above composition is 194 Mscf per ton of coke gasified. Combustion of this gas results in production of about 80% of the equivalent coke heating value. Recovery of sensible heat from the coke gas leaving the coke heater increases the recoverable heat to about 85% of the equivalent coke heating value.

5.7 CAPITAL COSTS AND UTILITIES FOR FLEXICOKING AND FLUID COKING

As a rough approximation it can be assumed that the investment for a fluid coking unit is about the same as that for a delayed coking unit for a given feedstock and that a Flexicoker costs about 30% more.

The utility requirements for Fluid Coking are significantly higher than those for delayed coking primarily because of the energy required to circulate the solids between fluid beds. The air blower in a Flexicoker requires more power than that for a Fluid Coker. The process Licensor should be consulted to determine reasonably accurate utility requirements.

5.8 VISBREAKING

Visbreaking is a relatively mild thermal cracking operation mainly used to reduce the viscosities and pour points of vacuum tower bottoms to meet No. 6 fuel oil specifications or to reduce the amount of cutting stock required to dilute the resid to meet these specifications. Refinery production of heavy fuel oils can be reduced from 20–35% and cutter stock requirements from 20–30% by visbreaking. The

gas oil fraction produced by visbreaking is also used to increase cat cracker feed stocks and increase gasoline yields.

Long paraffinic side chains attached to aromatic rings are the primary cause of high pour points and viscosities for paraffinic base residua. Visbreaking is carried out at conditions to optimize the breaking off of these long side chains and their subsequent cracking to shorter molecules with lower viscosities and pour points. The amount of cracking is limited, however, because if the operation is too severe, the resulting product becomes unstable and forms polymerization products during storage which cause filter plugging and sludge formation. The objective is to reduce the viscosity as much as possible without significantly affecting the fuel stability. For most feedstocks, this reduces the severity to the production of less than 10% gasoline and lighter materials.

The degree of viscosity and pour point reduction is a function of the composition of the residua feed to the visbreaker. Waxy feed stocks achieve pour point reductions from 15–35°F (−3 to 2°C) and final viscosities from 25–75% of the feed. High asphaltene content in the feed reduces the conversion ratio at which a stable fuel can be made [15], which results in smaller changes in the properties. The properties of the cutter stocks used to blend with the visbreaker tars also have an effect on the severity of the visbreaker operation. Aromatic cutter stocks, such as catalytic gas oils, have a favorable effect on fuel stability and permit higher visbreaker conversion levels before reaching fuel stability limitations [17].

The molecular structures of the compounds in petroleum which have boiling points above 1000°F (538°C) are highly complex and historically have been classified arbitrarily as oils, resins, and asphaltenes according to solubility in light paraffinic hydrocarbons. The oil fraction is soluble in propane the resin fraction is soluble (and the asphaltene fraction insoluble) in either pentane, hexane, n-heptane, or octane, depending upon the investigator. Usually either pentane or n-heptane is used. The solvent selected does have an effect on the amounts and properties of the fractions obtained, but normally little distinction is made in terminology. Chapter 9 (Catalytic Hydrocracking and Hydrocracking and Hydroprocessing) contains a more detailed discussion of the properties of these fractions.

Many investigators believe the asphaltenes are not in solution in the oil and resins, but are very small, perhaps molecular size, solids held in suspension by the resins, and there is a definite critical ratio of resins to asphaltenes below which the asphaltenes will start to precipitate. During the cracking phase some of the resins are cracked to lighter hydrocarbons and others are converted to asphaltenes. Both reactions affect the resin–asphaltene ratio and the resultant stability of the visbreaker tar product and serve to limit the severity of the operation.

The principal reactions [17] which occur during the visbreaking operation are:

1. Cracking of the side chains attached to cycloparaffin and aromatic rings at or close to the ring so the chains are either removed or shortened to methyl or ethyl groups.
2. Cracking of resins to light hydrocarbons (primarily olefins) and compounds which convert to asphaltenes.
3. At temperatures above 900°F (480°C), some cracking of naphthalene rings. There is little cracking of naphthenic rings below 900°F (480°C).

The severity of the visbreaking operation can be expressed in several ways: the yield of material boiling below 330°F (166°C), the reduction in product viscosity, and the amount of standard cutter stock needed to blend the visbreaker tar to No. 6 fuel oil specifications as compared with the amount needed for the feedstock [9]. In the United States usually the severity is expressed as the vol% product gasoline in a specified boiling range, and in Europe as the wt% yield of gas plus gasoline (product boiling below 330°F, or 165°C).

There are two types of visbreaker operations, coil and furnace cracking and soaker cracking. As in all cracking processes, the reactions are time-temperature dependent (see Table 5.12), and there is a trade-off between temperature and reaction time. Coil cracking uses higher furnace outlet temperatures [885–930°F (473–500°C)] and reaction times from one to three minutes, while soaker cracking uses lower furnace outlet temperatures [800–830°F (427–443°C)] and longer reaction times. The product yields and properties are similar, but the soaker operation with its lower furnace outlet temperatures has the advantages of lower energy consumption and longer run times before having to shut down to remove coke from the furnace tubes. Run times of 3–6 months are common for furnace visbreakers and 6–18 months for soaker visbreakers. This apparent advantage for soaker visbreakers is at least partially balanced by the greater difficulty in cleaning the soaking drum [2].

Table 5.12 Visbreaking
Time-Temperature Relationship
(Equal Conversion Conditions)

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

Source: Ref. 3.

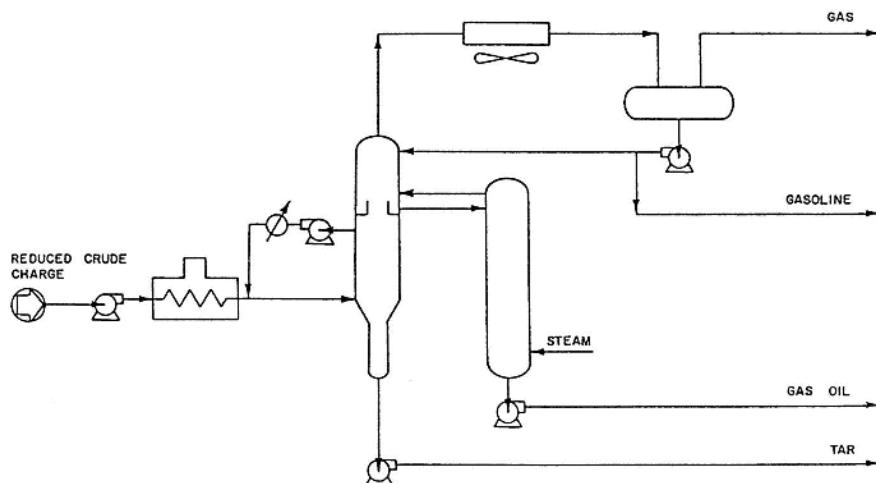
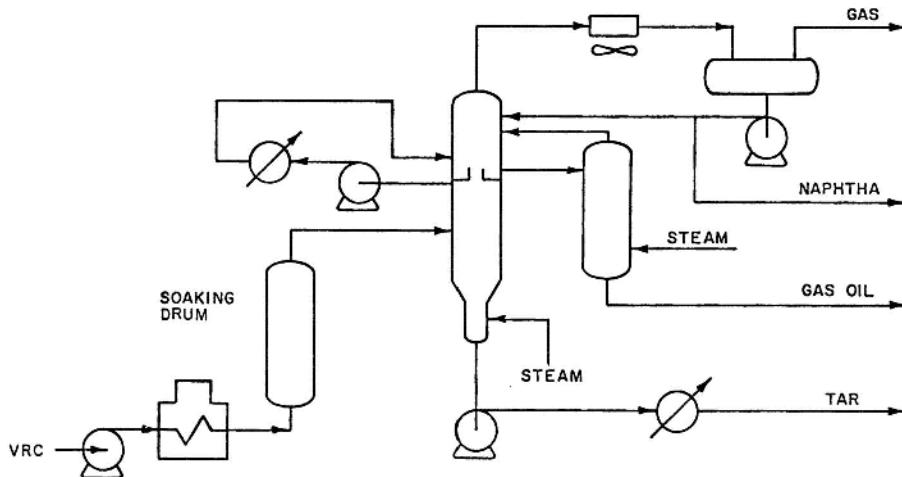


Figure 5.4 Coil visbreaker.

Process flow diagrams are shown in Figures 5.4 and 5.5. The feed is introduced into the furnace and heated to the desired temperature. In the furnace or coil cracking process the feed is heated to cracking temperature [885–930°F (474–500°C)] and quenched as it exits the furnace with gas oil or tower bottoms to stop the cracking reaction. In the soaker cracking operation, the feed leaves the furnace between 800 and 820°F (427–438°C) and passes through a soaking drum, which provides the additional reaction time, before it is quenched. Pressure is an important design and operating parameter with units being designed for pressures as high as 750 psig (5170 kPa) for liquid-phase visbreaking and as low as 100–300 psig (690–2070 kPa) for 20–40% vaporization at the furnace outlet [8]. Typical yields and product properties from visbreaking operations are shown in Tables 5.13 and 5.14.

For furnace cracking, fuel consumption accounts for about 80% of the operating cost with a net fuel consumption equivalent of 1–1.5 wt% on feed. Fuel requirements for soaker visbreaking are about 30–35% lower [3]. (See Table 5.15.)

Many of the properties of the products of visbreaking vary with conversion and the characteristics of the feedstocks. However, some properties, such as diesel index and octane number, are more closely related to feed qualities; and others, such as density and viscosity of the gas oil, are relatively independent of both conversion and feedstock characteristics [16].

**Figure 5.5** Soaker visbreaker.**Table 5.13** Visbreaking Results, Kuwait Long Resid

	Feed	Product
<i>Yields, wt%</i>		
Butane and lighter		2.5
C ₅ – 330°F naphtha		5.9
Gas oil, 660°F EP		13.5
Tar		78.1
<i>Product properties</i>		
Naphtha		
°API		65.0
Sulfur, wt%		1.0
RONC		
Gas oil		
°API		32.0
Sulfur, wt%		2.5
Tar or feed		
% on crude		
°API	14.4	11.0
Sulfur, wt%	4.1	4.3
Viscosity, cSt, 50°C	720	250

Source: Ref. 17.

Table 5.14 Visbreaking Results, Agha-Jari Short Resid

	Feed	Product
<i>Yields, wt%</i>		
Butane & lighter		2.4
C ₅ – 330°F naphtha		4.6
Gas oil, 660°F EP		14.5
Tar		78.5
<i>Product properties</i>		
Naphtha		
°API		
Sulfur, wt%		
RONC		
Gas Oil		
°API		32.2
Sulfur, wt%		
Tar or feed		
% on crude		
°API	8.2	5.5
Sulfur, wt%	—	
Viscosity, cSt, 122°F (50°C)	100,000	45,000

Source: Ref. 16.

Table 5.15 Coil and Soaker Visbreaking

	Coil	Soaker
Furnace outlet temperature, °F (°C)	900 (480)	805 (430)
Fuel consumption, relative	1.0	0.85
Capital cost, relative	1.0	0.90

5.9 CASE-STUDY PROBLEM: DELAYED COKER

See Section 4.6 for statement of problem and Table 4.7 for feed to delayed coker. The delayed coker material balance is calculated from the equations given in Table 5.3. The results are tabulated in Table 5.16.

Although at this time the only feed available for the delayed coker is the vacuum tower bottoms stream, other process units in the refinery produce heavy product streams that either can be blended into heavy fuel oil or sent to the delayed coker. The market for heavy fuel oil is limited and, for this example problem, no heavy fuel oil is produced. The heavy products from the fluid cata-

Table 5.16 Delayed Coker Material Balance: 100,000 BPCD Alaska North Slope Crude Oil Basis

Component	vol%	BPD	°API	(lb/hr)/BPD	lb/hr	wt% S	lb/hr S
<i>Feed</i>							
1050+ VRC	88.4	18,003	8.7	14.72	265,162	2.17	5,757
PCC HGO	11.5	2,338	-0.6	15.75	36,820	0.32	117
Alky Tar	0.1	25			468		
Total	100.0	20,366	7.4	14.85	302,450	1.94	5,875
<i>Products</i>							
Gas (C_4-), wt%	(22.7)				29,776	5.92	1,762
Light naphtha	7.6	1,551	65.0	10.51	16,303	0.36	59
Heavy naphtha	14.1	2,868	50.1	11.36	32,575	0.72	235
LCGO	37.3	7,587	30.0	12.78	96,967	0.93	905
HCGO	20.1	4,103	14.3	14.16	58,114	1.98	1,151
Coke, wt%	(22.7)				68,717	2.56	1,762
Total		16,110			302,450		5,875

Note. Conradson carbon, 1050+ °F RC = 14.2% (from Table 4.6).

lytic cracking unit (HGO) and the alkylation unit (tar) are sent to the delayed coker for processing. These streams are included in the feed to coker in this problem.

Calculations of yields:

$$\text{Coke} = 1.6 \text{ (14.2)} = 22.72 \text{ wt\%}.$$

$$\text{Gas } (C_4-) = 7.8 + 0.144 \text{ (14.2)} = 9.84 \text{ wt\%}.$$

$$\text{Naphtha} = 11.29 + 0.343 \text{ (14.2)} = 16.16 \text{ wt\%}.$$

$$\text{Naphtha} = [186.5/(131.5 + 7.4)](16.16) = 21.7 \text{ vol\%}.$$

$$\text{Gas oil} = 100.0 - (22.7 + 9.8 + 16.2) = 51.3 \text{ wt\%}.$$

$$\text{Gas oil} = [(155.5/138.9)](51.3) = 57.4 \text{ vol\%}.$$

Sulfur distribution is obtained from Table 5.9 and gas (C_4-) composition from Table 5.8.

Table 5.17 Coker Utility Requirements (Basis: 825 Tons Coke Per Day)

Steam, Mlb/day	577
Power, MkWh/day	25
Cooling water, gpm	990
Fuel, MMBtu/day	2851

Coker gas balance:

Total gas = 28,855 lb/hr
 Sulfur in gas = 1,758 lb/hr
 Sulfur-free gas = 27,097 lb/hr

Using composition of sulfur-free gas from Table 5.6, total lb mol/hr is $27,097 / 22.12 = 1,225$ and sulfur-free composition is calculated as follows:

Component	mol%	mol/hr
C ₁	51.4	650.9
C ₂ =	1.5	19.0
C ₂	15.9	201.4
C ₃ =	3.1	39.3
C ₃	8.2	103.8
C ₄ =	2.4	30.4
i-C ₄	1.0	12.7
n-C ₄	2.6	32.9
H ₂	13.7	173.5
CO ₂ ''	0.2	2.5
	100.0	1226.4

It is now necessary to adjust this gas composition to allow for the sulfur content. In actual operations some of the sulfur will be combined as mercaptan molecules (R-S-H) but for preliminary calculations it is sufficiently accurate to assume that all the sulfur in the gas fraction is combined as H₂S. Since there are 1758 lb/hr of sulfur (equivalent to 54.8 mol/hr), the free hydrogen must be reduced by 54.8 mol/hr so the final coker gas balance is as follows:

Component	mol/hr	MW	lb/hr	(lb/hr)/BPD	BPD
C ₁	650.9	16	10,415		
C ₂ =	19.0	28	532		
C ₂	201.4	30	6,041		
C ₃ =	39.3	42	1,649	7.61	217
C ₃	103.8	44	4,569	7.42	616
C ₄ =	30.4	56	1,702	8.76	194
iC ₄	12.7	58	735	8.22	89
nC ₄	32.9	58	1,910	8.51	224
H ₂	118.5	2	237		
CO ₂	2.5	44	111		
H ₂ S	55.1	34	1,873		
Total	1,266.4		29,773		1,341

PROBLEMS

1. For the crude oil in Figures 3.5 and 3.9 estimate the Conradson carbon of the 1050+°F (566°C) residual crude oil fraction.
2. Estimate the coke yields for the crude oil fraction of problem 1 and make a material balance around the delayed coking unit. The 1050+°F (566°C) fraction contains 0.38% sulfur by weight.
3. Using the information from problem 2, estimate the capital cost of a 7500 BPSD delayed coking unit and its utility requirements.
4. Using Bureau of Mines distillation data from Appendix C, calculate the coke yield and make a material balance from a Torrence Field, California crude oil residuum having an API gravity of 23.8° and a sulfur content of 1.84 wt%.
5. Estimate the capital and operating costs for a 10,000 BPSD delayed coker processing the reduced crude of problem 4. Assume four workers per shift at an average of \$20.50/hr per worker.
6. Calculate the long tons per day of coke produced by charging 30,000 barrels of 1050+°F (566°C) residuum from the assigned crude oil to a delayed coking unit.
7. If 95% of the hydrogen sulfide present in the coker gas product stream can be converted to elemental sulfur, how many long tons of sulfur will be produced per day when charging 30,000 barrels of 1050+°F (566°C) residuum from the assigned crude oil to the delayed coker?
8. Make a material balance around the delayed coker for the charge rate and the crude oil of problems 6 and 7. Also estimate the utility requirements.
9. Estimate the capital and operating costs for a 30,000 BPSD delayed coker processing the assigned reduced crude. Assume four workers per shift at an average of \$20.50/hr per worker.

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6

Catalytic Cracking

Catalytic cracking is the most important and widely used refinery process for converting heavy oils into more valuable gasoline and lighter products, with 10.6 MMBPD (over 1 million tons/day) of oil processed in the world [29]. Originally cracking was accomplished thermally but the catalytic process has almost completely replaced thermal cracking because more gasoline having a higher octane and less heavy fuel oils and light gases are produced [28]. The light gases produced by catalytic cracking contain more olefins than those produced by thermal cracking (Table 6.1).

The cracking process produces carbon (coke) which remains on the catalyst particle and rapidly lowers its activity. To maintain the catalyst activity at a useful level, it is necessary to regenerate the catalyst by burning off this coke with air. As a result, the catalyst is continuously moved from reactor to regenerator and back to reactor. The cracking reaction is endothermic and the regeneration reaction exothermic. Some units are designed to use the regeneration heat to supply that needed for the reaction and to heat the feed up to reaction temperature. These are known as “heat balance” units.

Average riser reactor temperatures are in the range 900 to 1000°F (480–540°C), with oil feed temperatures from 500 to 800°F (260–425°C) and regenerator exit temperatures for catalyst from 1200 to 1500°F (650–815°C).

The catalytic-cracking processes in use today can all be classified as either moving-bed or fluidized-bed units. There are several modifications under each of the classes depending upon the designer or builder, but within a class the basic operation is very similar. The Thermafor catalytic cracking process (TCC) is representative of the moving-bed units and the fluid catalytic cracker (FCC) of the fluidized-bed units. There are very few TCC units in operation today and the FCC unit has taken over the field. The FCC units can be classified as either bed or riser (transfer line) cracking units depending upon where the major fraction of the cracking reaction occurs.

Table 6.1 Thermal Versus Catalytic Cracking Yields on Similar Topped Crude Feed

	Thermal cracking		Catalytic cracking	
	wt%	vol%	wt%	vol%
Fresh feed	100.0	100.0	100.0	100.0
Gas	6.6		4.5	
Propane	2.1	3.7	1.3	2.2
Propylene	1.0	1.8	2.0	3.4
Isobutane	.8	1.3	2.6	4.0
n-Butane	1.9	2.9	0.9	1.4
Butylene	1.8	2.6	2.6	3.8
C ₅ + gasoline	26.9	32.1	40.2	46.7
Light cycle oil	1.9	1.9	33.2	32.0
Decant oil			7.7	8.7
Residual oil	57.0	50.2		
Coke	0		5.0	
Total	100.0	96.5	100.0	102.2

The process flows of both types of processes are similar. The hot oil feed is contacted with the catalyst in either the feed riser line or the reactor. As the cracking reaction progresses, the catalyst is progressively deactivated by the formation of coke on the surface of the catalyst. The catalyst and hydrocarbon vapors are separated mechanically, and oil remaining on the catalyst is removed by steam stripping before the catalyst enters the regenerator. The oil vapors are taken overhead to a fractionation tower for separation into streams having the desired boiling ranges.

The spent catalyst flows into the regenerator and is reactivated by burning off the coke deposits with air. Regenerator temperatures are carefully controlled to prevent catalyst deactivation by overheating and to provide the desired amount of carbon burn-off. This is done by controlling the air flow to give a desired CO₂/CO ratio in the exit flue gases or the desired temperature in the regenerator. The flue gas and catalyst are separated by cyclone separators and electrostatic precipitators. The catalyst in some units is steam-stripped as it leaves the regenerator to remove adsorbed oxygen before the catalyst is contacted with the oil feed.

6.1 FLUIDIZED-BED CATALYTIC CRACKING

The FCC process employs a catalyst in the form of very fine particles [average particle size about 70 micrometers (microns)] which behave as a fluid when aer-

ated with a vapor. The fluidized catalyst is circulated continuously between the reaction zone and the regeneration zone and acts as a vehicle to transfer heat from the regenerator to the oil feed and reactor. Two basic types of FCC units in use today are the "side-by-side" type, where the reactor and regenerator are separate vessels adjacent to each other, and the Orthoflow, or stacked type, where the reactor is mounted on top of the regenerator. Typical FCC unit configurations are shown in Figures 6.1 to 6.8 and photos 6 and 7, Appendix E.

One of the most important process differences in FCC units relates to the location and control of the cracking reaction. Until about 1965, most units were designed with a discrete dense-phase fluidized-catalyst bed in the reactor vessel. The units were operated so most of the cracking occurred in the reactor bed. The extent of cracking was controlled by varying reactor bed depth (time) and temperature. Although it was recognized that cracking occurred in the riser feeding the reactor because the catalyst activity and temperature were at their highest there, no significant attempt was made to regulate the reaction by controlling riser conditions. After the more reactive zeolite catalysts were adopted by refineries, the amount of cracking occurring in the riser (or transfer line) increased to levels requiring operational changes in existing units. As a result, most recently constructed units have been designed to operate with a minimum bed level in

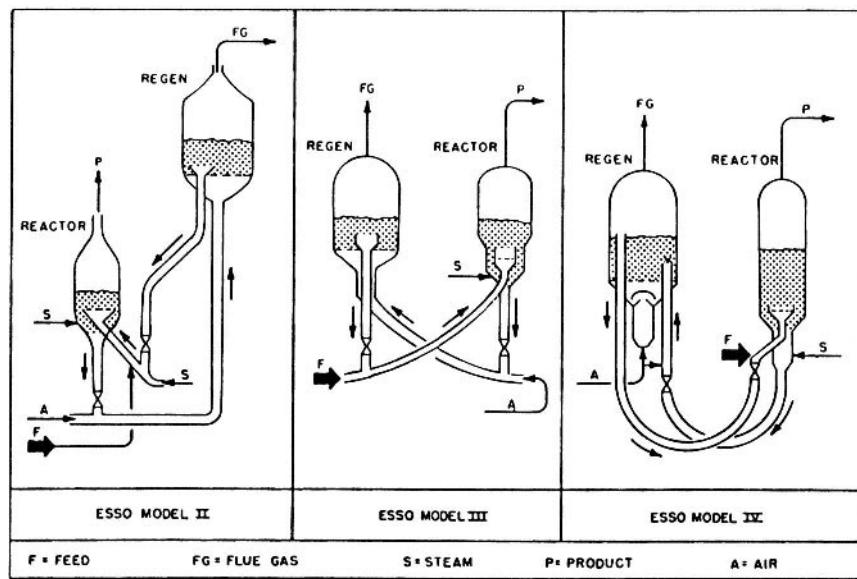


Figure 6.1a Older fluid catalytic-cracking (FCC) unit configurations.

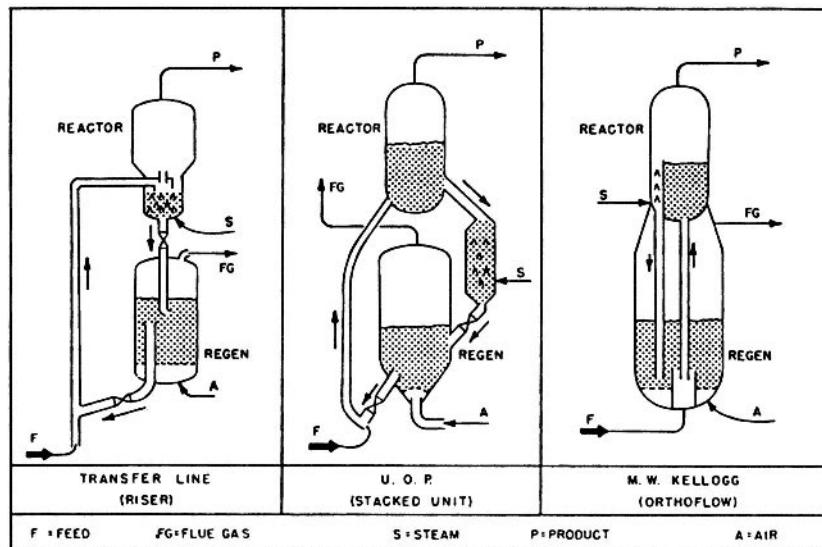


Figure 6.1b Older fluid catalytic-cracking (FCC) unit configurations.

the reactor and with control of the reaction being maintained by a varying catalyst circulation rate. Many older units have been modified to maximize and control riser cracking. Units are also operating with different combinations of feed-riser and dense-bed reactors, including feed-riser followed by dense-bed, feed-riser in parallel with dense-bed, and parallel feed-riser lines (one for fresh feed and the other for recycle) [31]. The major changes have been to take advantage of improvements in catalysts and to get more efficient contact of heavy feedstocks with the catalyst particles. The results have been higher conversion levels with better selectivity (higher gasoline yields at given conversion levels) by shorter and better controlled reaction times (1–3 sec), closed cyclones, and improved feed distribution systems. These have been summarized by James R. Murphy [26]. Alvaro Murcia reviewed reactor–regenerator configurations from the initial commercial FCC unit through today’s residue processing units [25]. Most of the designs are similar to those shown in Figures 6.1 through 6.8.

The fresh feed and recycle streams are preheated by heat exchangers or a furnace and enter the unit at the base of the feed riser where they are mixed with the hot regenerated catalyst. The heat from the catalyst vaporizes the feed and brings it up to the desired reaction temperature. The mixture of catalyst and hydrocarbon vapor travels up the riser into the reactors. The cracking reactions start when the feed contacts the hot catalyst in the riser and continues until the oil

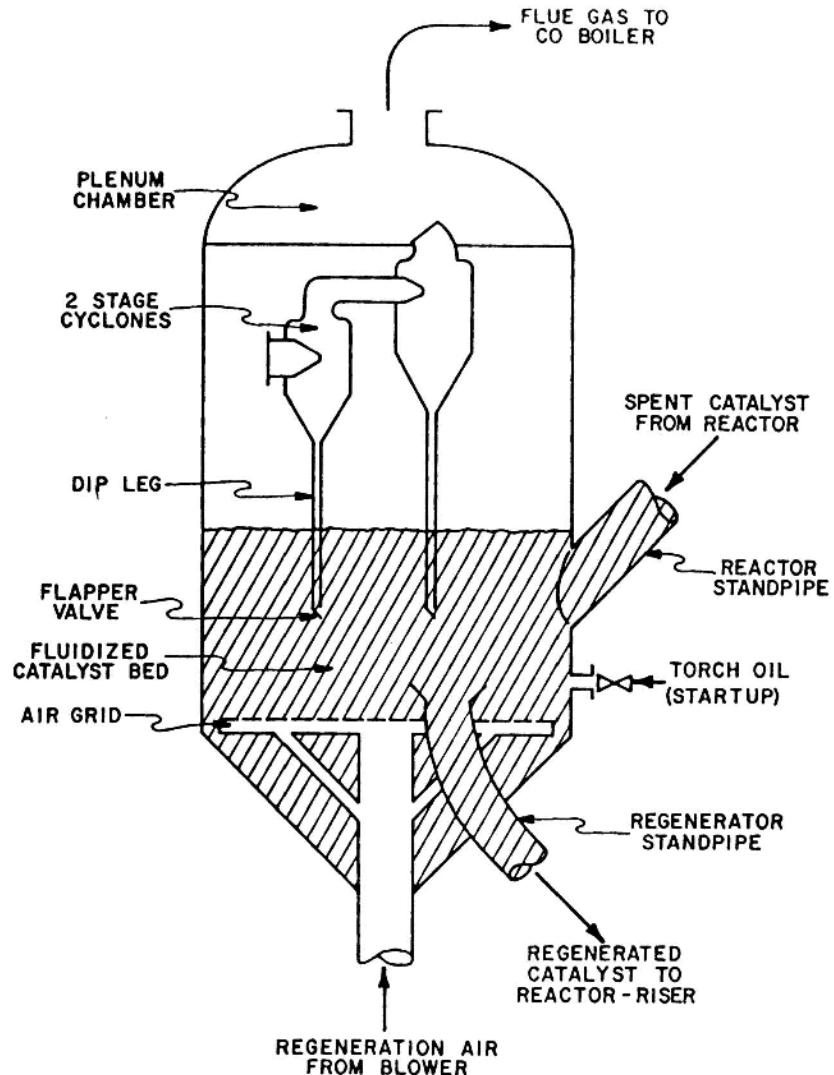


Figure 6.2 FCC regenerator.

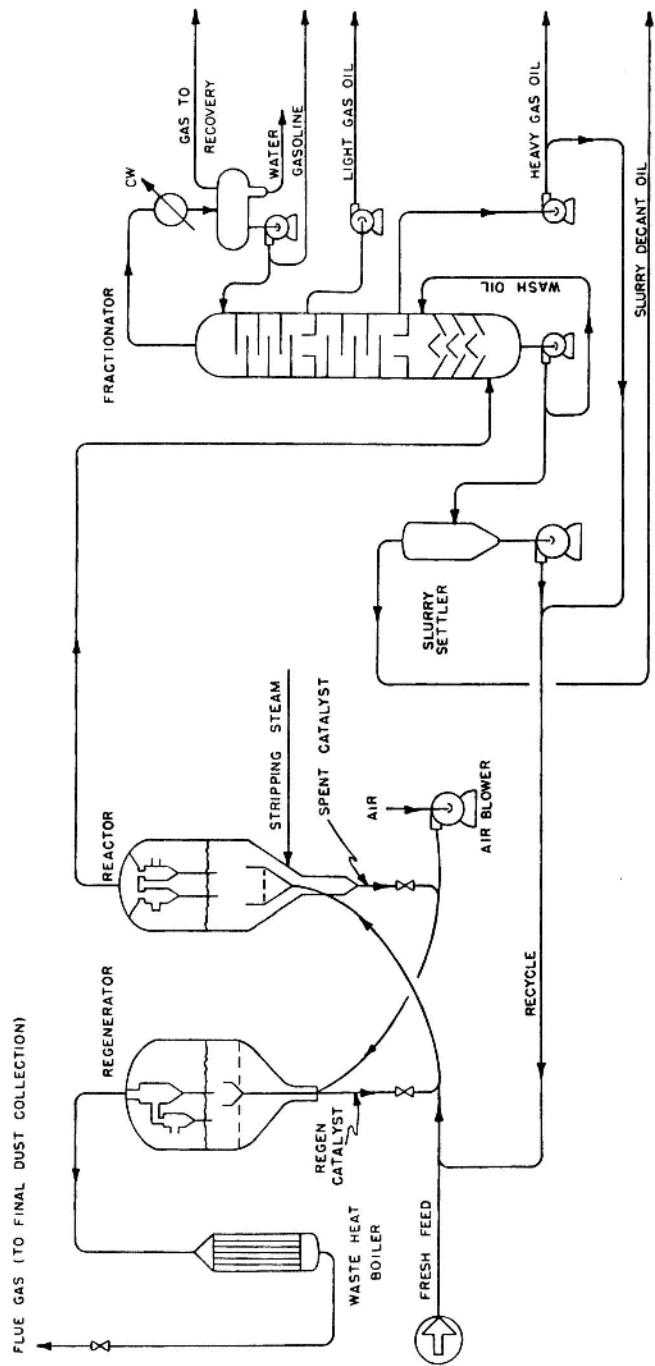


Figure 6.3 FCC unit, Model III.

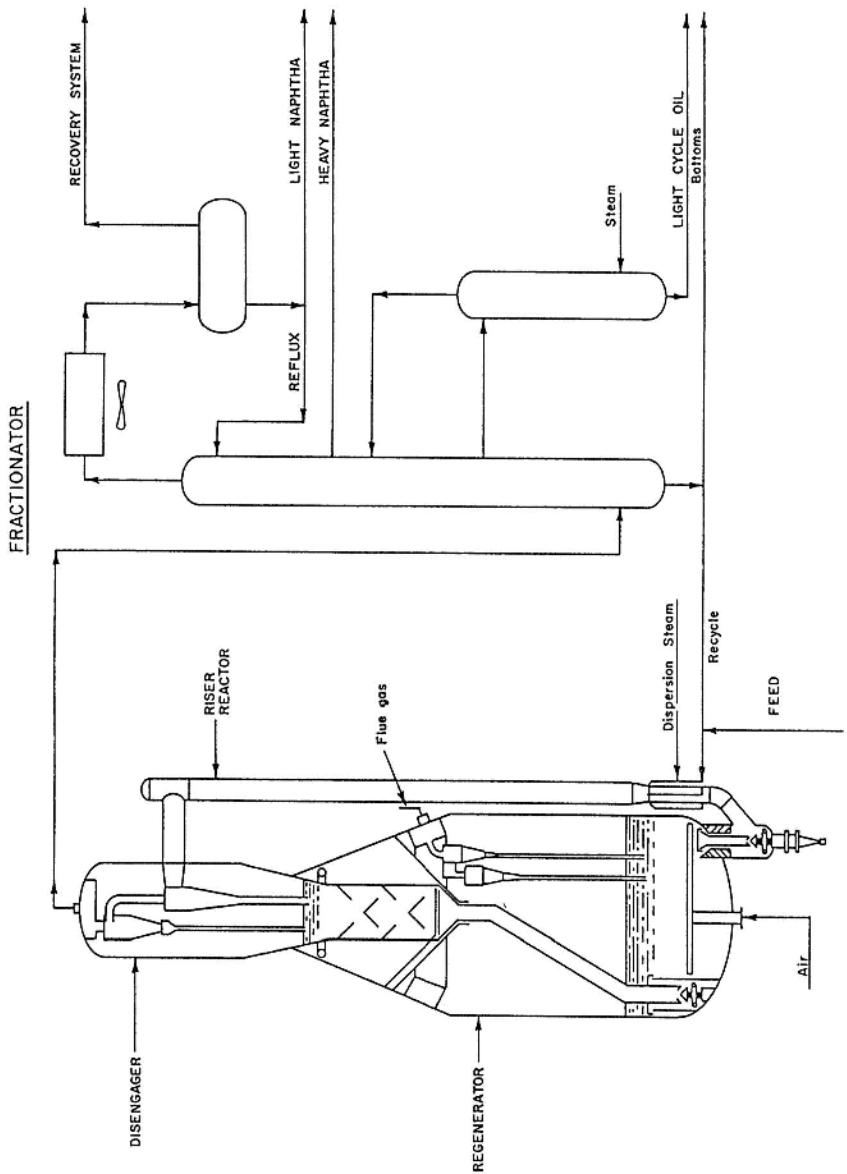


Figure 6.4 FCC unit, M. W. Kellogg design.

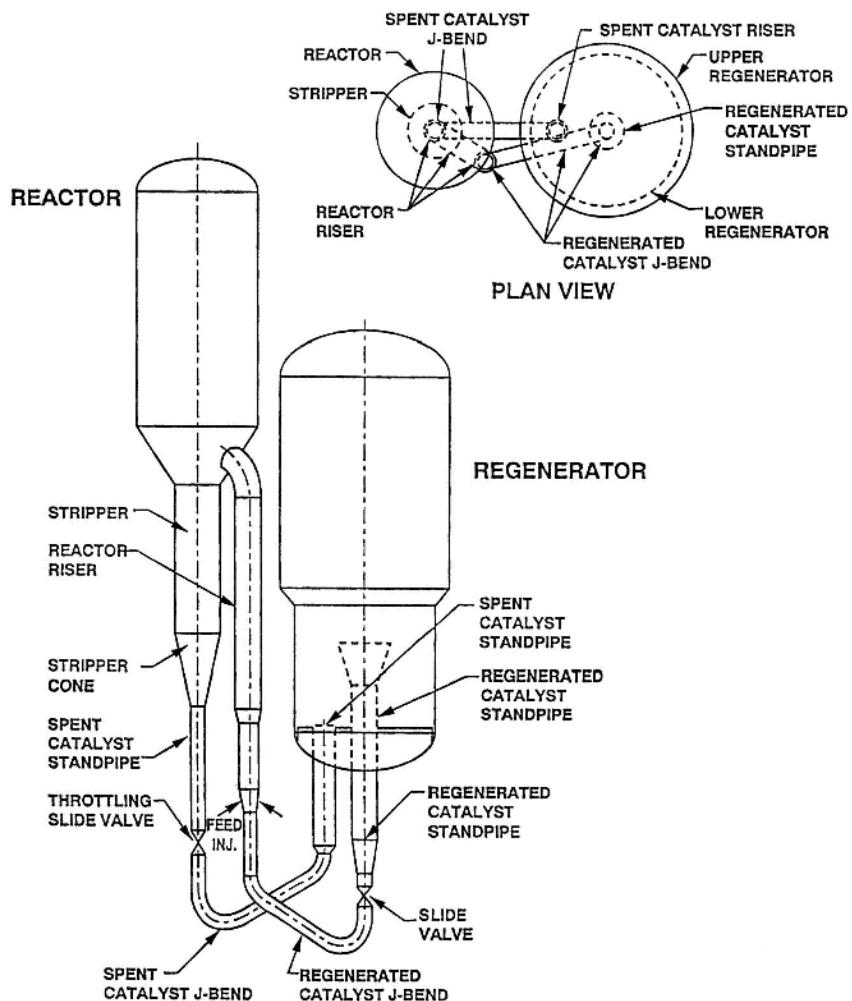


Figure 6.5 Exxon FLEXICRACKING IIIR FCC unit. (Courtesy of Exxon Research and Engineering.)

vapors are separated from the catalyst in the reactor. The hydrocarbon vapors are sent to the synthetic crude fractionator for separation into liquid and gaseous products.

The catalyst leaving the reactor is called spent catalyst and contains hydrocarbons adsorbed on its internal and external surfaces as well as the coke deposited by the cracking. Some of the adsorbed hydrocarbons are removed by steam

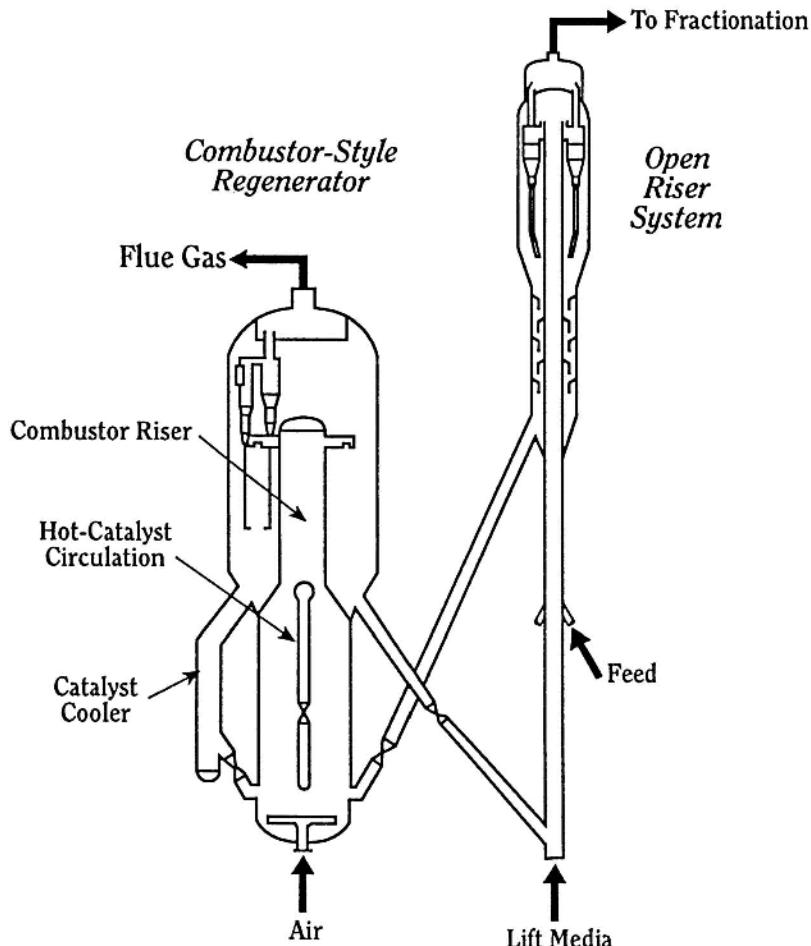


Figure 6.6a UOP FCC style unit. (Courtesy of UOP, LLC.)

stripping before the catalyst enters the regenerator. In the regenerator, coke is burned from the catalyst with air. The regenerator temperature and coke burn-off are controlled by varying the air flow rate. The heat of combustion raises the catalyst temperature to 1150 to 1550°F (620–845°C) and most of this heat is transferred by the catalyst to the oil feed in the feed riser. The regenerated catalyst contains from 0.01 to 0.4 wt% residual coke depending upon the type of combustion (burning to CO or CO₂) in the regenerator.

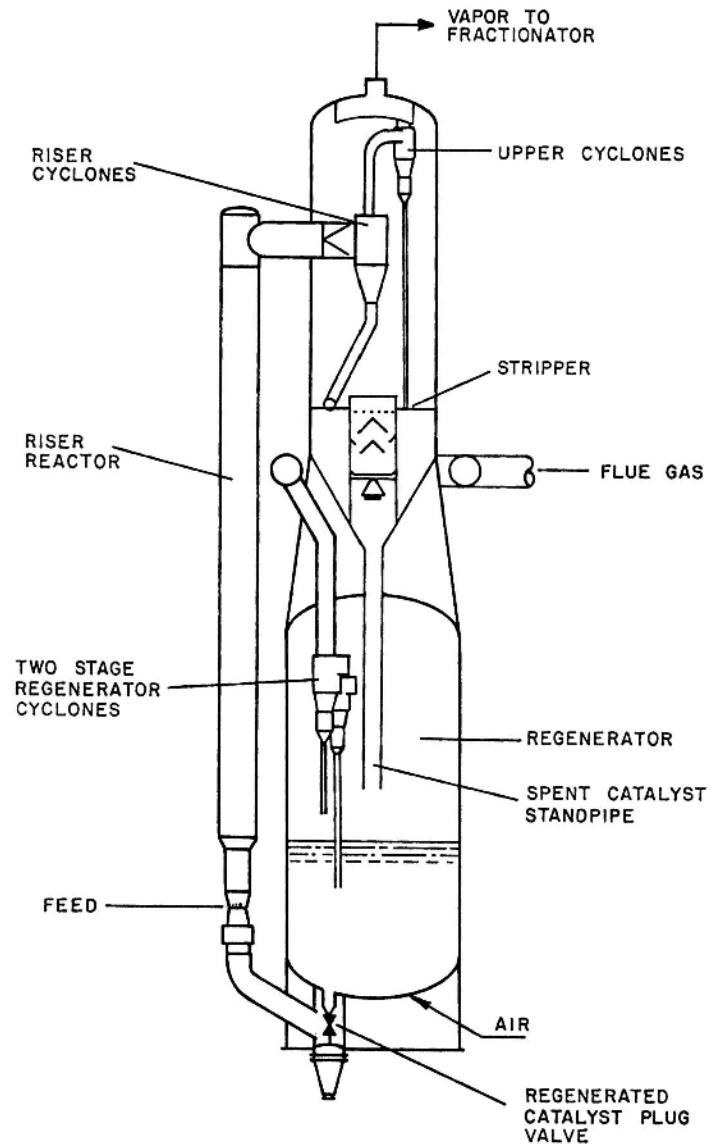


Figure 6.6b M. W. Kellogg design, riser FCC unit.

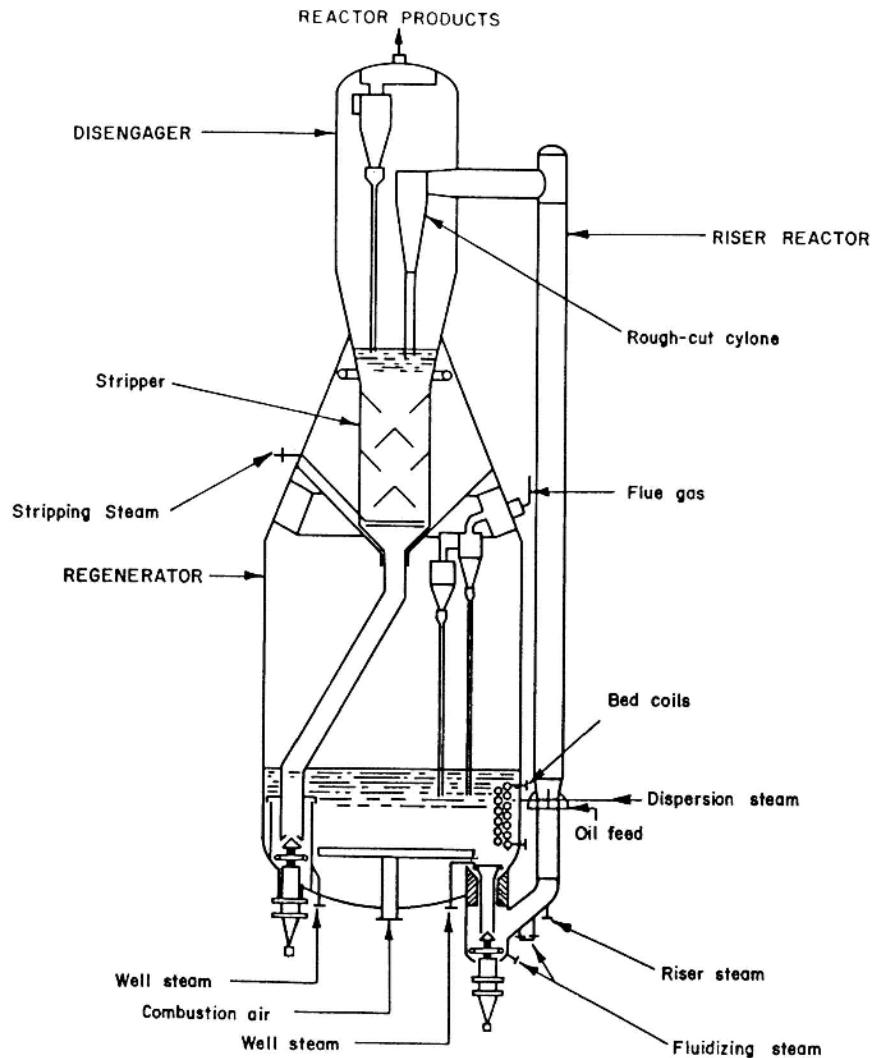


Figure 6.7 M. W. Kellogg resid fluid catalytic cracking (RFCC) unit.

The regenerator can be designed and operated to burn the coke on the catalyst to either a mixture of carbon monoxide and carbon dioxide or completely to carbon dioxide. Older units were designed to burn to carbon monoxide to minimize blower capital and operating costs because only about half as much air had to be compressed to burn to carbon monoxide rather than to carbon diox-

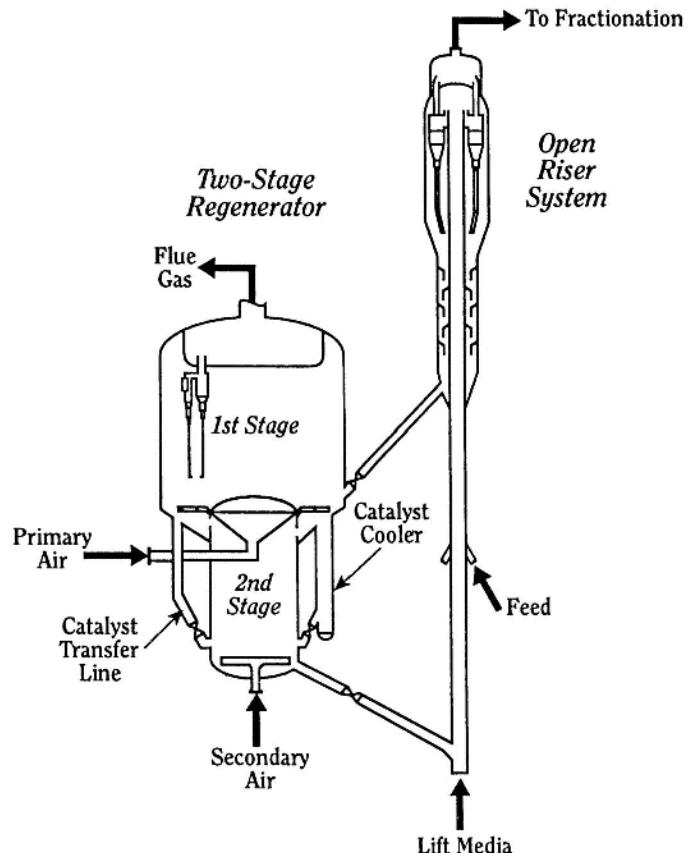


Figure 6.8 UOP RCC reduced crude cracking unit. (Courtesy of UOP, LLC.)

ide. Newer units are designed and operated to burn the coke to carbon dioxide in the regenerator because they can burn to a much lower residual carbon level on the regenerated catalyst. This gives a more reactive and selective catalyst in the riser and a better product distribution results at the same equilibrium catalyst activity and conversion level.

For units burning to carbon monoxide, the flue gas leaving the regenerator contains a large quantity of carbon monoxide which is burned to carbon dioxide in a CO furnace (waste heat boiler) to recover the available fuel energy. The hot gases can be used to generate steam or to power expansion turbines to compress the regeneration air and generate electric power. A schematic diagram of a typical

FCC reactor and regenerator is shown in Figure 6.2, a flow diagram for a Model III FCC unit is given in Figure 6.3, and of a Kellogg FCC unit in Figure 6.4.

6.2 NEW DESIGNS FOR FLUIDIZED-BED CATALYTIC CRACKING UNITS

Zeolite catalysts have a much higher cracking activity than amorphous catalysts, and shorter reaction times are required to prevent overcracking of gasoline to gas and coke. This has resulted in units which have a catalyst-oil separator in place of the fluidized-bed reactor to achieve maximum gasoline yields at a given conversion level. Many of the newer units are designed to incorporate up to 25% reduced crude in the FCC unit feed. Schematic drawings of Exxon Research and Engineering's FLEXICRACKING IIIR design are shown in Figure 6.5 [6,17]. These units incorporate a high height-to-diameter ratio lower regenerator section for more efficient single-stage regeneration and an offset side-by-side or stacked vessel design. UOP-designed units utilize high velocity, low inventory regenerators (Fig. 6.6a), and Kellogg-designed units use plug valves to minimize erosion by catalyst containing streams (Fig. 6.6b). All units are now designed for both complete combustion to CO₂ and CO combustion control.

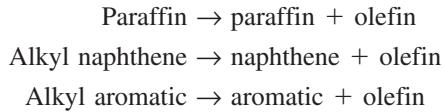
The large differential value between residual fuel and other catalytic cracking feed stocks has caused refiners to blend atmospheric and vacuum tower bottoms into the FCC feed. Residual feed stocks have orders of magnitude higher metals contents (especially nickel and vanadium) and greater coke forming potential (Ramsbottom and Conradson carbon values) than distillate feeds. These contaminants reduce catalyst activity, promote coke and hydrogen formation, and decrease gasoline yield. It has been shown that catalyst activity loss due to metals is caused primarily by vanadium deposition, and increased coke and hydrogen formation is due to nickel deposited on the catalyst [6,7]. The high coke laydown creates problems because of the increased coke burning requirement with the resulting increased air or oxygen demand, higher regenerator temperatures, and greater heat removal. For feeds containing up to 15 ppm Ni + V, passivation of nickel catalyst activity can be achieved by the addition of organic antimony compounds to the feed [7] with reductions in coke and hydrogen yields up to 15% and 45%, respectively. For feeds containing > 15 ppm metals and having Conradson carbon contents above 3%, hydroprocessing of the FCC feed may be required to remove metals, reduce the carbon forming potential, and increase the yield of gasoline and middle distillates by increasing the hydrogen content of the feed.

Designs of FCC units have been modified for higher carbon burning, heat removal, and gas product rates by larger equipment sizing and introduction of

steam generation coils. Kellogg's resid fluid catalytic cracking unit (RFCC), formerly called the heavy oil cracking (HOC) FCC unit, developed with Phillips Petroleum Company is shown in Figure 6.7 [33].

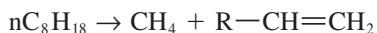
6.3 CRACKING REACTIONS

The products formed in catalytic cracking are the result of both primary and secondary reactions [14]. Primary reactions are designed as those involving the initial carbon–carbon bond scission and the immediate neutralization of the carbonium ion [24]. The primary reactions can be represented as follows:

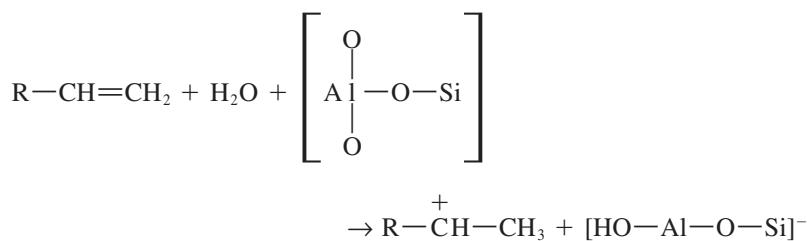


Thomas [37] suggested the mechanism that carbonium ions are formed initially by a small amount of thermal cracking of n-paraffins to form olefins. These olefins add a proton from the catalyst to form large carbonium ions which decompose according to the beta rule (carbon–carbon bond scission takes place at the carbon in the position beta to the carbonium ions and olefins) to form small carbonium ions and olefins. The small carbonium ions propagate the chain reaction by transferring a hydrogen ion from a n-paraffin to form a small paraffin molecule and a new large carbonium ion [11,31]. As an example of a typical n-paraffin hydrocarbon cracking reaction, we may look at the following sequence for n-octane (where R = CH₃CH₂CH₂CH₂CH₂–).

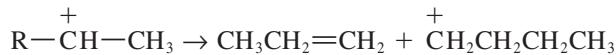
Step 1: Mild thermal cracking initiation reaction.



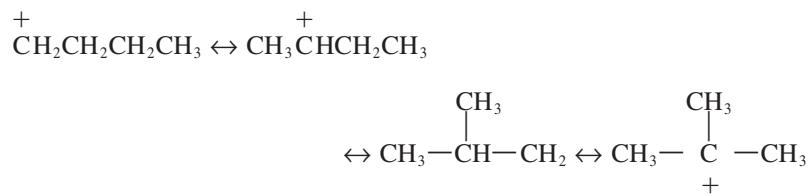
Step 2: Proton shift.



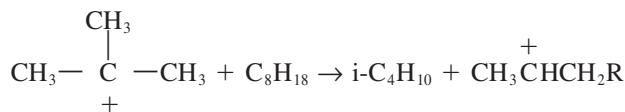
Step 3: Beta scission.



Step 4: Rearrangement toward more stable structure. The order of carbonium ion stability is tertiary > secondary > primary.



Step 5: Hydrogen ion transfer.



Thus another large carbonium ion is formed and the chain is ready to repeat itself.

Even though the basic mechanism is essentially the same, the manner and extent of response to catalytic cracking differs greatly among the various hydrocarbon types.

6.4 CRACKING OF PARAFFINS

The catalytic cracking of paraffins is characterized by high production of C₃ and C₄ hydrocarbons in the cracked gases, reaction rates and products determined by size and structure of paraffins, and isomerization to branched structures and aromatic hydrocarbons formation resulting from secondary reactions involving olefins [13]. In respect to reaction rates, the effect of the catalyst is more pronounced as the number of carbon atoms in the molecule increases, but the effect is not appreciable until the number of carbon atoms is at least six.

The cracking rate is also influenced by the structure of the molecule, with those containing tertiary carbon atoms cracking most readily, while quaternary carbon atoms are most resistant. Compounds containing both types of carbon atoms tend to neutralize each other on a one-to-one basis. For example, 2,2,4-trimethylpentane (one tertiary and one quaternary) cracks only slightly faster than

n-octane, while 2,2,4,6,6-pentamethylheptane (one tertiary and two quaternary) cracks at a slower rate than does n-dodecane.

6.5 OLEFIN CRACKING

The catalytic cracking rates of olefinic hydrocarbons are much higher than those of the corresponding paraffins. The main reactions are [11]:

1. Carbon–carbon bond scissions
2. Isomerization
3. Polymerization
4. Saturation, aromatization, and carbon formation

Olefin isomerization followed by saturation and aromatization are responsible for the high octane number and lead susceptibility of catalytically cracked gasolines. The higher velocity of hydrogen transfer reactions for branched olefins results in ratios of iso- to normal paraffins higher than the equilibrium ratios of the parent olefins. In addition, naphthenes act as hydrogen donors in transfer reactions with olefins to yield isoparaffins and aromatics.

6.6 CRACKING OF NAPHTHENIC HYDROCARBONS

The most important cracking reaction of naphthenes in the presence of silica-alumina is dehydrogenation to aromatics. There is also carbon–carbon bond scission in both the ring and attached side chains but at temperatures below 1000°F (540°C) the dehydrogenation reaction is considerably greater. Dehydrogenation is very extensive for C₉ and larger naphthenes and a high-octane gasoline results. The non-ring liquid products and cracked gases resulting from naphthenic hydrocarbon cracking are more saturated than those resulting from cracking paraffins.

6.7 AROMATIC HYDROCARBON CRACKING

Aromatic hydrocarbons with alkyl groups containing less than three carbon atoms are not very reactive. The predominant reaction for aromatics with long alkyl chains is the clean splitting off of side chains without breaking the ring. The carbon–carbon bond ruptured is that adjacent to the ring, and benzene compounds containing alkyl groups can be cracked with nearly quantitative recovery of benzene [11].

6.8 CRACKING CATALYSTS

Commercial cracking catalysts can be divided into three classes: (1) acid-treated natural aluminosilicates, (2) amorphous synthetic silica-alumina combinations, and (3) crystalline synthetic silica-alumina catalysts called zeolites or molecular sieves [1]. Most catalysts used in commercial units today are either class 3 or mixtures of classes 2 and 3 catalysts [15]. See Tables 6.2 and 6.3. The advantages of the zeolite catalysts over the natural and synthetic amorphous catalysts are:

1. Higher activity
2. Higher gasoline yields at a given conversion
3. Production of gasolines containing a larger percentage of paraffinic and aromatic hydrocarbons
4. Lower coke yield (and therefore usually a larger throughput at a given conversion level)
5. Increased isobutane production
6. Ability to go to higher conversions per pass without overcracking

Table 6.2 Comparison of Amorphous and Zeolite Catalysts

	Amorphous	Zeolite
Coke, wt%	4	4
Conversion, vol%	55	65
C ₅ + gasoline, vol%	38	51
C ₃ - gas, wt%	7	6
C ₄ 's, vol%	17	16

Source: Ref. 4.

Table 6.3 Y Zeolite Types in Catalyst

Type Y zeolite	Major attributes
Rare earth exchanged Y (REY)	Highest gasoline yield
Ultrastable Y (USY)	Highest octane, low H-transfer, best coke selectivity (resid)
Rare earth exchanged USY (RE USY)	Gasoline-octane balance, better coke selectivity

Source: Ref. 3.

The high activity of zeolitic cracking catalyst permits short residence time cracking and has resulted in most cracking units being adapted to riser cracking operations [15]. Here the adverse effects of carbon deposits on catalyst activity and selectivity are minimized because of the negligible amount of catalyst back-mixing in the riser. In addition, separate risers can be used for cracking the recycle stream and the fresh feed so that each can be cracked at their own optimum conditions.

The catalytic effects of zeolitic catalysts can be achieved with only 10 to 25% of the circulating catalyst as zeolites [18] and the remainder amorphous silica-alumina cracking catalyst. Amorphous catalysts have higher attrition resistance and are less costly than zeolitic catalysts. Most commercial catalysts contain approximately 15% zeolites and thus obtain the benefits of the higher activity and gasoline selectivity of the zeolites and the lower costs and make-up rates of the amorphous catalysts. Lower attrition rates also greatly improve particulate emission rates.

Basic nitrogen compounds, iron, nickel, vanadium, and copper in the oil act as poisons to cracking catalysts [1]. The nitrogen reacts with the acid centers on the catalyst and lowers the catalyst activity. The metals deposit and accumulate on the catalyst and cause a reduction in throughput by increasing coke formation and decreasing the amount of coke burn-off per unit of air by catalyzing coke combustion to CO_2 rather than to CO .

It is generally accepted that nickel has about four times as great an effect on catalyst activity and selectivity as vanadium, and some companies use a factor of $4\text{Ni} + \text{V}$ (expressed in ppm) to correlate the effects of metals loading while others use $\text{Ni} + \text{V}/4$ or $\text{Ni} + \text{V}/5$ [13,24,35].

Although the deposition of nickel and vanadium reduces catalyst activity by occupying active catalytic sites, the major effects are to promote the formation of gas and coke and reduce the gasoline yield at a given conversion level. Tolen [39] and others [15] have discussed the effects of nickel and vanadium deposits on equilibrium catalysts (Fig. 6.9a and b). Metals loadings on equilibrium catalysts are now as high as 10,000 ppm and, in 1998, the mean was over 3000 ppm of nickel plus vanadium [34]. The effects of nickel can be partially offset by the addition of passivators, such as antimony and barium compounds, to the feed and catalysts containing tin, barium and strontium titanates, and magnesium oxide have been developed which act as metal traps for vanadium [21]. Metals removal processes can also be used to reactivate the catalyst by cycling a slip stream through a metals removal system (Demet). This permits the equilibrium catalyst metals concentrations to be controlled at the level at which the fresh catalyst required to maintain activity and selectivity equals catalyst losses [9].

A range of catalysts is available from catalyst manufacturing companies that are compounded to give high gasoline octanes (0.5 to 1.5 RON improvement), resist deactivation due to sulfur or metals in the feed, and to transfer sulfur

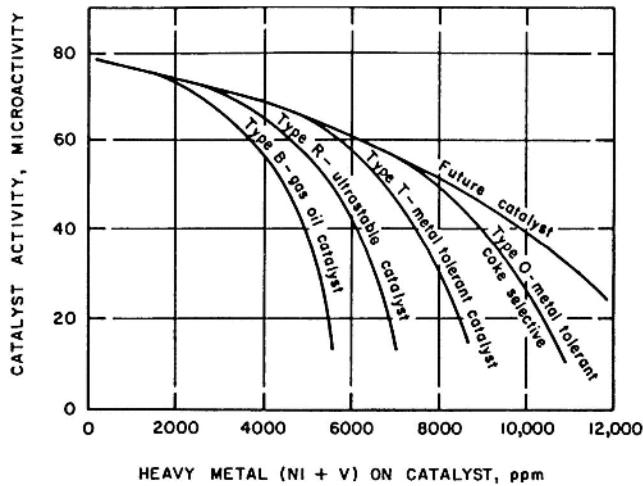


Figure 6.9a Catalyst activity loss from heavy metals. (From Ref. 39.)

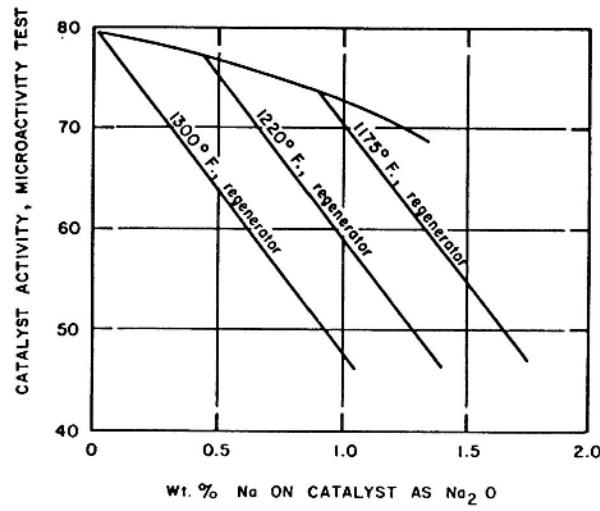


Figure 6.9b Catalyst activity loss from sodium contamination. (From Ref. 39.)

from the regenerator to the reactor (to reduce SO_x in the regenerator flue gas) [18]. For each operation and feed, economic and/or environmental considerations affect the catalyst used.

The average microactivity of FCC catalyst in North and South America in 1998 was between 67 and 70, while world activity averaged between 65 and 70. In the United States approximately two-thirds of the FCC units supply propylene to the chemicals market and supply about 50% of the U.S. propylene demand. Additives are available which increase the percentage of propylene in the butane and lighter gases from the FCC unit. By operating at higher conversion levels the butylene and propylene production (as well as total butane and lighter gas yields) can be increased at the expense of naphtha. The naphtha has 1–2 higher blending octane numbers because the additives crack the low octane straight chain and lightly branched paraffins and olefins to propylenes and butylenes [35].

The zeolite content of catalysts ranges from 15 to 40 wt% [3].

Catalysts for the processing of resids in specially designed FCC units have to be designed with a range of pore size distributions to handle the large molecules ($>30 \text{ \AA}$) present and also smaller pores to give higher activities. Avidan [3] summarizes the need for high matrix activity to increase bottoms conversion along with a distribution of large liquid-catching pores ($>100 \text{ \AA}$) with lower activity to control coke and gas make, meso pores ($30\text{--}100 \text{ \AA}$) with higher activity, and small pores ($<20 \text{ \AA}$) with very high activity. The meso pores are most effective for reducing bottoms yields for aromatic and naphthenic feedstocks and small pores for paraffinic feedstocks.

6.9 FCC FEED PRETREATING

The trend toward low sulfur and nitrogen contents in gasolines and diesel fuels requires that either the FCC unit feed or products be treated to reduce sulfur and nitrogen. Treating feed to the FCC unit offers the advantages that the sulfur and nitrogen in the gasoline and diesel fuel products are reduced and, by adding hydrogen to the feed, naphtha and LCO yields are increased without lowering the olefins content and octanes of the naphtha fraction [42]. For refineries that do not hydrotreat the FCC feed or naphtha products, over 95% of the sulfur in the gasoline blending pool is from the FCC naphtha.

The hydrotreating unit can be operated in several ways: as a hydrodesulfurization (HDS) unit, a mild hydrocracking (MHC) unit, or a partial-conversion hydrocracking unit. In all cases the product sulfur content has to be less than 135 wppm to produce a refinery gasoline blending pool with less than 50 wppm sulfur and less than 85 wppm to produce a refinery gasoline blending pool of less than 30 wppm.

If operated as an HDS or MHC unit, the operating pressure is in the 800–1000 psig (55–70 barg) range. Higher operating pressures [1400–1600 psig (95–110 barg)] are necessary to provide the aromatic ring hydrogenation necessary for partial-conversion hydrocracking (Fig. 6.10) [43]. The partial-conversion hydrocracking unit also produces distillates with 50 cetane indices (CI), less than 50 wppm sulfur, and smoke points of 15–19 mm. The capital costs of the units designed for 1000 and 1500 psig (70 and 102 barg) are from 15 to 110% higher than the HDS unit designed for 900 psig (60 barg) [43].

Using MHC or partial-conversion hydrocracking instead of hydrocracking offers greater flexibility by increasing the yield of higher-value products such as diesel fuel and jet fuel. MHC, because of its lower operating pressure and less hydrogenation of aromatic rings, typically produces diesel fuels with cetane indices from 39–42 and the kerosine smoke points well below the 19 mm smoke point required for jet fuels. Partial-conversion hydrocracking, operating at 1400–

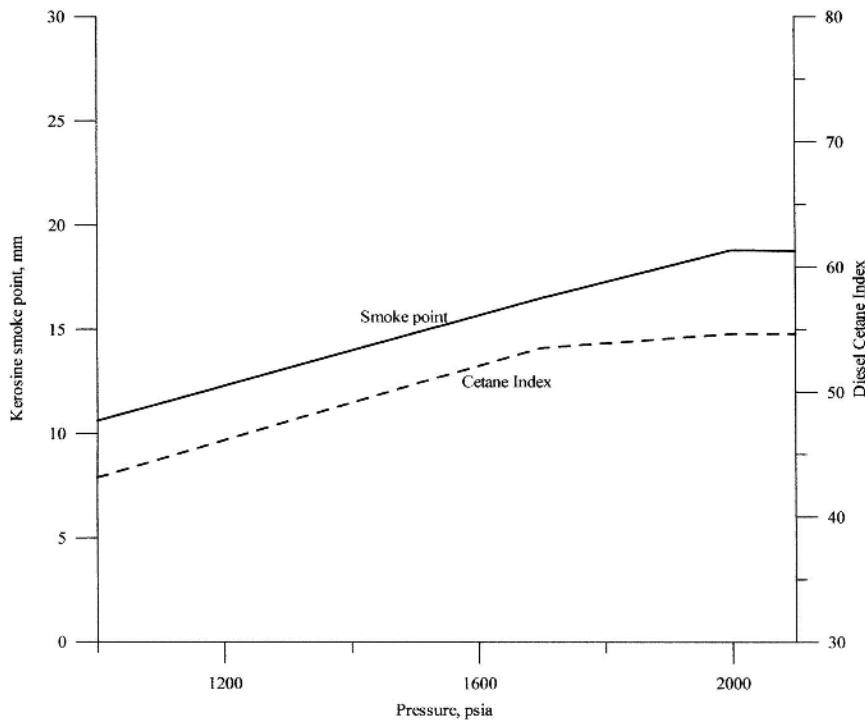


Figure 6.10 Effects of pressure on smoke point and cetane index. (From Ref. 43.)

1600 psig (95–110 barg) and 40% conversion to diesel or diesel plus naphtha, produces diesel with cetane indices near 50 and kerosine smoke points close to 19 [43].

6.10 PROCESS VARIABLES

In addition to the nature of the charge stock, the major operating variables effecting the conversion and product distribution are the cracking temperature, catalyst/oil ratio, space velocity, catalyst type and activity, and recycle ratio. For a better understanding of the process, several terms should be defined.

Activity: Ability to crack a gas oil to lower boiling fractions.

Catalyst/oil ratio (C/O) = lb catalyst/lb feed.

Conversion = 100 (volume of feed – volume of cycle stock)/volume of feed.

Cycle stock: Portion of catalytic-cracker effluent not converted to naphtha and lighter products [generally the material boiling above 430°F (220°C)]

Efficiency = (% gasoline) × conversion.

Recycle ratio = Volume recycle/volume fresh feed.

Selectivity: The ratio of the yield of desirable products to the yield of undesirable products (coke and gas).

Space velocity: Space velocity may be defined on either a volume (LHSV) or a weight (WHSV) basis. In a fluidized-bed reactor, the LHSV has little meaning because it is difficult to establish the volume of the bed.

The weight of the catalyst in the reactor can be easily determined or calculated from the residence time and C/O ratio.

LHSV = Liquid hour space velocity in volume feed/(volume catalyst) (hr).

WHSV = (Weight hour space velocity in lb feed)/(lb catalyst) (hr). If *t* is the catalyst residence time in hours, then *WHSV* = 1/(*t*)(C/O).

Within the limits of normal operations, increasing

1. Reaction temperature
2. Catalyst/oil ratio
3. Catalyst activity
4. Contact time

results in an increase in conversion, while a decrease in space velocity increases conversion. It should be noted that an increase in conversion does not necessarily mean an increase in gasoline yield, as an increase in temperature above a certain

level can increase conversion, coke and gas yields, and octane number of the gasoline but decrease gasoline yield [13,25]. In many FCC units, conversion and capacity are limited by the regenerator coke burning ability. This limitation can be due to either air compression limitations or to the afterburning temperatures in the last stage regenerator cyclones. In either case FCC units are generally operated at the maximum practical regenerator temperature with the reactor temperature and throughput ratio selected to minimize the secondary cracking of gasoline to gas and coke. With the trend to heavier feedstocks, the carbon forming potential of catalytic cracker feeds is increasing, and some units limited in carbon burning ability because of limited blower capacity are adding oxygen to the air to the regenerator to overcome this limitation. Oxygen contents of the gases to the regenerator are being increased to 24–30% by volume and are limited by regenerator temperature capability and heat removal capacity [26,27].

In fluidized-bed units, the reactor pressure is generally limited to 15 to 20 psig by the design of the unit and is therefore not widely used as an operating variable. Increasing pressure increases coke yield and the degree of saturation of

Table 6.4 Comparison of Fluid, Thermafor, and Houdry Catalytic Cracking Units

	FCC	TCC	HCC
Reactor space velocity	1.1–13.4 ^a	1–3 ^b	1.5–4 ^b
C/O	5–16 ^c	2–7 ^d	3–7 ^d
Recycle/fresh feed, vol	0–0.5	0–0.5	0–0.5
Catalyst requirement, lb/bbl feed	0.15–0.25	0.06–0.13	0.06–0.13
Cat. crclt. rate, ton cat./bbl total feed	0.9–1.5	0.4–0.6	0.4–0.6
On-stream efficiency, %	96–98		
Reactor temp., °F	885–950 ^e	840–950	875–950
Regenerator temp., °F	1200–1500	1100–1200	1100–1200
Reactor pressure, psig	8–30 ^e	8–12	9–10
Regenerator pressure, psig	15–30		
Turndown ratio			2:1
Gasoline octane, clear			
RON	92–99	88–94	88–94
MON	80–85		

^a lb/hr/lb.

^b v/hr/v.

^c wt.

^d vol.

^e One company has operated at 990°F and 40 psig to produce a 98 RON (clear) gasoline with a C₃ – 650°F liquid yield of 120 vol% on feed (once-through); there was approximately 90% yield of the C₅ – 650°F product.

the gasoline but decreases the gasoline octane. It has little effect on the conversion.

The initial catalyst charge to a FCC unit using riser cracking is about 3 to 5 tons of catalyst per 1000 BPSD charge rate. Catalyst circulation rate is approximately 1 ton/min per MBPD charge rate. Typical operations of these units are given in Table 6.4.

6.11 HEAT RECOVERY

Fuel and energy costs are a major fraction of the direct costs of refining crude oils, and as a result of large increases in crude oil and natural gas prices there is a great incentive to conserve fuel by the efficient utilization of the energy in the off-gases from the catalytic cracker regenerator. Temperature control in the regenerator is easier if the carbon on the catalyst is burned to carbon dioxide rather than carbon monoxide but much more heat is evolved and regenerator temperature limits many be exceeded. A better yield structure with lower coke laydown and higher gasoline yield is obtained at a given conversion level when burning to carbon dioxide to obtain a lower residual carbon on the catalyst. In either case, the hot gases are at high temperature [1100 to 1250°F (595–675°C in the former case and 1250 to 1500°F (675–815°C) in the latter] and at pressures of 15 to 25 psig (103–172 kPa). Many catalytic crackers include waste heat boilers which recover the sensible heat by steam generation and others use power recovery turbines to generate electric power or compress the air used in the catalytic cracker regenerator. Some refineries recover the heat of combustion of the carbon monoxide in the flue gas by installing CO-burning waste heat boilers in place of those utilizing only the sensible heat of the gases. An even higher rate of energy recovery can be achieved by using a power recovery turbine prior to the CO or waste heat boiler, although when regenerator pressures are less than 15 psig, power recovery turbines usually are not economic.

Assuming a regenerator flue gas discharge pressure of 20 psig (138 kPa) and 1000°F (538°C), the available horsepower per pound per second of gas flow for the various schemes are:

	hp	kW
Waste heat boiler only	45	34
Power recovery only	78	58
Power recovery plus waste heat boiler	106	79
CO burning waste heat boiler	145	108
Power recovery plus CO burning waste heat boiler	206	154

6.12 YIELD ESTIMATION

Correlations have been developed to estimate the product quality and yields from the catalytic cracking of virgin gas oils. The correlations are very useful for estimating typical yields for preliminary studies and to determine yield trends when changes are made in conversion levels. The yield structure is very dependent upon catalyst type. Figures 6.11 through 6.16 are for silica-alumina catalyst and Figures 6.17 through 6.27 are for zeolitic or molecular-sieve catalyst. If the feedstocks contain sulfur, Figure 6.28 can be used to estimate the distribution of sulfur in the product streams.

It is necessary to make a weight balance in order to obtain product distribution and properties as the cycle gas oil yields are obtained by difference. When using molecular-sieve catalyst, the procedure is as follows (gravities shown on curves are those of the fresh feed):

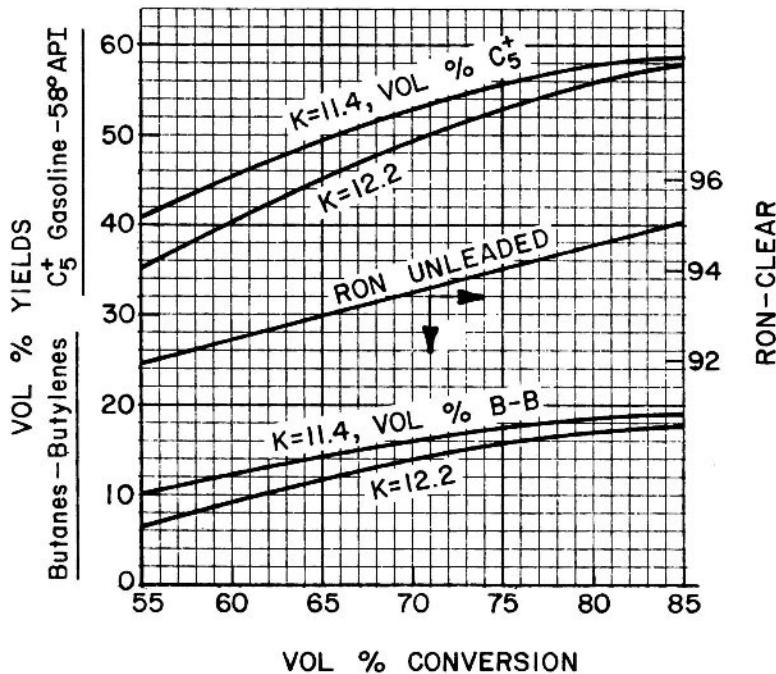


Figure 6.11 Catalytic cracking yields. Silica-alumina catalyst (butanes, butylenes, C_5^+ gasoline). The butane–butylene fraction typically contains about 40 vol% isobutane, 12 vol% n- butane, and 48 vol% butylenes.

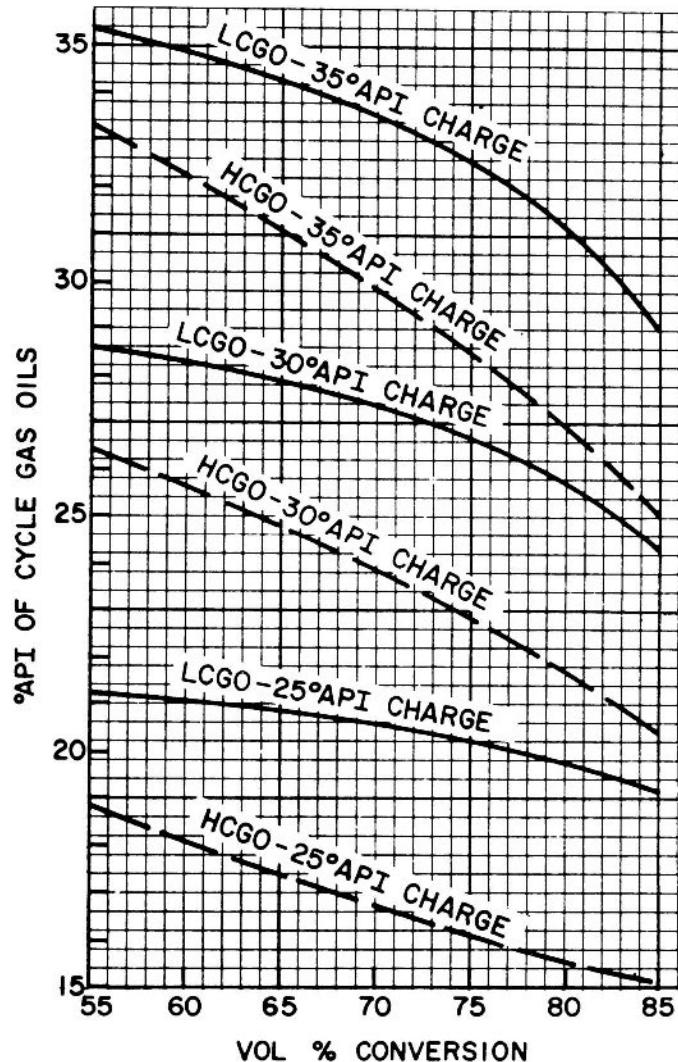


Figure 6.12 Catalytic cracking yields. Silica-alumina catalyst (cycle gas oils).

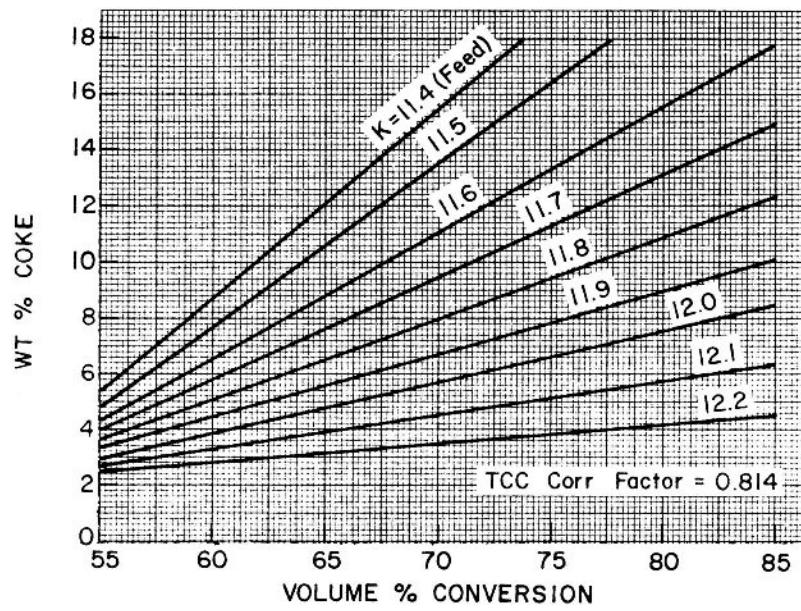


Figure 6.13 Catalytic cracking yields. Silica-alumina catalyst (coke).

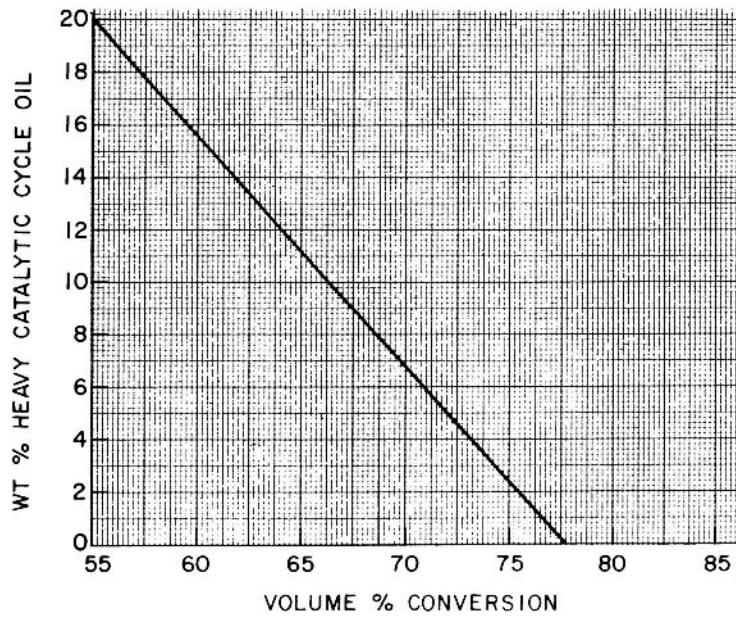


Figure 6.14 Catalytic cracking yields. Silica-alumina catalyst (heavy catalytic cycle oil).

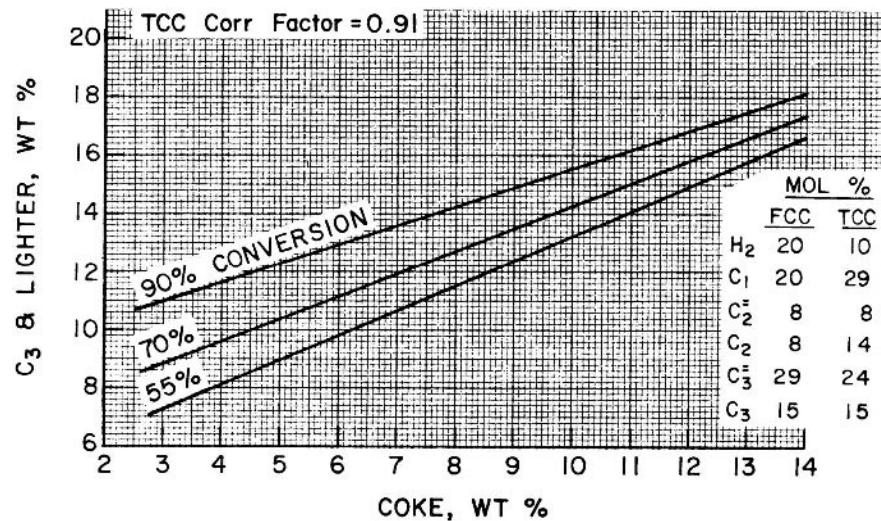


Figure 6.15 Catalytic cracking yields. Silica-alumina catalyst (C₃ and lighter).

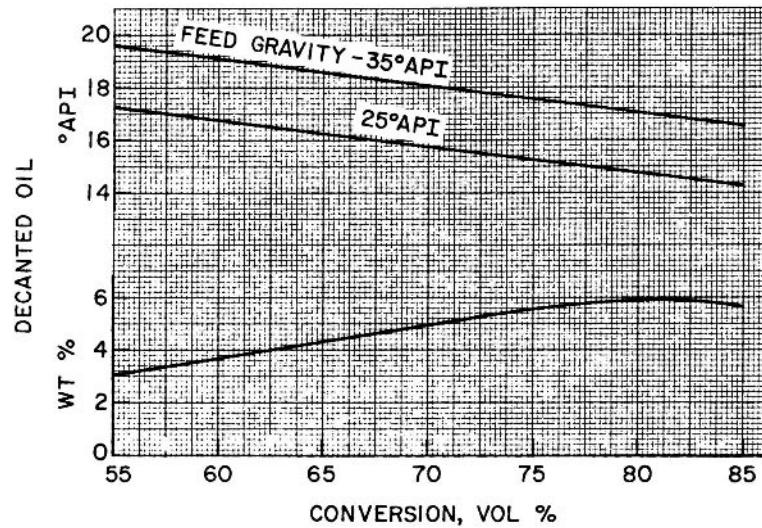


Figure 6.16 Catalytic cracking yields. Silica-alumina catalyst (decanted oil).

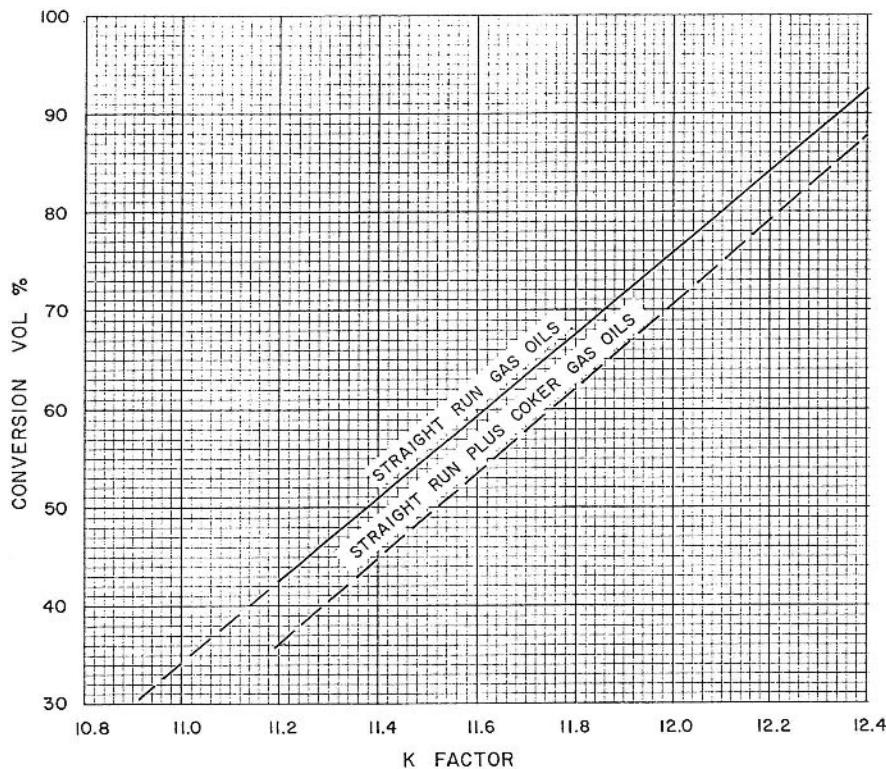


Figure 6.17 Effect of feed composition on conversion at constant operating conditions.

1. Calculate weight of feed.
2. Determine yields and weights of all products except gasoline from Figures 6.17 through 6.19.
3. Use Figures 6.20 and 6.21 to obtain the split of LPG components and adjust to total LPG as shown by Figure 6.19.
4. Determine weight of TCGO by use of Figure 6.26, then gasoline by difference.
5. Using Figure 6.26 to estimate gasoline gravity, calculate volume of gasoline produced and check against yield estimated by Figure 6.22.
6. From Figures 6.23 and 6.24 and feed rate, calculate the volume of heavy cycle gas oil (HGO).
7. Subtract volume of HGO from volume of total cycle gas oil (100 – conversion) to obtain volume yield of light cycle gas oil (LGO).
8. Use Figure 6.26 to estimate HGO gravity and calculate weight yield of HGO.

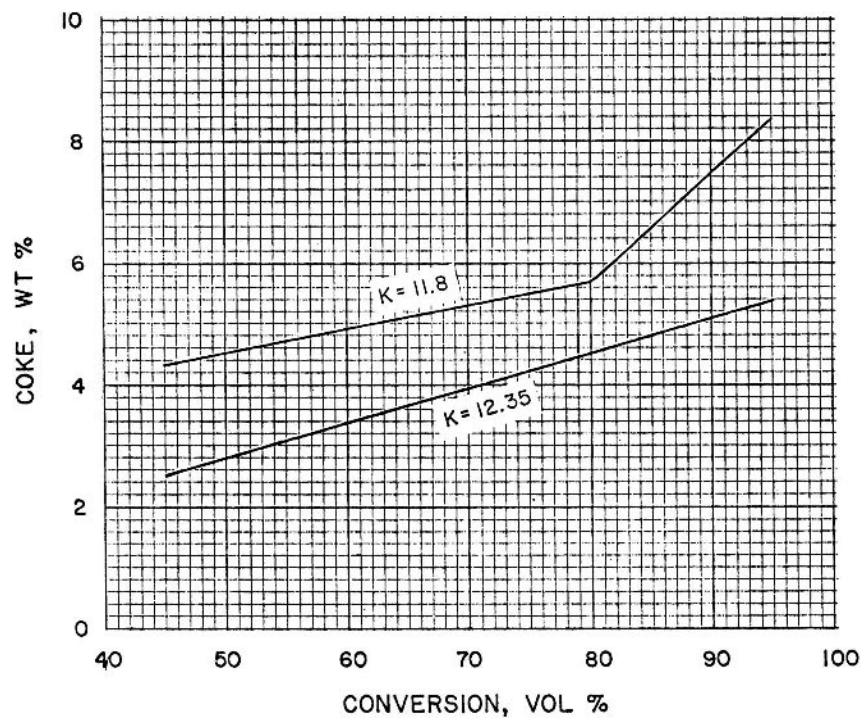


Figure 6.18 Catalytic cracking yields. Zeolite catalyst (coke).

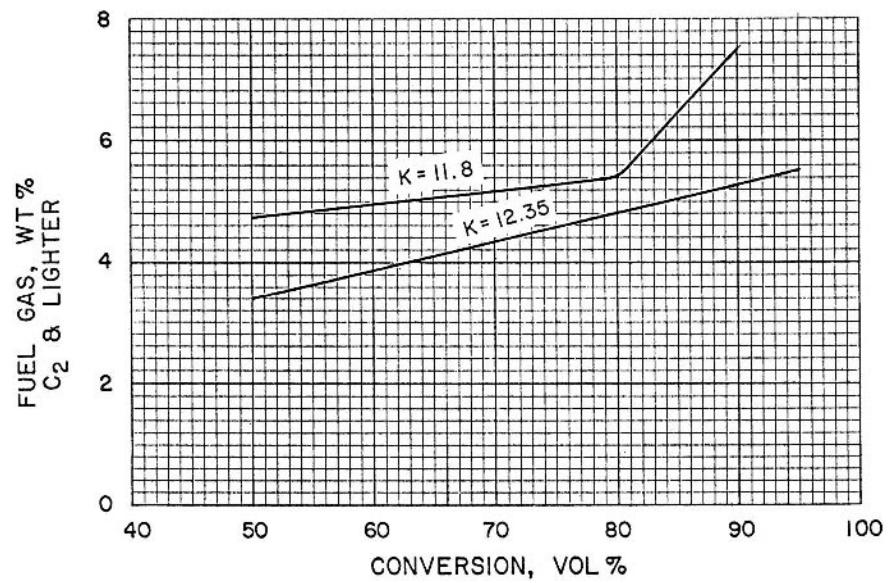


Figure 6.19 Catalytic cracking yields. Zeolite catalyst (fuel gas).

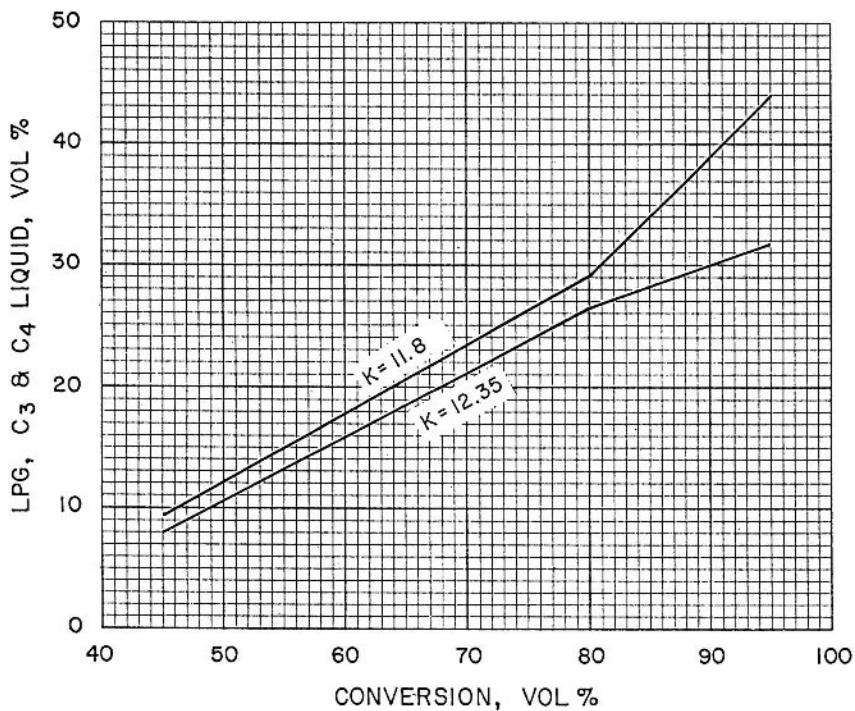


Figure 6.20 Catalytic cracking yields. Zeolite catalyst (C₃ and C₄).

9. Subtract weight yield of HGO from weight of total cycle gas oil to obtain weight yield of LGO.
10. Divide weight yield of LGO by volume yield of LGO (step 7) to obtain density of LGO. Use tables to find API gravity.

Product yields and properties are obtained in a similar manner when silica-alumina catalyst is used in the reactor, except the gravity of the LGO can be obtained from Figure 6.10 and the yield of HGO from Figure 6.12. It is necessary to find the weight yield of LGO by difference.

6.13 CAPITAL AND OPERATING COSTS

Capital construction and operating costs for a fluid catalytic cracking unit can be estimated using Figure 6.27 and its accompanying descriptive material (Table 6.5). Multiplying factors can be found in Chapter 17 (Cost Estimation).

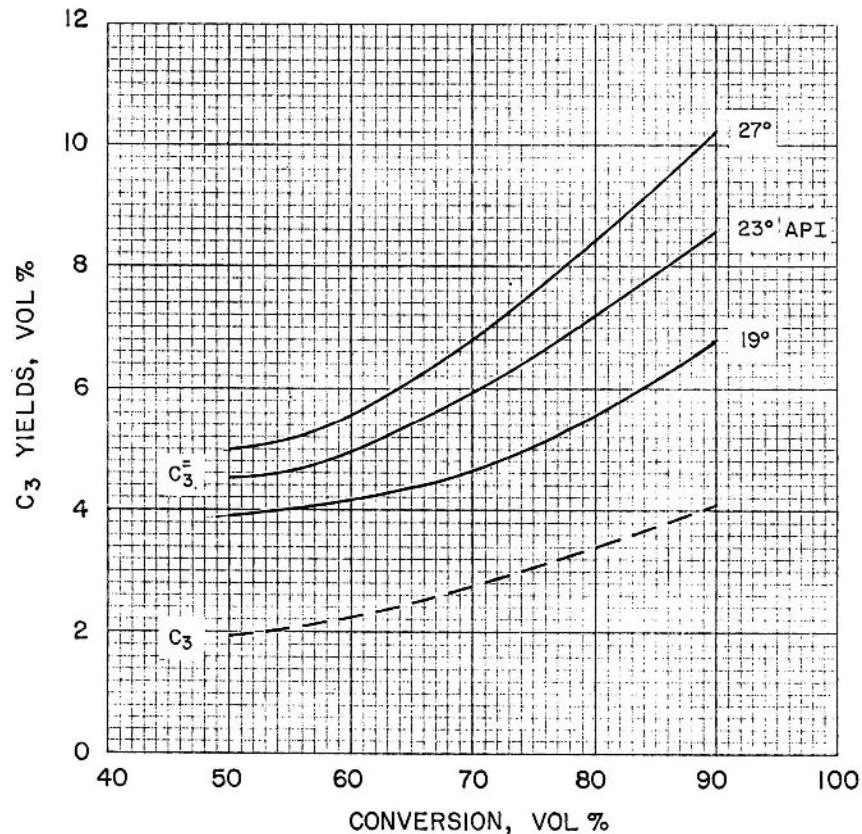


Figure 6.21 Catalytic cracking yields. Zeolite catalyst (C₃ ratios).

6.14 CASE-STUDY PROBLEM: CATALYTIC CRACKER

The choice of feedstocks for a catalytic cracking unit should be based on an economic evaluation of alternative uses of the hydrocarbon streams. This is especially important in the case of a refinery having both catalytic cracking and hydrocracking units. For this example, both the heavy gas oil from the atmospheric pipe still and the vacuum gas oil from the vacuum unit are used as FCC feedstocks, although it is quite possible the vacuum gas oil might give a better return if used as hydrocracker feed.

The selection of a 75% conversion level was made because of the high boiling characteristics of the feed. Checks should be made at higher and lower

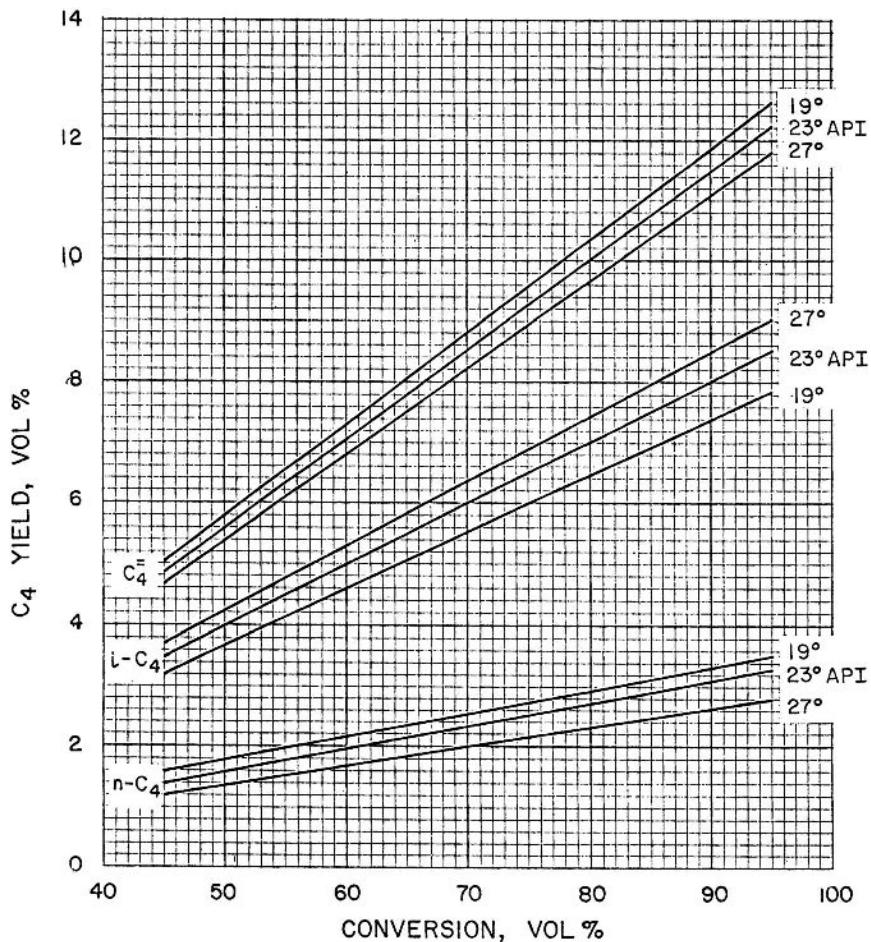


Figure 6.22 Catalytic cracking yields. Zeolite catalyst (C₄ ratios).

conversion levels to determine the level of conversion giving the best economic return.

The gravity of the combined charge stock is obtained by dividing the total pounds of charge by the volume. If the gravity is to be used for the calculation of a characterization factor (K_W) for yield prediction, the weight of sulfur and nitrogen should be subtracted from the weight of feed before dividing by the volume. If this is not done, the characterization factor will not be representative of the types of hydrocarbon compounds present in the feedstocks.

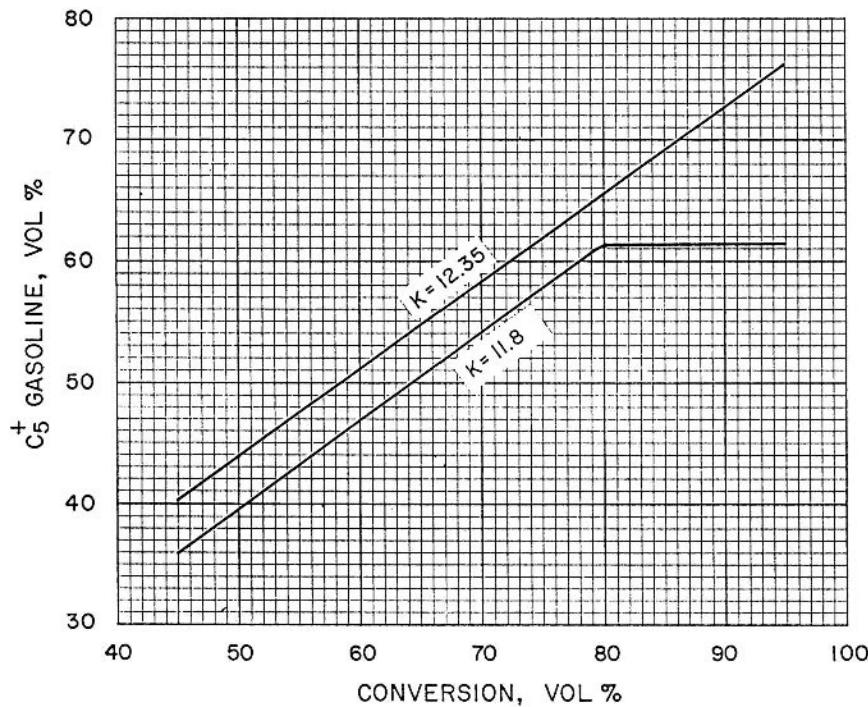


Figure 6.23 Catalytic cracking yields. Zeolite catalyst (C_5^+ gasoline).

The yields for the various product streams are obtained from Figures 6.9 through 6.14 for silica-alumina catalyst and from Figures 6.15 through 6.21 for zeolitic catalyst. The sulfur distribution in the products is estimated from Figure 6.22. In the case of the C_4 and lighter stream shown in Figure 6.22, it is assumed the sulfur is in the form of hydrogen sulfide (H_2S).

The weight of the total cycle gas oil (TGO) product stream is determined by difference, the gravity from Figure 6.21, and the volume by dividing the weight by the gravity. This volume is then used to check the conversion. In this example, the conversion obtained is 75.2% versus the 75% used as the base. This is a satisfactory check. If it does not check within +1%, some other method of determining product yields may better fit the characteristics of the feed.

The material balance is shown in Table 6.6.

Utility requirements are estimated from Table 6.5 and are listed in Table 6.7.

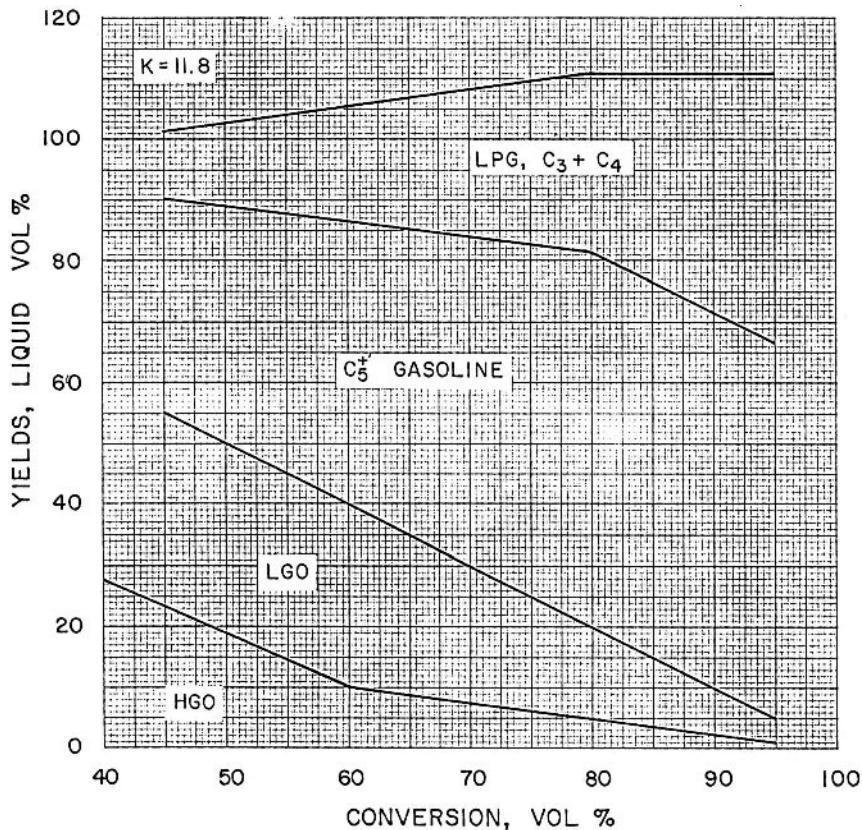


Figure 6.24 Catalytic cracking yields. Zeolite catalyst (heavy gas oil, feed $K = 11.8$).

PROBLEMS

1. For a 27.0° API catalytic cracker feedstock with a boiling range of 650 to 900°F and a sulfur content of 1.2% by weight, make an overall weight and volume material balance for 10,000 BPD feed rate when operating at a 65% conversion level and a once-through operation with:
 - a. Zeolite catalyst.
 - b. Silica-alumina catalyst
2. If the catalytic gas oil produced in Problem 1 is recycled to extinction (no products heavier than kerosine or No. 1 fuel oil are withdrawn

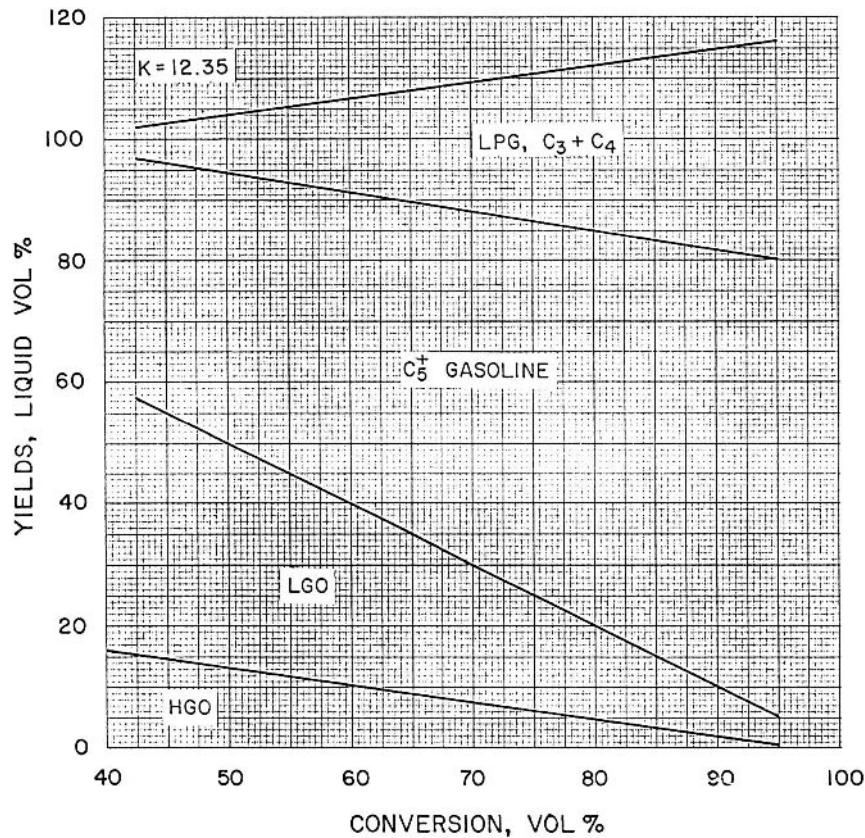


Figure 6.25 Catalytic cracking yields. Zeolite catalyst (heavy gas oil, feed K = 12.35).

from the unit), how much will gasoline production be increased? Coke laydown?

3. Estimate the direct operating cost, including royalty, per barrel of feed for a 20,000 BPD catalytic cracking unit if labor costs are \$900/day, electric power is \$0.05/kWh, steam is \$3.15/MMBtu, fuel is \$2.25/MMBtu, silica-alumina catalyst is \$900/ton, a mixture of silica-alumina and zeolite catalysts is \$2000/ton, and zeolite catalyst is \$3000/ton.
4. Using today's construction costs for a 20,000 BPD catalytic cracking unit and double-rate declining-balance depreciation, estimate the cost per barrel of feed added by depreciation costs. Assume a 20-year life

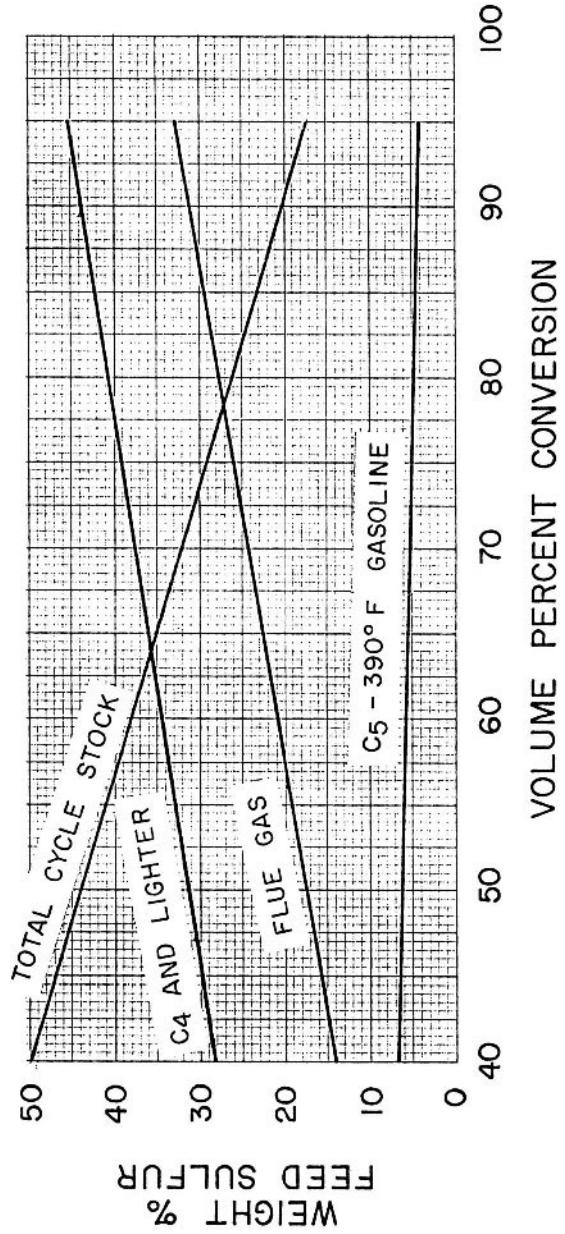


Figure 6.26 Distribution of sulfur in catalytic cracking products. (From Ref. 10.)

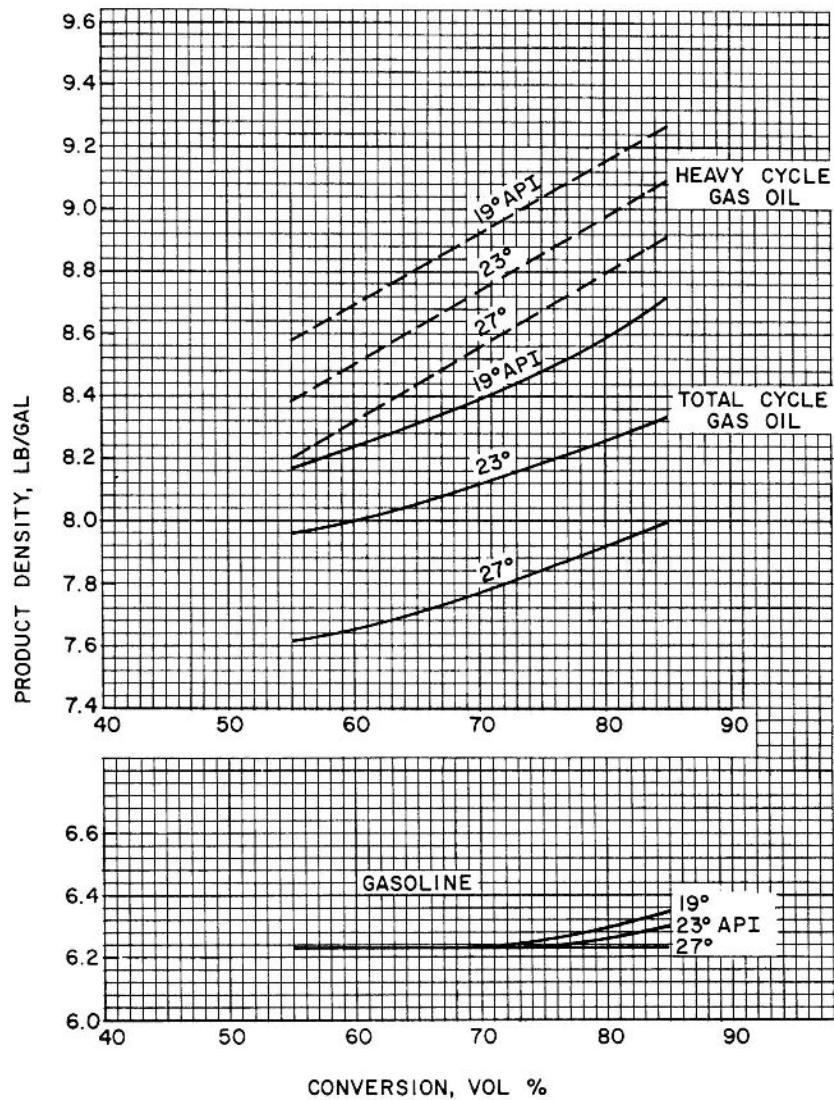


Figure 6.27 FCC product gravity. Zeolite catalyst.

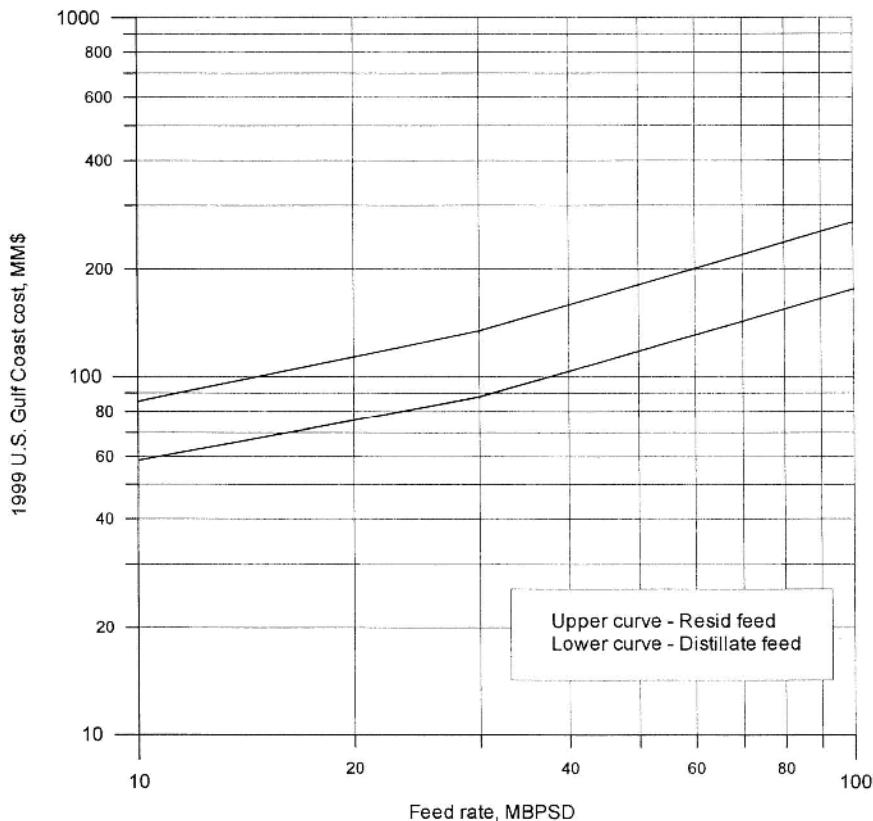


Figure 6.28 Fluid catalytic cracking units investment cost: 1999 U.S. Gulf Coast. (See Table 6.5.)

and a salvage value equal to dismantling costs. Calculate for the first and fifth years of operation. Compare with depreciation costs per barrel when straight-line depreciation is used.

- For the following conditions, calculate the (a) wt% hydrogen in coke, (b) coke yield, and (c) catalyst-to-oil ratio.

Carbon on spent catalyst:	1.50 wt%
Carbon on regenerated catalyst:	0.80 wt%
Air from blower:	155,000 lb/hr
Hydrocarbon feed to reactor:	295,000 lb/hr

Table 6.5 Fluid Catalytic Cracking Unit Cost Data*Costs included*

1. Product fractionation
2. Gas compression and concentration for recovery of 95% and fractionation of C₄s and 80% of C₃
3. Complete reactor-regenerator section
4. Sufficient heat exchange to cool products to ambient temperatures
5. Central control system

Costs not included

1. Feed fractionation
2. Off-gas and product treating
3. Cooling water, steam, and power supply
4. Initial catalyst charge

Royalty

Running royalty about \$0.10/bbl
Paid-up royalty about \$110/BPD

Utility data (per bbl feed)

Steam, lb ^a	
Power, kWh ^b	6.0
Cooling water, gal (30FΔt)	500
Fuel (LHV), MMBtu	0.1
Catalyst Replacement, \$	0.15–0.50

^a Waste heat steam production usually is in excess of consumption by approximately 30 pounds of steam per barrel of fresh feed.

^b Includes electric drive for air blower and off-gas compressor.
Note: See Fig. 6.2.

Flue gas analysis (Orsat), vol%:

CO	12.0
CO ₂	6.0
O ₂	0.7
N ₂	81.3
	100.0

6. Estimate the cost, including royalty, per gallon of gasoline boiling range product for a 20,000 BPSD catalytic cracking unit if labor costs are \$1150/day, electric power is \$0.06/kWh, steam is \$2.25/M lb, fuel is \$2.49/MM Btu, silica-alumina catalyst is \$900/ton, zeolite catalyst is \$3000/ton, and depreciation is \$625,000/yr. The on-stream factor is 96.5%. The C₅⁺ gasoline yield is 58% at 85% conversion level.
7. For a 24.0° API catalytic cracker feedstock with a boiling range of 617°F (325°C) to 950°F (510°C) and a sulfur content of 0.45% by

Table 6.6 FCC Material Balance: 100,000 BPCD Alaska North Slope Crude Oil Basis (Severity, 75% Conversion; Zeolite Catalyst)

Component	vol%	BPD	°API	(lb/h)/BPD	lb/h	wt% S	lb/h S
Feed							
650–850°F	56.7	20,090	23.2	13.35	268,103	0.10	261
850–1050°F	43.3	15,331	16.5	13.95	213,857	0.29	630
KW = 11.67	100.0	35,421	20.0	13.61	481,960	0.18	891
Products							
Coke, wt%	5.80				27,954	0.83	232 ^a
C ₂ and lighter, wt%	5.50				26,508	1.30	344
C ₃ ⁼	5.30	1,877		7.61	14,286		
C ₃	2.90	1,027		7.42	7,591		
C ₄ ⁼	9.50	3,365		8.76	29,477		
iC ₄	6.10	2,161		8.22	17,718		
nC ₄	2.70	956		8.51	8,139		
C ₅ ⁺ naphtha	56.79	20,117	57.2	10.94	(220,115)	0.02	40
TGO	(25.0)	(8,855)	8.9	14.70	130,172	0.21	275
LGO	18.4	(6,517)	12.6	(14.32)	(93,352)	0.17	158
HGO	6.6	2,338	-0.6	15.75	36,820	0.32	117
Total		38,359			481,960		891

^a In flue gas as SO₂.

weight, make an overall weight and volume material balance for 25,000 BPSD feed rate when operating at an 85% conversion level and a once-through operation with zeolite catalyst.

- For the feedstock and conditions in problem 7, compare the relative cost per barrel of C₅⁺ gasoline produced at 75% conversion with that at 85% conversion assuming constant direct operating costs. Use *Oil and Gas Journal* values for other fuels

Table 6.7 FCC Catalyst and Utility Requirements

Power, MkWh/d	213
Cooling water, gpm	17,711
Fuel, MMBtu/d	3,542
Catalyst, \$/d	5,313
Steam, Mlb/d	(1,063)

9. For a 23.0° API catalytic cracker feedstock with a boiling range of 600–900°F (315–482°C) and containing 1.5 wt% sulfur, make an overall weight and volume material balance for 10,000 BPCD feed rate when operating at 70% conversion using a zeolite catalyst.

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7

Catalytic Hydrocracking

Although hydrogenation is one of the oldest catalytic processes used in refining petroleum, only in recent years has catalytic hydrocracking developed to any great extent in this country. This interest in the use of hydrocracking has been caused by several factors, including (1) the demand for petroleum products has shifted to high ratios of gasoline and jet fuel compared with the usages of diesel fuel and home heating oils, (2) by-product hydrogen at low cost and in large amounts has become available from catalytic reforming operations, and (3) environmental concerns limiting sulfur and aromatic compound concentrations in motor fuels have increased.

The hydrocracking process was commercially developed by I. G. Farben Industrie in 1927 for converting lignite into gasoline and was brought to this country by Esso Research and Engineering Company in the early 1930s for use in upgrading petroleum feedstocks and products, but the first modern distillate hydrocracker was put into commercial operation by Chevron in 1958 [2]. Improved catalysts have been developed which permit operations at relatively low pressures, and the demand for high-octane unleaded gasolines and kerosine-type jet fuels plus a decrease in demand for distillate fuel oils has promoted the conversion of higher-boiling petroleum materials to gasoline and jet fuels.

Product balance is of major importance to any petroleum refiner. There are a number of things that can be done to balance the products made with the demand, but there are relatively few operations that offer the versatility of catalytic hydrocracking. Some of the advantages of hydrocracking are:

1. Better balance of gasoline and distillate production
2. Greater gasoline yield
3. Improved gasoline pool octane quality and sensitivity
4. Production of relatively high amounts of isobutane in the butane fraction

5. Supplementing of fluid catalytic cracking to upgrade heavy cracking stocks, aromatics, cycle oils, and coker oils to gasoline, jet fuels, and light fuel oils

In a modern refinery catalytic cracking and hydrocracking work as a team. The catalytic cracker takes the more easily cracked paraffinic atmospheric and vacuum gas oils as charge stocks, while the hydrocracker uses more aromatic cycle oils and coker distillates as feed [10]. These streams are very refractory and resist catalytic cracking, while the higher pressures and hydrogen atmosphere make them relatively easy to hydrocrack. The new zeolite cracking catalysts help improve the gasoline yields and octanes from catalytic crackers as well as reduce the cycle stock and gas make. However, the cycle oil still represents a difficult fraction to crack catalytically to extinction. One alternative is to use the cycle stock as a component for fuel oil blending, but this is limited as it is a relatively poor burning stock and burns with a smoky flame. For this reason a limit is placed on the percentage that can be blended into distillate fuel oils. The cycle oils that result from cracking operations with zeolite catalysts tend to be highly aromatic and therefore make satisfactory feedstocks for hydrocracking. Vacuum and coker gas oils are also used as hydrocracker feed.

Sometimes diesel boiling range material is included in hydrocracker feed to make jet and motor gasoline products. Both straight-run and FCC LCO can be used and in some cases 100% LCO is used. In cases where 100% LCO is the feed, there is a follow-up with a high-pressure hydrotreater to reduce the aromatic content and increase the smoke point to meet specifications. When the feed contains large amounts of LCO, the major effects are increased heat release and lower smoke point of the jet fuel product [17].

In addition to middle distillates and cycle oils used as feed for hydrocracking units, it is also possible to process residual fuel oils and reduced crude by hydrocracking. This usually requires a different technology and for the purposes of our discussion the hydrocracking operation is broken into two general types of processes; those which operate on distilled feed (hydrocracking) and those which process residual materials (hydropyrolysis). These processes are similar and some licensed processes have been adapted to operate on both types of feedstocks. There are major differences, however, between the two processes in regard to the type of catalyst and operating conditions. During the design stages of the hydrocracker the process can be tailored to convert heavy residue into lighter oils or to change straight-run naphthas into liquefied petroleum gases. This is difficult to do after the unit is built as the processing of residual oil requires special consideration with respect to such factors as asphaltenes, ash, and metal contents of the feedstocks [8,16]. Hydropyrolysis is discussed in Chapter 8 and typical feedstocks and products for hydrocrackers are given in Table 7.1.

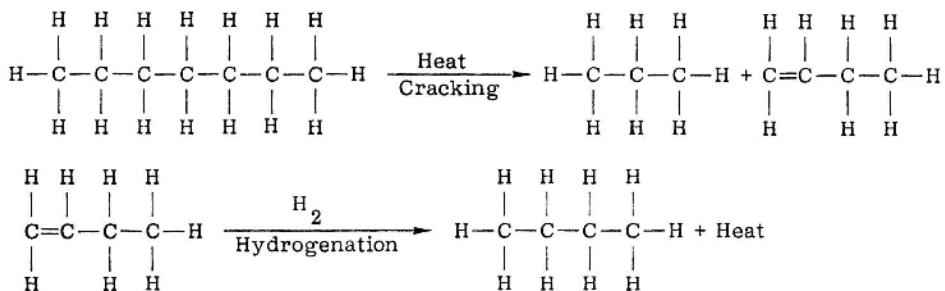
Table 7.1 Typical Hydrocracker Feedstocks

Feed	Products
Kerosine	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 LCGO	Naphtha and/or distillates
Coker HCGO	Naphtha and/or distillates

Source: Refs. 1 and 17.

7.1 HYDROCRACKING REACTIONS

Although there are hundreds of simultaneous chemical reactions occurring in hydrocracking, it is the general opinion that the mechanism of hydrocracking is that of catalytic cracking with hydrogenation superimposed (see Fig. 7.1). Catalytic cracking is the scission of a carbon–carbon single bond, and hydrogenation is the addition of hydrogen to a carbon–carbon double bond. An example of the scission of a carbon–carbon single bond followed by hydrogenation is the following:



This shows that cracking and hydrogenation are complementary, for cracking provides olefins for hydrogenation, while hydrogenation in turn provides heat for cracking. The cracking reaction is endothermic and the hydrogenation reaction is exothermic. The overall reaction provides an excess of heat because the amount of heat released by the exothermic hydrogenation reactions is much greater than the amount of heat consumed by the endothermic cracking reactions. This surplus

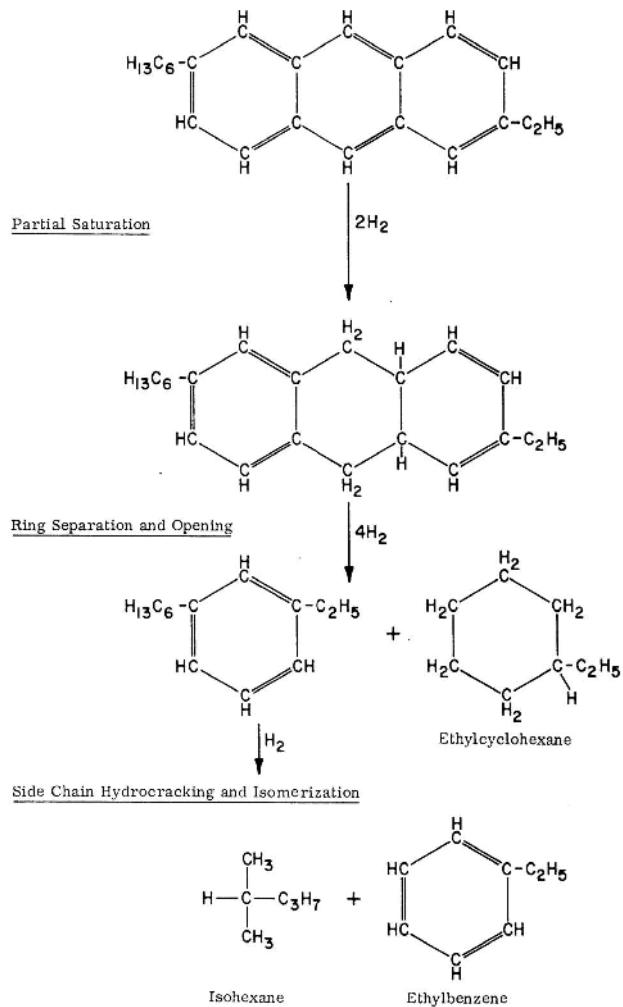


Figure 7.1 Typical hydrocracking reactions.

of heat causes the reactor temperature to increase and accelerate the reaction rate. This is controlled by injecting cold hydrogen as quench into the reactors to absorb the excess heat of reaction.

Another reaction that occurs and illustrates the complementary operation of the hydrogenation and cracking reactions is the initial hydrogenation of a condensed aromatic compound to a cycloparaffin. This allows subsequent cracking

to proceed to a greater extent and thus converts a low-value component of catalytic cycle oils to a useful product.

Isomerization is another reaction type that occurs in hydrocracking and accompanies the cracking reaction. The olefinic products formed are rapidly hydrogenated, thus maintaining a high concentration of high octane isoparaffins and preventing the reverse reaction back to straight-chain molecules. An interesting point in connection with the hydrocracking of these compounds is the relatively small amounts of propane and lighter materials that are produced as compared with normal cracking processes. The volumetric yield of liquid products can be as high as 125% of the feed because the hydrogenated products have a higher API gravity than the feed.

Hydrocracking reactions are normally carried out at average catalyst temperatures between 550 and 750°F (290 to 400°C) and at reactor pressures between 1200 and 2000 psig (8275 and 13,800 kPa). The circulation of large quantities of hydrogen with the feedstock prevents excessive catalyst fouling and permits long runs without catalyst regeneration. Careful preparation of the feed is also necessary in order to remove catalyst poisons and to give long catalyst life. Frequently the feedstock is hydrotreated to remove sulfur and nitrogen compounds as well as metals before it is sent to the first hydrocracking stage or, sometimes, the first reactor in the reactor train can be used for this purpose.

7.2 FEED PREPARATION

Hydrocracking catalyst is susceptible to poisoning by metallic salts, oxygen, organic nitrogen compounds, and sulfur in the feedstocks. The feedstock is hydrotreated to saturate the olefins and remove sulfur, nitrogen, and oxygen compounds. Molecules containing metals are cracked and the metals are retained on the catalyst. The nitrogen and sulfur compounds are removed by conversion to ammonia and hydrogen sulfide. Although organic nitrogen compounds are thought to act as permanent poisons to the catalyst, the ammonia produced by reaction of the organic nitrogen compounds with hydrogen does not affect the catalyst permanently. For some types of hydrocracking catalysts, the presence of hydrogen sulfide in low concentrations acts as a catalyst to inhibit the saturation of aromatic rings. This is a beneficial effect when maximizing gasoline production as it conserves hydrogen and produces a higher octane product.

In the hydrotreater a number of hydrogenation reactions, such as olefin saturation and aromatic ring saturation, take place, but cracking is almost insignificant at the operating conditions used. The exothermic heats of the desulfurization and denitrogenation reactions are high [about 65 to 75 Btu/scf of hydrogen consumed (2400 to 2800 kJ/std m³)]. If the nitrogen and sulfur contents of the feedstock are high, this effect contributes appreciably to the total heat of reaction.

Another reaction contributing to high heat release in the hydrotreating process is the saturation of olefins, as the heat of reaction for olefin saturation is about 140 Btu/scf of hydrogen consumed. For cracked feedstocks the olefin content is very high and olefin saturation is responsible for a large portion of the total heat of reaction. For virgin stocks, however, the olefin content is negligible and this is not an important contribution to heat of reaction. The overall heat of reaction for most hydrotreating reactors used for the preparation of hydrocracker feed is approximately 25,000 to 35,000 Btu per barrel (166 to 232 MJ/m³) feed.

In addition to the removal of nitrogen and sulfur compounds and metals, it is also necessary to reduce the water content of the feed streams to less than 25 ppm because, at the temperatures required for hydrocracking, steam causes the crystalline structure of the catalyst to collapse and the dispersed rare-earth atoms to agglomerate. Water removal is accomplished by passing the feed stream through a silica gel or molecular sieve dryer. Exceptions to this are the Unicracking and GOFining processes, which can tolerate water contents as high as 400 to 500 ppm and it is necessary only to remove free water from the feed.

On the average, the hydrogen treating process requires approximately 150 to 300 ft³ of hydrogen per barrel of feed (27 to 54 m³ hydrogen per m³ feed).

7.3 THE HYDROCRACKING PROCESS

There are a number of hydrocracking processes available for licensing and some of these are given in Table 7.2. With the exception of the H-Oil and LC-Fining processes, all hydrocracking and hydroprocessing processes in use today are fixed-bed catalytic processes with liquid downflow. The hydrocracking process may require either one or two stages, depending upon the process and the feed-

Table 7.2 Hydrocracking Processes Available for License

Process	Company	Ref.
Isomax	Chevron and UOP, LLC	18
Unicracking	UOP	
GOFining	Exxon Research and Engineering	
Ultracracking	BP Amoco	6
Shell	Shell Development Co.	
BASF-IFP hydrocracking	Badische Anilin und Soda Fabrik, and Institute Francais Petrole	
Unibon	UOP, LLC	

stocks used. The process flows of most of the fixed-bed processes are similar and the GOFining process will be described as a typical fixed-bed hydrocracking process.

The GOFining process is a fixed-bed regenerative process employing a molecular-sieve catalyst impregnated with a rare-earth metal. The process employs either single-stage or two-stage hydrocracking with typical operating conditions ranging from 660 to 785°F and from 1000 to 2000 psig (350–420°C and 6900–13,800 kPa). The temperature and pressure vary with the age of the catalyst, the product desired, and the properties of the feedstock.

The decision to use a single- or two-stage system depends upon the size of the unit and the product desired. For most feedstocks the use of a single stage will permit the total conversion of the feed material to gasoline and lighter products by recycling the heavier material back to the reactor. The process flow for a two-stage reactor is shown in Figure 7.2. If only one stage is used, the process flow is the same as that of the first stage of the two-stage plant except the fractionation tower bottoms is recycled to the reactor feed.

The fresh feed is mixed with makeup hydrogen and recycle gas (high in hydrogen content) and passed through a heater to the first reactor. If the feed has not been hydrotreated, there is a guard reactor before the first hydrocracking reactor. The guard reactor usually has a modified hydrotreating catalyst such as cobalt-molybdenum on silica-alumina to convert organic sulfur and nitrogen compounds to hydrogen sulfide, ammonia, and hydrocarbons to protect the precious metals catalyst in the following reactors. The hydrocracking reactor(s) is operated at a sufficiently high temperature to convert 40 to 50 vol% of the reactor effluent to material boiling below 400°F (205°C). The reactor effluent goes through heat exchangers to a high-pressure separator where the hydrogen-rich gases are separated and recycled to the first stage for mixing both makeup hydrogen and fresh feed. The liquid product from the separator is sent to a distillation column where the C₄ and lighter gases are taken off overhead, and the light and heavy naphtha, jet fuel, and diesel fuel boiling range streams are removed as liquid sidestreams. The fractionator bottoms are used as feed to the second-stage reactor system. The unit can be operated to produce all gasoline and lighter products or to maximize jet fuel or diesel fuel products. See Figure 7.3.

The bottoms stream from the fractionator is mixed with recycle hydrogen from the second stage and sent through a furnace to the second-stage reactor. Here the temperature is maintained to bring the total conversion of the unconverted oil from the first-stage and second-stage recycle to 50 to 70 vol% per pass. The second-stage product is combined with the first-stage product prior to fractionation.

Both the first- and second-stage reactors contain several beds of catalysts. The major reason for having separate beds is to provide locations for injecting

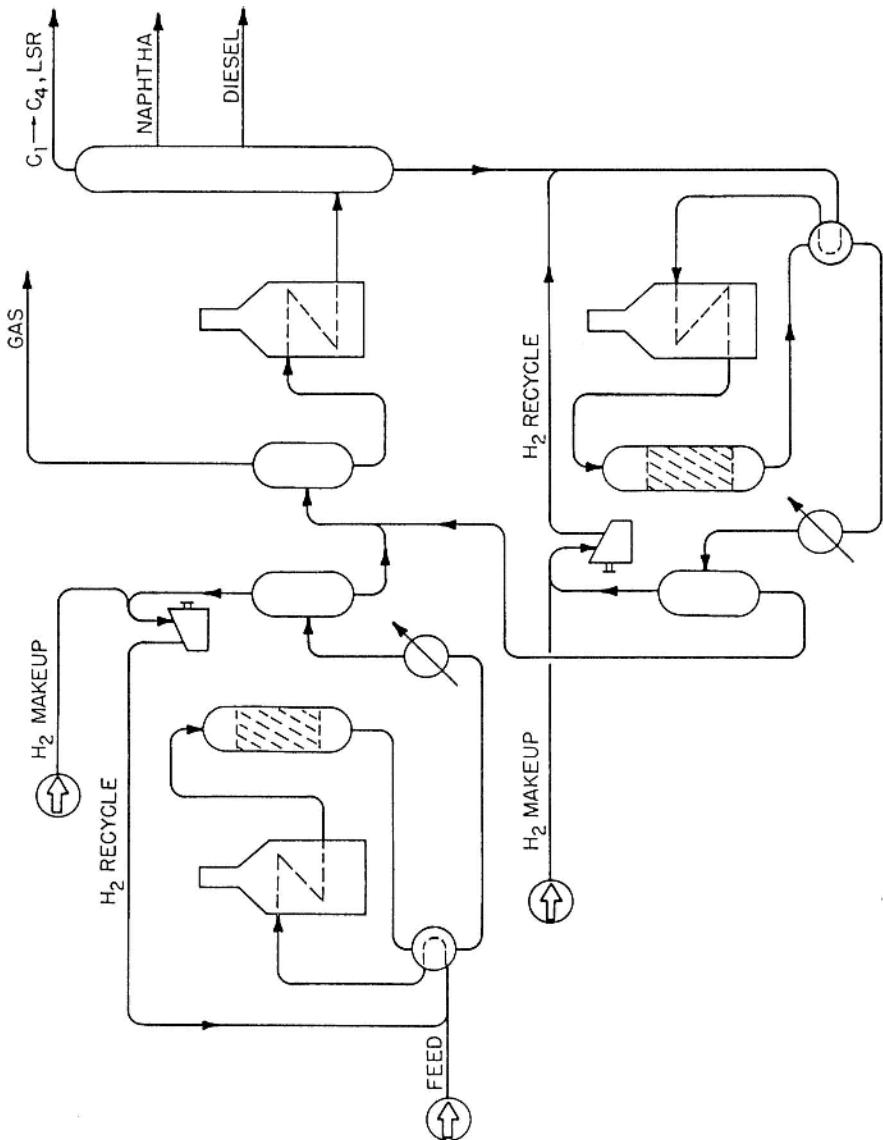


Figure 7.2 Two-stage hydrocracker.

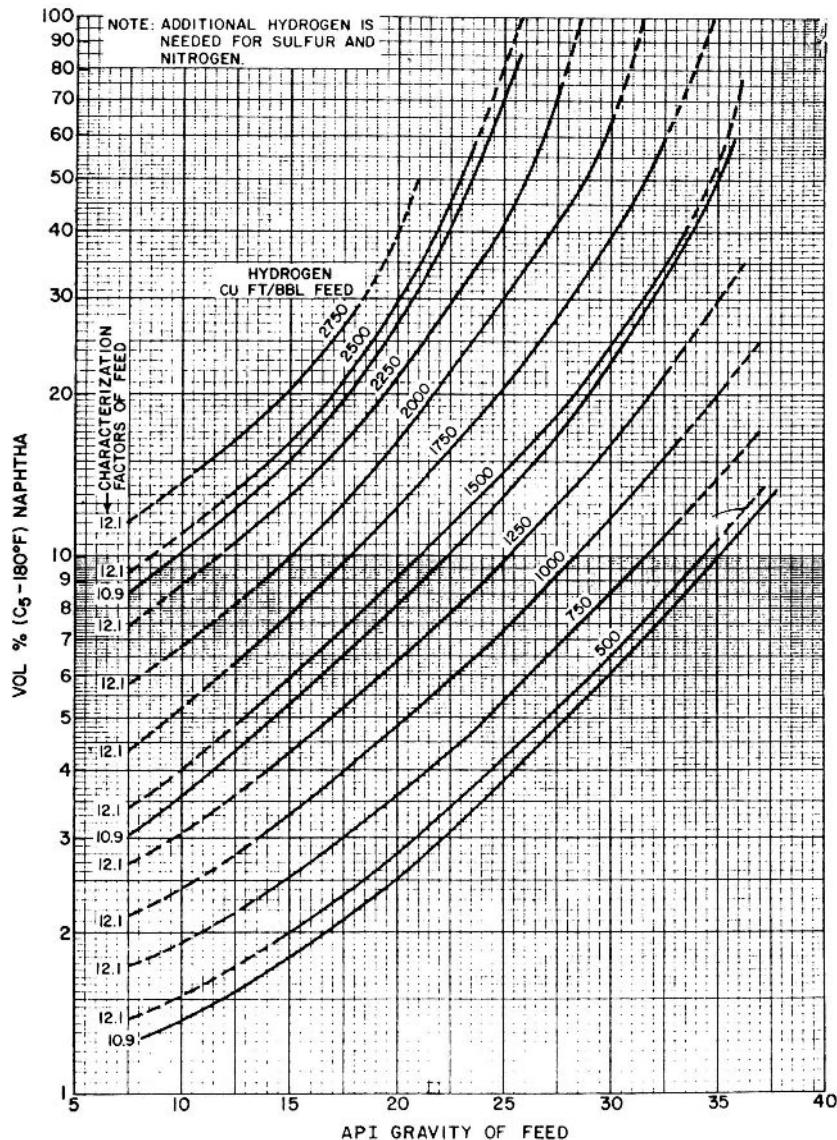


Figure 7.3 Approximate hydrogen required for hydrocracking. (From Ref. 11.)

cold recycled hydrogen into the reactors for temperature control. In addition, redistribution of the feed and hydrogen between the beds helps to maintain a more uniform utilization of the catalyst.

When operating hydrocrackers for total conversion of distillate feeds to gasoline, the butane-and-heavier liquid yields are generally from 120 to 125 vol% of fresh feed.

7.4 HYDROCRACKING CATALYST

There are a number of hydrocracking catalysts available and the actual composition is tailored to the process, feed material, and the products desired. Most of the hydrocracking catalysts consist of a crystalline mixture of silica-alumina with a small uniformly distributed amount of rare earths contained within the crystalline lattice. The silica-alumina portion of the catalyst provides cracking activity while the rare-earth metals promote hydrogenation. Catalyst activity decreases with use, and reactor temperatures are raised during a run to increase reaction rate and maintain conversion. The catalyst selectivity also changes with age and more gas is made and less naphtha produced as the catalyst temperature is raised to maintain conversion. With typical feedstocks it will take from two to four years for catalyst activity to decrease from the accumulation of coke and other deposits to a level which will require regeneration. Regeneration is accomplished by burning off the catalyst deposits, and catalyst activity is restored to close to its original level. The catalyst can undergo several regenerations before it is necessary to replace it.

Almost all hydrocracking catalysts use silica-alumina as the cracking base but the rare-earth metals vary according to the manufacturer. Those in most common use are platinum, palladium, tungsten, and nickel.

7.5 PROCESS VARIABLES

The severity of the hydrocracking reaction is measured by the degree of conversion of the feed to lighter products. Conversion is defined as the volume percent of the feed which disappears to form products boiling below the desired product end point. In order to compare operation severities it is necessary to equate conversions to the same product end point. A given percent conversion at a low product end point represents a more severe operation than does the same percent conversion at a higher product end point.

The primary reaction variables are reactor temperature and pressure, space velocity, hydrogen consumption, nitrogen content of feed, and hydrogen sulfide content of the gases. The effects of these are as follows:

Reactor Temperature

Reactor temperature is the primary means of conversion control. At normal reactor conditions a 20°F (10°C) increase in temperature almost doubles the reaction rate, but does not affect the conversion level as much because a portion of the reaction involves material that has already been converted to materials boiling below the desired product end point. As the run progresses it is necessary to raise the average temperature about 0.1 to 0.2°F per day to compensate for the loss in catalyst activity.

Reactor Pressure

The primary effect of reactor pressure is in its effects on the partial pressures of hydrogen and ammonia. An increase in total pressure increases the partial pressures of both hydrogen and ammonia. Conversion increases with increasing hydrogen partial pressure and decreases with increasing ammonia partial pressure. The hydrogen effect is greater, however, and the net effect of raising total pressure is to increase conversion.

Space Velocity

The volumetric space velocity is the ratio of liquid flow rate, in barrels per hour, to catalyst volume, in barrels. The catalyst volume is constant, therefore the space velocity varies directly with feed rate. As the feed rate increases, the time of catalyst contact for each barrel of feed is decreased and conversion is lowered. In order to maintain conversion at the proper level when the feed rate is increased, it is necessary to increase the temperature.

Nitrogen Content

The organic nitrogen content of the feed is of great importance as the hydrocracking catalyst is deactivated by contact with organic nitrogen compounds. An increase in organic nitrogen content of the feed causes a decrease in conversion.

Hydrogen Sulfide

At low concentrations the presence of hydrogen sulfide acts as a catalyst to inhibit the saturation of aromatic rings. This conserves hydrogen and produces a product with a higher octane number because the aromatic naphtha has a higher octane than does its naphthenic counterpart. However, hydrocracking in the presence of a small amount of hydrogen sulfide normally produces a very low-smoke-point

jet fuel. At high hydrogen sulfide levels corrosion of the equipment becomes important and the cracking activity of the catalyst is also affected adversely.

Heavy Polynuclear Aromatics (HPNA)

Heavy polynuclear aromatics are formed in small amounts from hydrocracking reactions and, when the fractionator bottoms is recycled, can build up to concentrations that cause fouling of heat exchanger surfaces and equipment. Steps such as reducing feed end point or removal of a drag stream may be necessary to control this problem [15].

7.6 HYDROCRACKING YIELDS

Yields from the hydrocracker are functions of the type of crude oil, previous processing operations, type and activity of catalyst used, and operating conditions. Representative yields for straight-run and cracked feedstocks are given in Table 7.3.

For the purpose of the example problem, the yields for hydrocracking to produce gasoline as the primary product can be calculated from charts and equations developed by W. L. Nelson [11–13]. The data needed to start the calcula-

Table 7.3 Hydrocracking Yields

	Naphtha	Jet	Diesel
<i>Yields on Coker Gas Oil and FCC Decanted Oil (vol% on feed)</i>			
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
<i>Yields on Coker Gas Oil and FCC Decant Oil (vol% on feed)</i>			
Butanes		5.2	
C ₅ -185°F		8.8	
180–435°F		31.8	
435–650°F, diesel		33.8	
650°F+, gas oil		35.0	
Total		114.6	

Source: Ref. 1.

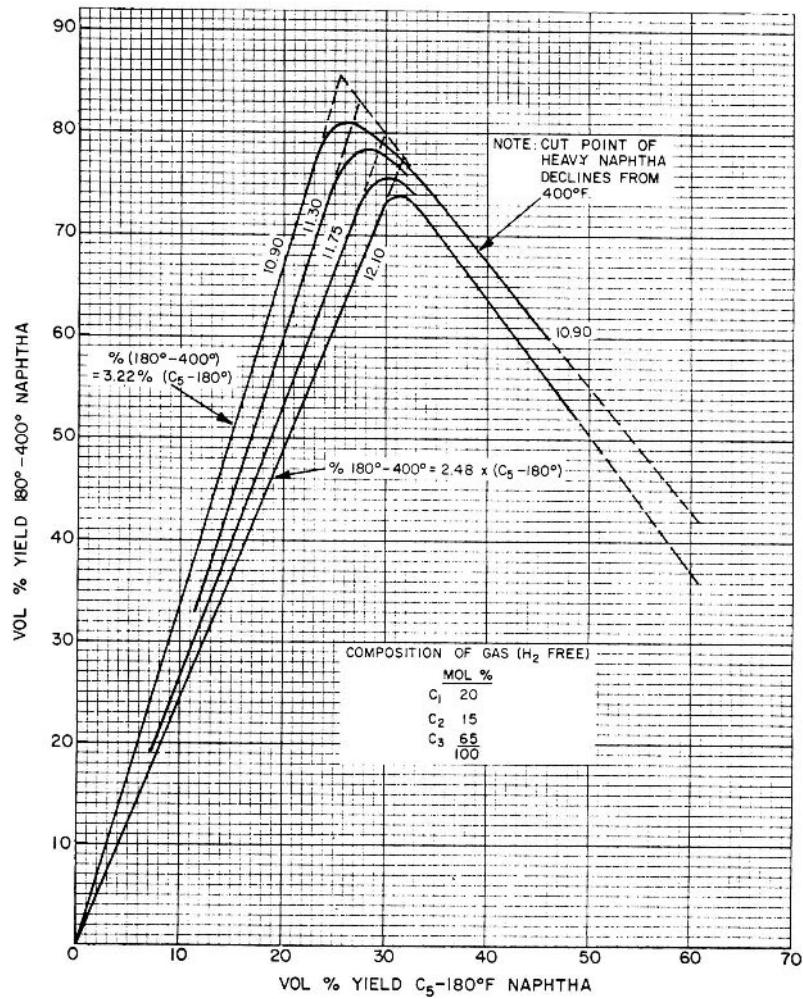


Figure 7.4 Relationship between yields of C₅-180°F and 180-400°F hydrocrackates. (From Ref. 11.)

tions are the Watson characterization factor (K_w) of the feed and the hydrogen consumption in scf/bbl feed. With this information proceed as follows:

1. Use Figure 7.4 to determine the vol% (C₅-180°F) naphtha.
2. With Figure 7.5 use the vol% (C₅-180°F) naphtha and feed K_w to obtain vol% (180 to 400°F) naphtha.

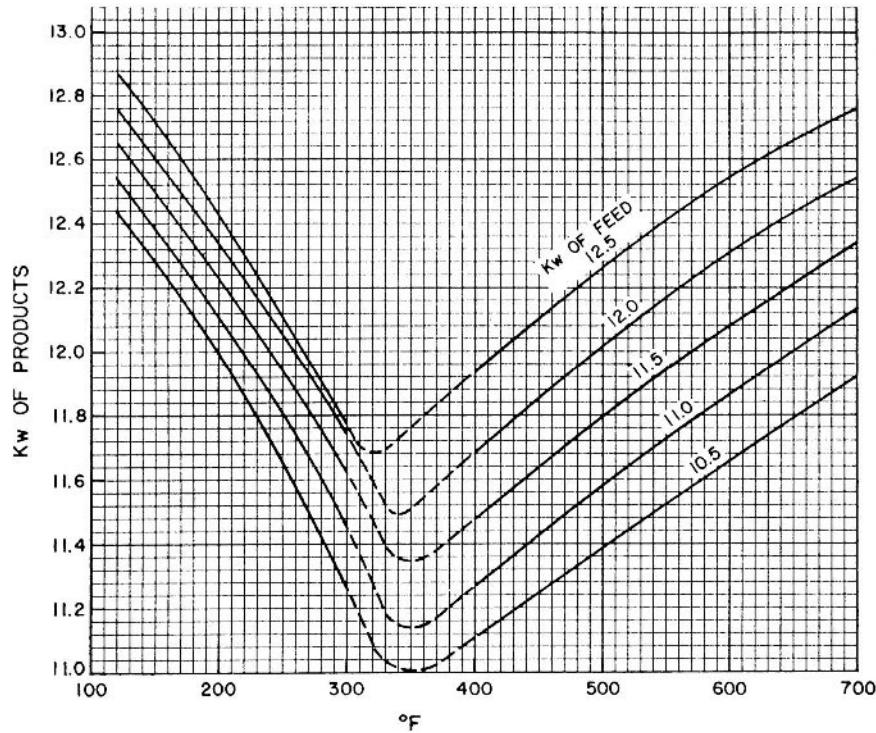


Figure 7.5 Characterization factor of hydrocracker products. (From Ref. 12.)

3. Calculate the liquid volume % butanes formed from:

$$\begin{aligned} \text{LV\% iC}_4 &= 0.377 [\text{LV\% (C}_5\text{-}180^\circ\text{F)}] \\ \text{LV\% nC}_4 &= 0.186 [\text{LV\% (C}_5\text{-}180^\circ\text{F)}] \end{aligned}$$

4. Calculate the wt% of propane and lighter from:

$$\text{wt\% C}_3 \text{ and lighter} = 1.0 + 0.09 [\text{LV\% (C}_5\text{-}180^\circ\text{F)}].$$

It is necessary to make both weight and hydrogen balances on the unit. The gravities of the product streams can be calculated using the K_w factors of the product streams obtained from Figure 7.5 and average mid-boiling points of 131°, 281°, and 460°F for the C₅-180°F naphtha, 180 to 400°F naphtha, and 400+°F streams, respectively. The weight of the 400+°F stream is obtained by

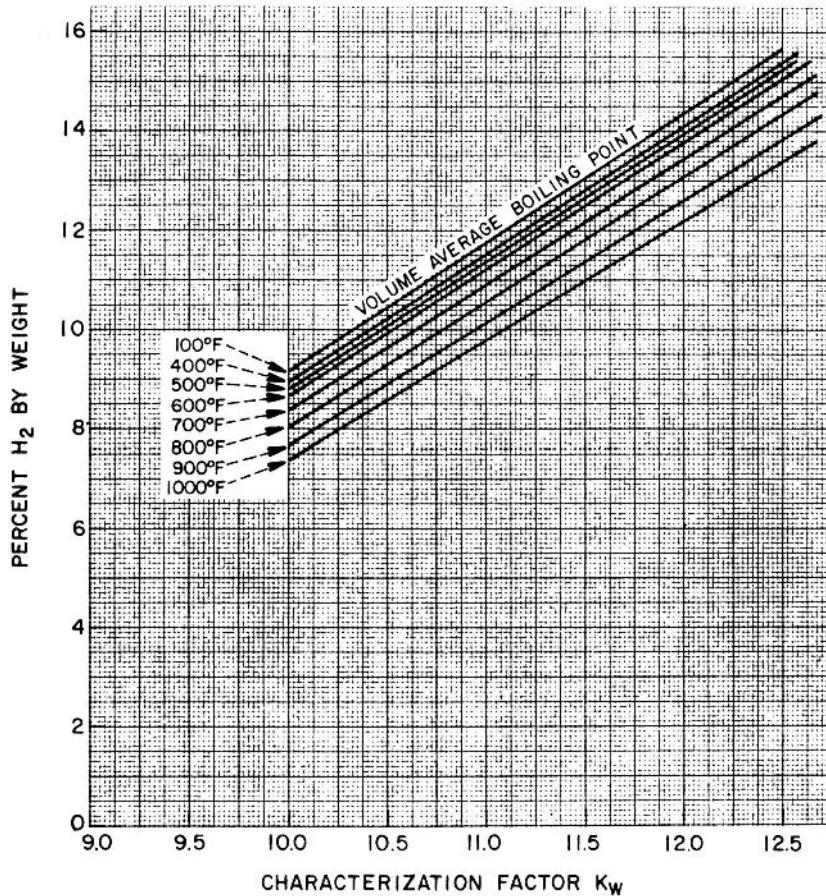


Figure 7.6 Hydrogen content of hydrocarbons. (From Ref. 21.)

difference. The chemical hydrogen consumed should be included with the total weight of the feed.

Hydrogen contents of the streams can be estimated using the wt% hydrogen for each stream, except the heavy hydrocrackate (180 to 400°F), obtained from Figure 7.6 [7]. The heavy hydrocrackate is highly naphthenic and contains from 13.3 to 14.5 wt% hydrogen (avg. 13.9%). Assume hydrogen loss by solution in products of 1 lb/bbl feed (range 0.8 to 1.3 lb H₂/bbl feed) [11].

It should be noted that if the yield of C₅-180°F naphtha is greater than 25

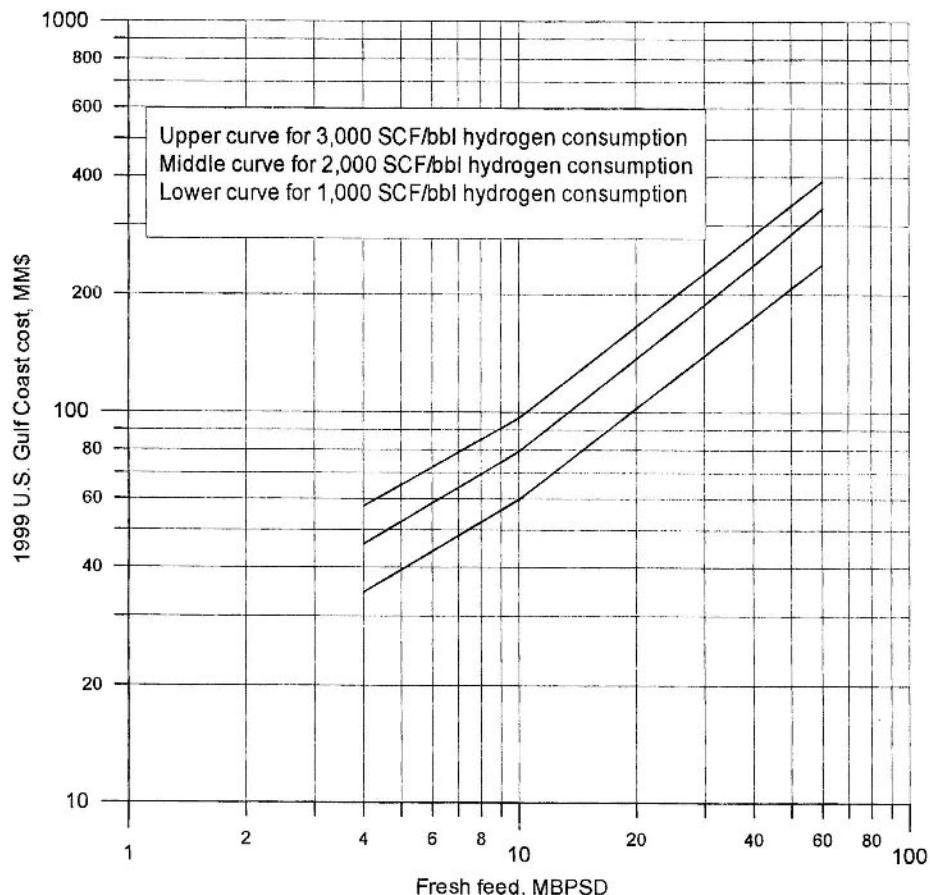


Figure 7.7 Catalytic hydrocracking unit investment cost: 1999 U.S. Gulf Coast. (See Table 7.4.)

to 30 vol%, the yield of heavy hydrocrackate (180 to 400°F naphtha) will be determined from a curve having a negative slope. This indicates an economically unattractive situation because heavy hydrocrackate is being cracked to lighter materials. A less severe operation should be used.

The composition of the C₃ and lighter stream will vary depending upon feedstock properties and operating conditions. For the purpose of preliminary studies, the following composition can be assumed:

	mol%	wt%
C ₁	20	8.8
C ₂	15	12.4
C ₃	65	78.8
Total	100	100.0

These values were determined by averaging the compositions obtained when processing thirteen feedstocks ranging from virgin gas oil to coker and fluid catalytic cracker gas oil. Within the precision of the data, the same average composition was found for the C₃ and lighter streams when operating to obtain all gasoline or maximum jet fuel liquid products.

7.7 INVESTMENT AND OPERATING COSTS

Capital investment costs for catalytic hydrocracking units can be estimated from Figure 7.7. Table 7.4 lists the items included in the investment cost obtained from Figure 7.7 and also the utility requirements for operation.

7.8 MODES OF HYDROCRACKER OPERATION

Full-conversion hydrocracking operations are very expensive in terms of both original capital cost and direct operating cost because of the high pressures at which the units operate [1800–2500 psig (120–170 barg)]. As a result, units designed to operate at lower pressures are being used to obtain some of the benefits of hydrocracking at lower costs. These units are called mild hydrocracking (MHC) units or moderate pressure hydrocracking (MPHC) units. UOP refers to the MPHC units as partial-conversion units [19]. The MHC units operate at pressures in the range of 800–1200 psig (55–82 barg) and the MPHC units at pressures in the range 1400–1500 psig (95–102 barg).

The MHC units are frequently used to reduce the sulfur and nitrogen contents of fluid catalytic cracking unit feedstocks while also increasing the amount of middle distillate fuel (diesel) blending stocks. Yields of up to 30% full-range diesel fuel with cetane indices between 30 and 40 can be produced from virgin vacuum gas-oil feedstocks [20].

The MPHC units, operating at higher pressures and costing from 1.5 to 1.8 times the cost of a MHC unit, can produce from 35–40% full-range diesel blending stocks with cetane indices of 45–50. They can also be operated to produce 10–20% kerosene blending stocks with smoke points of 15–20 [19].

Table 7.4 Catalytic Hydrocracking Unit Cost Data*Costs included*

1. Stabilization of gasoline
2. Fractionation into two products
3. Complete preheat, reaction, and hydrogen circulation facilities
4. Hydrogen sulfide removal from hydrogen recycle
5. Sufficient heat exchange to cool products to ambient temperature
6. Central control system
7. Electric motor–driven hydrogen recycle compressors

Costs not included

1. Initial catalyst charge, approximately \$150/BPD of feed
2. Hydrogen generation and supply facilities
3. Spare hydrogen recycle compressors
4. Recovery of butanes, propane, etc., from gas
5. Feed fractionation
6. Conversion of hydrogen sulfide to sulfur
7. Cooling water, steam, and power supply
8. Paid-up royalty

Royalty

Running royalty is about \$0.15 to 0.25/bbl.

Paid-up royalty is about \$150 to 250/BPD.

Utility data (per bbl feed)

	1000	2000	3000
Hydrogen consumption, scf.	1000	2000	3000
Steam, lb	50	75	100
Power, kWh ^a	8	13	18
Cooling water, gal crclt. (30°FΔt)	300	450	600
Fuel (LHV), MMBtu	0.1	0.2	0.3
Catalyst replacement, \$	0.05	0.1	0.2

^a Includes electric drive for hydrogen recycle compressors.

Note: See Fig. 7.8.

The MHC and MPHC units offer refineries the flexibility of producing higher yields of high-quality middle distillate products with capital and operating costs from 50–80% of those of a full-conversion hydrocracker.

7.9 CASE-STUDY PROBLEM: HYDROCRACKER

Table 7.5 shows the hydrocracker material balance. Hydrocracker catalyst and utility requirements are shown in Table 7.6.

Table 7.5 Hydrocracker Material Balance: 100,000 BPCD, Alaska North Slope Crude Oil Basis (10,621 BPCD Fresh Feed; Severity, 2,000 scf H₂/bbl)

Component	vol%	BPD	°API	(lb/hr)/BPD	lb/hr	wt% S	lb/hr S	Kw
<i>Feed</i>								
Coker GO	38.6	4,103	14.3	14.16	58,114	1.98	1,151	10.56
FCC LCO	61.4	6,517	12.6	14.32	93,352	0.17	158	10.44
Combined	100.0	10,621	13.3	14.26	151,456		1,309	
Hydrogen, scfb	2,000				4,671			
Total					156,137			
<i>Products</i>								
H ₂ S, wt%	0.89				1,391		1,309	
C ₃ and lighter, wt%	1.72				1,603			
iC ₄	2.89	307		8.22	2,523			
nC ₄	1.43	151		8.51	1,289			
C ₅ -180°F	7.7	817	77.1	9.90	8,096		12.37	
180-400°F	28.12	2,937	47.1	11.56	34,519		11.42	
400-520°	79.5	8,441	32.2	12.61	106,716		11.25	
Total	120.9	12,841			156,137			
<i>Hydrogen balance</i>								
<i>Out</i>								
H ₂ S					1,391		82	
C ₃ and lighter				20.0	1,603		321	
C ₄				17.2	3,805		654	
C ₅ -180°F				15.3	8,053		1,231	
180-400°F				13.9	34,519		4,798	
400-520°F				12.1	106,439		12,870	
H ₂ in soln. (1 lb/bbl feed)							443	
Total							20,399	
<i>In</i>								
Coker GO				10.0	58,114		5,791	
FCC LCGO				9.9	93,352		9,235	
Hydrogen				100.0	4,671		4,671	
Total							19,697	
Added H ₂ ^a							702	
Total							20,399	

^a Increase H₂ consumption by 702 lb/hr to give 2,301 scfb H₂ used.

Table 7.6 Hydrocracker Catalyst and Utility Requirements

Steam, Mlb/day	797
Power, MkWh/day	138
Cooling water, Mgpn	3.3
Fuel, MMBtu/day	2124
Catalyst, \$/day	1062

PROBLEMS

1. A hydrocracker feedstock has a boiling range of 650 to 920°F, an API gravity of 23.7°, and contains 1.7 wt% sulfur. If the hydrocracking hydrogen consumption is 1500 scf/bbl of feed and the feed rate is 7500 BPSD, determine (a) total hydrogen consumption, (b) barrels of gasoline, and (c) barrels of jet fuel produced per day.
2. For the feed of problem 1, calculate the feed rate in barrels per day needed to produce sufficient isobutane for an alkylation unit producing 3500 BPD of alkylate. Assume the hydrocracking hydrogen consumption is 1750 scf/bbl of feed, and 0.65 bbl of isobutane is needed to produce 1 bbl of alkylate.
3. For the feedstock and under the conditions of problem 1, estimate the characterization factors of the gasoline and jet fuel fractions produced by the hydrocracker.
4. Make an overall material balance, including a hydrogen balance for a 10,000 BPSD hydrocracker with a 26.5° API feedstock having a characterization factor of 12.1 and containing 0.7% sulfur, 0.3% nitrogen, and 0.15% oxygen by weight. The hydrocracking hydrogen consumption is 2000 scf/bbl of feed.
5. Calculate direct operating costs, excluding labor, per barrel of feed for a 10,000 BPSD hydrocracker that has a total hydrogen consumption of 1780 scf/bbl of feed, and hydrogen has a value of \$3.00/Mscf.
6. Calculate the total hydrogen consumption for hydrocracking 10,000 BPSD of 24.0° API, 617°F (325°C) to 950°F (510°C) boiling range feedstock containing 0.45% sulfur, 0.18% nitrogen, and 0.11% oxygen by weight to a total gasoline liquid product.
7. Using the cost figures in problem 6 of chapter 6 and assuming labor costs are equal on the two units, compare the costs per barrel of gasoline product for hydrocracking and fluid catalytic cracking the feedstocks in problems 6 and 7 of chapter 6. The cost of hydrogen is \$3.00/Mscf.

8. Calculate the hydrogen consumption and jet fuel production for the feedstock in problem 6 if the hydrocracker were operated to maximize jet fuel production (45° API fraction). How much gasoline would be produced?
9. Using the cost figures in problem 6 of chapter 6 and product prices in a current issue of the *Oil and Gas Journal*, estimate the hydrocracking processing costs per barrel of liquid product and the value added per barrel of product.

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8

Hydroprocessing and Resid Processing

The term resid refers to the bottom of the barrel and is usually the atmospheric tower bottoms (atmospheric reduced crude, or ARC) with an initial boiling point of 650°F (343°C) or vacuum tower bottoms (vacuum reduced crude, or VRC) with an initial boiling point of 1050°F (566°C). In either case, these streams contain higher concentrations of sulfur, nitrogen, and metals than does the crude oil from which they were obtained, and hydrogen/carbon ratios in the molecules are much lower. These concentrations are much higher in the case of the VRC.

In recent years the density and sulfur contents of crude oils charged to U.S. refineries have been increasing and consequently a higher percentage of the crude oils are in the 1050+°F (566+°C) boiling range. In the past this resid has been sold as asphalt (if the qualities of the crude permit) or as heavy fuel oil (No. 6 or bunker fuel oil). Stricter environmental emission standards have made it much more difficult and costly to use these heavy oils for fuels, and more of these must be converted in the refinery to feedstocks for refining processes that will convert them to transportation fuel blending stocks.

High carbon forming potentials of resids, caused by the low hydrogen/carbon ratios in the molecules and as indicated by the Conradson and Ramsbottom carbon residues, cause rapid catalyst deactivation and high catalyst costs, and the nickel and vanadium in the resids act as catalysts for reactions creating carbon and light gaseous hydrocarbons. As a result, catalytic processes for converting resids usually use ARC for their feedstocks, and VRC feedstocks are usually processed by noncatalytic processes. The processes most commonly used for processing ARC are reduced crude catalytic cracking units and hydroprocessing units. Thermal cracking processes such as delayed coking and Flexicoking or solvent extraction processes for VRC feedstocks.

8.1 COMPOSITION OF VACUUM TOWER BOTTOMS

Vacuum tower bottoms are complex mixtures of high molecular weight and high boiling point compounds containing thousands of hydrocarbon and organic compounds. All of the bad processing features of refinery feedstocks are present in the bottoms streams in greater concentrations than in any of the distillate feedstocks [6]. Because they are so complex it has been difficult to express the compositions in ways meaningful to processing operations.

Several investigators have reported the results of studies using solubility techniques to separate vacuum resids into fractions whose properties can be related to processing techniques and results [10,27]. Liquid propane is used to extract the oil fraction from vacuum tower bottoms, and liquid n-pentane, n-hexane, or n-heptane is then used to extract the resin fraction from the residue from the propane extraction. The material insoluble in either the propane or the higher hydrocarbons is termed the asphaltene fraction.

A. L. Hensley and his associates from Amoco Research summarized the properties of the fractions in a report given at a meeting of the American Institute of Chemical Engineers [10] from which the following description is derived.

The asphaltene fraction has a very low hydrogen-to-carbon ration and consists of highly condensed ring compounds with predominating molecular weights, as determined by solution techniques, in the 5000 to 10,000 range (mass spectrometer techniques estimate molecular weights about an order of magnitude lower). The molecule is built up of sheets of these highly condensed ring structures held together by valence bonds between hetero atoms such as sulfur, oxygen, and metals. Support to this structure is given by work reported by Bonné [2]. An asphaltene molecule contains three to five unit sheets consisting of condensed aromatic and naphthenic rings with paraffinic side chains. These sheets are held together by hetero atoms such as sulfur or nitrogen and/or polymethylene bridges, thio-ether bonds, and vanadium and nickel complexes. Separation into unit sheets is accompanied by sulfur and vanadium removal. A significant feature of the asphaltene fraction is that 80 to 90% of the metals in the crude (nickel and vanadium) are contained in this material. Apparently 25 to 35% of these metals are held in porphyrin structures and the remainder in some undetermined type of organic structure. The asphaltene fraction contains a higher content of sulfur and nitrogen than does the vacuum resid and also contains higher concentrations of carbon forming compounds (as shown by Conradson and Ramsbottom carbon residues). A hypothetical asphaltene molecule structure developed by A. G. Bridge and his coworkers at Chevron is depicted in Figure 8.1. Vacuum resids from crude oils examined by Hensley using extraction by n-heptane contained from 2 to 15 wt% asphaltenes. Results on similar crude oils by Rossi and his

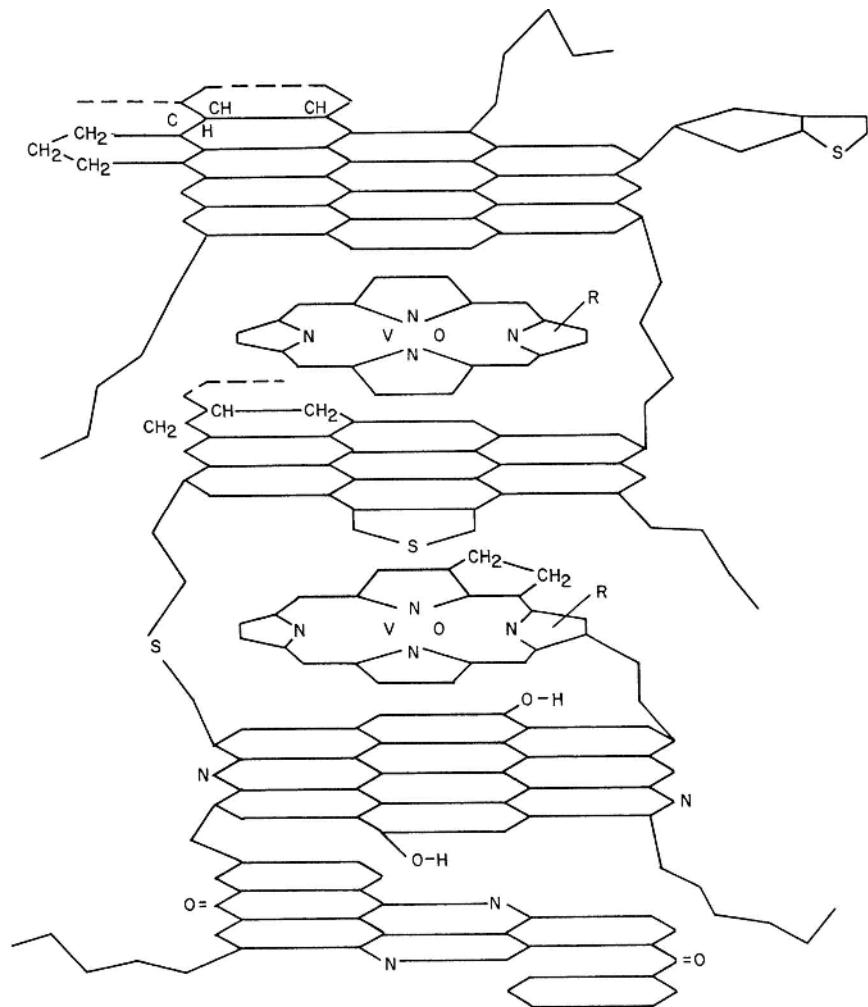


Figure 8.1 Hypothetical asphaltene molecule structure. (From Ref. 3.)

coworkers from Chevron using n-pentane as the solvent gave asphaltene contents up to 25 wt% [27].

The resin fraction contains certain condensed-ring aromatics but also has a substantial amount of paraffinic structures and serves as a solvent for the asphaltenes. Average molecular weights from 600 to 5000 were determined by solvent

techniques. Sulfur concentrations are approximately the same as the vacuum resids from which they are derived, so there is no significant concentration of sulfur in this fraction. The resins contain 10 to 20 wt% of the metals in the crude so the oil fraction is almost free of metals contamination.

The oil fraction is highly paraffinic, usually contains no metals, and has lower sulfur and nitrogen contents than the vacuum resid.

8.2 PROCESSING OPTIONS

Although there have been improvements in existing processes for converting resids to more salable products or reducing the quantity of material difficult to sell, the main processes used have been available for many years but the economics have changed. The processes are classified as catalytic or noncatalytic. The catalytic processes normally use atmospheric reduced crude as the feedstock and include fixed-bed hydroprocessing, ebullated- or expanded-bed hydroprocessing, moving-bed hydroprocessing, and reduced crude fluid catalytic cracking. The noncatalytic processes typically use vacuum reduced crude as the feedstock and include solvent extraction, delayed coking, and Flexicoking.

8.3 HYDROPROCESSING

The term hydroprocessing is used to denote those processes used to reduce the boiling range of the feedstock as well as to remove substantial amounts of impurities such as metals, sulfur, nitrogen, and high carbon forming compounds. As presently practiced fixed-bed processes—such as Residfining, ARDS, VRDS, and RESID HDS, and the ebullated- or expanded-bed processes H-Oil and LC-finining—fall into this category rather than hydrocracking. In hydroprocessing processes, feed conversion levels of 25 to 65% can be attained. Other names applied to this operation are hydroconversion, hydrorefining, and resid HDS.

In U.S. refineries, hydroprocessing units are used to prepare residual stream feedstocks for cracking and coking units. Although vacuum resids can be used as feedstocks, most units use atmospheric resids as feeds because the lower viscosities and impurity levels give better overall operations and greater impurity reductions in the $1050+^{\circ}\text{F}$ ($566+^{\circ}\text{C}$) fractions. Typically the heavy naphtha fraction of the products will be catalytically reformed to improve octanes, the atmospheric gas oil fraction hydrotreated to reduce aromatic content and improve cetane number, the vacuum gas oil fraction used as conventional FCC unit feed, and the vacuum tower bottoms sent to a heavy oil cracker or coker.

With the exception of H-Oil, LC-finining HYCON, and OCR, the processes have fixed-bed reactors and usually require the units to be shut down to have the

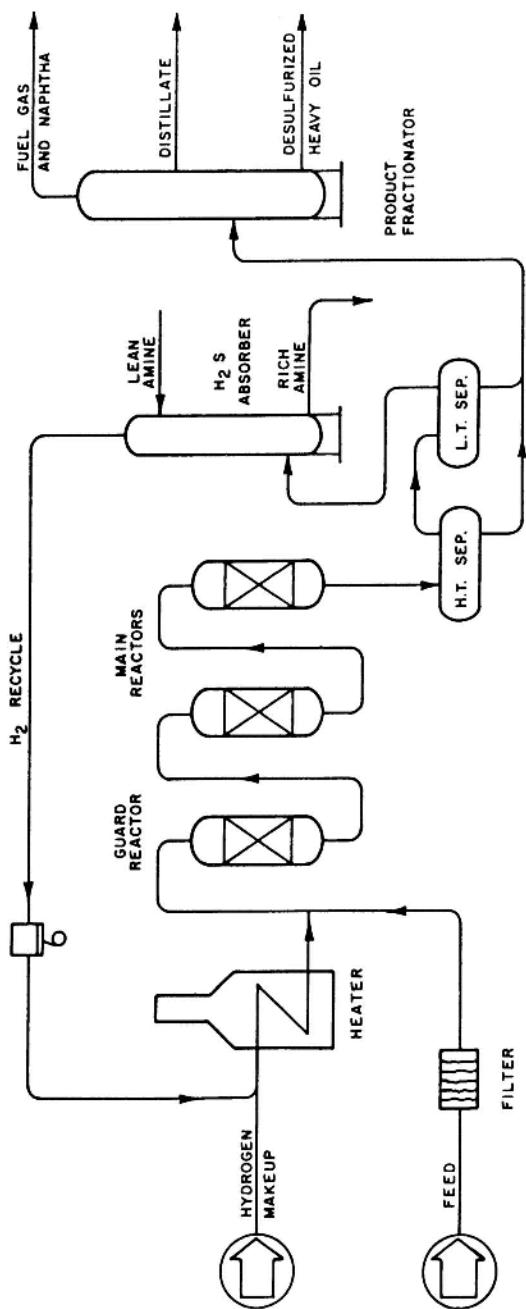


Figure 8.2 EXXON RESIDfining hydropyrolysis unit. (Courtesy Exxon Research and Engineering.)

catalyst changed when catalyst activity declines below the accepted level of activity. A typical fixed-bed process flow diagram is shown in Figure 8.2. Ebullated- or expanded-bed processes have similar overall flow diagrams in terms of sequence of operations.

All units operate at very high pressures, above 2000 psig (13.8 MPa) and usually near 3000 psia (20.7 MPa), and low space velocities of 0.2 to 0.5 v/hr/v. The low space velocities and high pressures limit charge rates to 30,000 to 40,000 BPSD (4760–6360 M³/SD) per train of reactors. Typically each train will have a guard reactor to reduce the metals contents and carbon forming potential of the feed, followed by three to four hydroprocessing reactors in series. The guard reactor's catalyst is a large-pore-size (150–200 Å) silica-alumina catalyst with a low-level loading of hydrogenation metals such as cobalt and molybdenum. The catalysts in the other reactors are tailor-made for the feedstocks and conversion levels desired and may contain catalysts with a range of pore and particle sizes as well as different catalytic metal loadings and types (e.g., cobalt and molybdenum or nickel and molybdenum). Typical pore sizes will be in the 80 to 100 Å range.

The process flow, as shown on Figure 8.2 [7,27], is very similar to that of a conventional hydrocracking unit except for the amine absorption unit to remove hydrogen sulfide from the recycle hydrogen stream and the guard reactor to protect the catalyst in the reactor train. The heavy crude oil feed to the atmospheric distillation unit is desalted in a two- or three-stage desalting unit to remove as much of the inorganic salts and suspended solids as possible because these will be concentrated in the resids. The atmospheric resids are filtered before being fed to the hydroprocessing unit to remove solids greater than 25 Å in size, mixed with recycle hydrogen, heated to reaction temperature, and charged into the top of the guard reactor. Suspended solids in the feed will be deposited in the top section of the guard reactor and most of the metals will be deposited on the catalyst. There is a substantial reduction in the Conradson and Ramsbottom car-

Table 8.1 Results from Hydroprocessing Jobo Crude

	Feed	Product
Gravity, °API	8.5	22.7
Sulfur, wt%	4.0	0.8
Nickel, ppm	89	5
Vanadium, ppm	440	19
Residue, wt%	13.8	2.8

Source: Ref. 6.

bons in the guard reactor, and the feed to the following reactors is low in metals and carbon forming precursors.

The three or four reactors following the guard reactor are operated to remove sulfur and nitrogen and to crack the $1050+^{\circ}\text{F}$ ($566+^{\circ}\text{C}$) material to lower boiling compounds. Recycle hydrogen is separated and the hydrocarbon liquid stream fractionated in atmospheric and vacuum distillation columns. Results of hydroprocessing a heavy Venezuelan crude oil (Jobo) are shown in Table 8.1.

8.4 EXPANDED-BED HYDROCRACKING PROCESSES

There are two expanded- or ebullated-bed processes available for license today. These are the H-Oil and LC-finishing processes, which were developed by Hydrocarbon Research Incorporated (HRI) and Cities Service and C-E Lummus. The LC-finishing and H-Oil processes are designed to process heavy feeds such as atmospheric tower bottoms or vacuum reduced crude and use catalysts with metals removal, hydrotreating, and cracking activities. A simplified process flow diagram for the LC-finishing process is shown in Figure 8.3a and b. (See also Photo 9, Appendix E)

The terms ebullated bed and expanded bed are names given by HRI and C-E Lummus to a fluidized-bed type operation which utilizes a mixture of liquids and gases to expand the catalyst bed rather than just gases (definition of fluidized

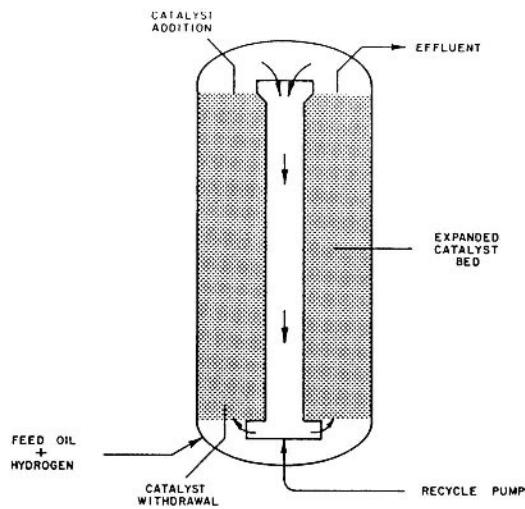


Figure 8.3a Expanded- or ebullated-bed reactor. (From Ref. 4.)

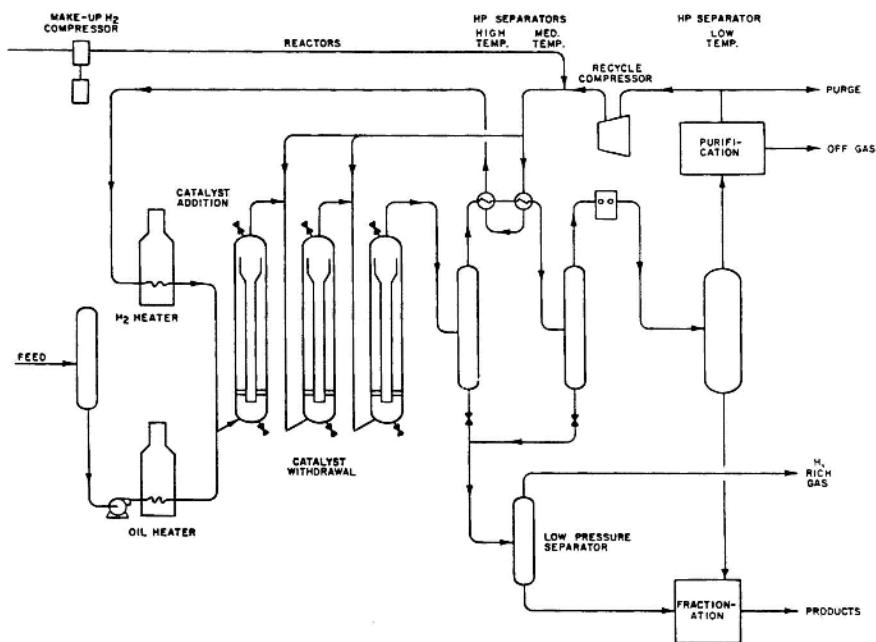


Figure 8.3b LC-finishing expanded-bed hydroprocessing unit. (From Ref. 4.)

bed). Both HRI and Lummus use similar technologies but offer different mechanical designs [4,25,26].

The preheated feed, recycle, and makeup hydrogen are charged to the first reactor of the unit. The liquid passes upward through the catalyst, which is maintained as an ebullient bed. The first-stage reactor effluent is sent to the second-stage reactor for additional conversion. The product from the second reactor passes through a heat exchanger to a high-pressure separator where the recycle gas is removed. The liquid from the high-pressure separator is sent to a low-pressure flash drum to remove additional gases. The liquid stream at low pressure then goes to a rectification column for separation into products. The operating pressure for an H-Oil unit is a function of feed boiling point with operating pressures up to 3000 psig used when charging vacuum tower residuum. The operating temperature is a function of charge stock and conversion but is normally in the range of 800 to 850°F.

One of the main advantages of the ebullated-bed reactor process is the ability to add and remove catalyst during operation. This permits operators to regenerate catalyst while remaining on-stream and to maintain catalyst activity by either regeneration or the addition of fresh catalyst. Because the unit operates

from start-of-run to end-of-run with an equilibrium activity catalyst, with a constant quality feedstock, and constant operating conditions, the product yields and quality will also be constant. This significantly improves refinery operation and efficiency.

Another advantage to the ebullated-bed reactor system is that small solid particles are flushed out of the reactor and do not contribute to plugging or increase in pressure drop through the reactor.

It is necessary to recycle effluent from each of the reactor's catalyst beds into the feed to that reactor in order to have sufficiently high velocities to keep the catalyst bed expanded, to minimize channeling, to control the reaction rates, and to keep heat released by the exothermic hydrogenation reactions to a safe level. This back-mixing dilutes the concentrations of the reactants and slows the rates of reactions as compared with fixed-bed (plug-flow) reactors. Based on work reported by Shell [20], ebullated-bed reactors require up to three times as much catalyst per barrel of feed to obtain the same conversion level as fixed-bed reactors.

Typical product yields from LC-finishing cracking are given in Table 8.2.

8.5 MOVING-BED HYDROPROCESSORS

Shell and Chevron have developed technology which combines the advantages of fixed-bed and ebullated-bed hydroprocessing. These systems use reactors designed for catalyst flow by gravity from top to bottom with mechanisms designed to allow spent catalyst to be removed continuously or periodically from the bottom and fresh catalyst added to the top. This permits low-activity high-metals catalyst to be removed from the reactor and replaced with fresh catalyst without taking the unit off-stream. Lower catalyst consumption rates are required than with the ebullated-bed systems because, in the ebullated-bed system, equilibrium-activity and metals-loaded catalyst is removed rather than the lowest-activity-spent catalyst. As there is no recycling of product from the reactor outlets to the reactor inlet, the reactors operate in a plug-flow condition and reaction rates are the same as in a fixed-bed operation. Shell technology is known as the HYCON process and the Chevron process is called OCR.

8.6 SOLVENT EXTRACTION

Solvent extraction technology is used to extract up to two-thirds of the vacuum reduced crude to be used as a good quality feed for a fluid catalytic cracking unit to convert into gasoline and diesel fuel (home heating oil) blending stocks. There are a number of processes licensed but the two most common are the DEMEX

Table 8.2 LC-finining Yields

	Long resid	Short resid
<i>Feed stocks</i>		
Gravity, °API	15.7	10.7
Sulfur, wt%	2.7	3.2
RCR, wt%	9.4	
<i>Metals:</i>		
Vanadium, ppm	110	147
Nickel, ppm	27	35
IBP-1050°F, vol%	55	33.2
1050+°F, vol%	45	66.8
<i>Yields</i>		
Gas, C ₃ -, scf/bbl	350	590
Naphtha, C ₄ -400°F, vol%	17.8	13.1
Gravity, °API	61.0	64.0
Sulfur, wt%	<0.1	0.04
Kerosine		
400–500°F, vol%	10.2	8.9
Gravity, °API	38.8	37.2
Sulfur, wt%	0.1	0.1
AGO, 500–600°F, vol%	19.7	14.3
Gravity, °API	31.8	30.1
Sulfur, wt%	0.25	0.18
VGO, 650–1050°F, vol%	37.1	36.1
Gravity, °API	22.4	23.0
Sulfur, wt%	0.6	0.6
Pitch, 1050+°F, vol%	20.0	32.7
Gravity, °API	7.7	7.0
Sulfur, wt%	1.3	2.3
H ₂ consumption, scf/bbl	985	1310
Catalyst consumption, lb/bbl	0.15	0.12

Source: Ref. 4.

process licensed by UOP and the ROSE process licensed by Kerr-McGee. Both technologies use light hydrocarbons (propane to pentanes) as the solvents and use subcritical extraction but use supercritical techniques to recover the solvents. A simplified process flow diagram of the UOP DEMEX process is shown in Figure 8.4.

Light hydrocarbons have reverse solubility curves; that is, as temperature increases the solubility of higher molecular weight hydrocarbons decreases. Also paraffinic hydrocarbons have higher solubilities than aromatic hydrocarbons. A

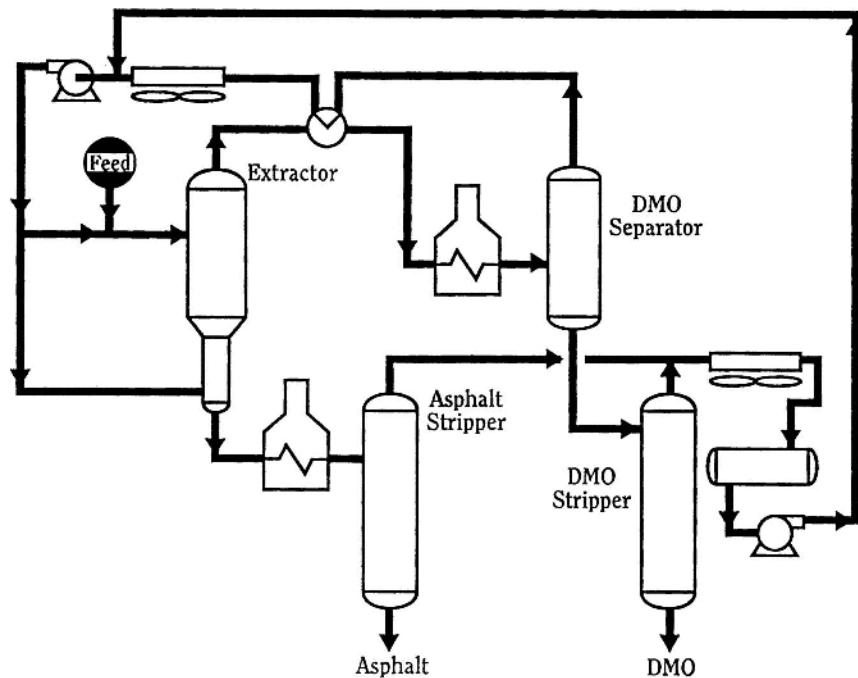


Figure 8.4 UOP DEMEX solvent extraction unit flow. (Courtesy of UOP LLC.)

temperature can be selected at which all of the paraffins go into solution along with the desired percentage of the resin fraction. The higher molecular weight resins precipitate along with the asphaltenes. The extract is then separated from the precipitated raffinate fraction and stripped of the solvent by increasing the temperature to just above the critical temperature of the solvent. At the critical temperature, the oil-plus-resin portion will separate from the solvent and the solvent can be recovered without having to supply latent heat of vaporization. This reduces energy requirements by 20–30% as compared with solvent recovery by evaporation.

The hydrocarbon solvent used is feedstock-dependent. As the molecular weight of the solvent increases (propane to pentane), the amount of solvent needed for a given amount of material extracted decreases but the selectivity of the solvent also decreases. Therefore, the choice of solvent is an economic one because; for a given recovery of FCC unit feedstock from a particular resid, propane will give a better quality extract but will use more solvent. Solvent recovery costs will be greater than if the higher molecular weight solvent is used be-

cause more solvent has to be recovered. The higher molecular weight solvents give lower solvent recovery costs but, for a given feedstock and yield, give a lower quality extract and have higher capital costs because the critical pressure of the solvent increases with molecular weight and a higher equipment design pressure must be used.

As 80–90% of the metals in the crude oil are in the asphaltenes, and most of the remaining metals are in the resin fraction, a good quality FCC unit feedstock can be obtained. As shown in Figure 8.5, the quality of the extract decreases as the percent extracted increases. Typically, extract is limited to 50–65% of the VRC.

The asphaltene fraction is a very hard asphalt (0.1 penetration) and is usually blended into asphalt or residual fuels.

8.7 SUMMARY OF RESID PROCESSING OPERATIONS

The selection of the most economic method of processing the portion of crude oil boiling above 1050°F (566°C) is a very complex matter because political, environmental, and technical issues are all involved. Unlike decisions driven by the market, criteria which are difficult to evaluate from an economic viewpoint must also be included. As a result, the “best” decision for one refinery may be the “worst” for another refinery even in the same company. A summary of the advantages and disadvantages of the processes illustrates the complexity of the matter.

Thermal processes (delayed coking and Flexicoking) have the advantage that the vacuum reduced crude is eliminated so there is no residual fuel for disposal, and most of the VRC is converted to lower-boiling hydrocarbon fractions suitable for feedstocks to other processing units to convert them into transportation fuels. However, for high-sulfur crude oils, delayed coking produces a fuel grade coke of high sulfur content. This coke may be very difficult to sell. The alternative is to hydroprocess the feed to the coker to reduce the coker feed sulfur level and make a low-sulfur coke. This can add a great deal to the cost.

Flexicoking is more costly than delayed coking, both from a capital and operating cost viewpoint, but has the advantage of converting the coke to a low heating value fuel gas to supply refinery energy needs and elemental sulfur for which there is a market. A disadvantage is that the fuel gas produced is more than the typical refinery can use and energy of compression does not permit it to be transported very far. It can be used for cogeneration purposes or sold to nearby users.

Hydroprocessing reduces the sulfur and metal contents of the VRC and improves the hydrogen/carbon ratio of the products by adding hydrogen, but the products are very aromatic and may require a severe hydrotreating operation to

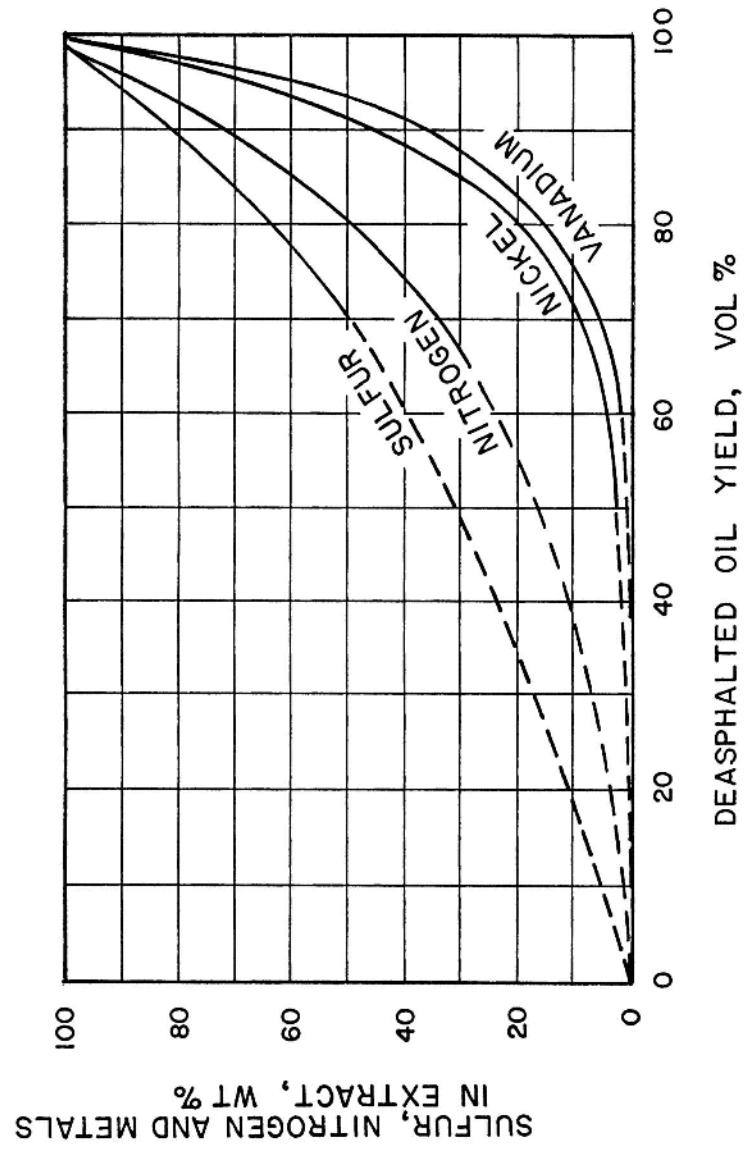


Figure 8.5 Extract quality varies with extract quantity. (Courtesy of UOP, LLC.)

obtain satisfactory middle distillate fuel blending stocks. Crude oils with high sulfur and metal levels will also have high catalyst replacement costs.

Solvent extraction recovers 55–70% of the VRC for FCC or hydrocracker feedstocks to be converted into transportation fuel blending stocks, but the asphaltene fraction can be difficult process or sell.

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9

Hydrotreating

The terms hydrotreating, hydroprocessing, hydrocracking, and hydrodesulfurization are used rather loosely in the industry because, in the processes hydrodesulfurization and hydrocracking, cracking and desulfurization operations occur simultaneously and it is relative as to which predominates. In this text, hydrotreating refers to a relatively mild operation whose primary purpose is to saturate olefins and/or reduce the sulfur and/or nitrogen content (and not to change the boiling range) of the feed. Hydrocracking refers to processes whose primary purpose is to reduce the boiling range and in which most of the feed is converted to products with boiling ranges lower than that of the feed. Hydrotreating and hydrocracking set the two ends of the spectrum and those processes with a substantial amount of sulfur and/or nitrogen removal and a significant change in boiling range of the products versus the feed are called hydroprocessing in this text.

Hydrotreating is a process to catalytically stabilize petroleum products and/or remove objectionable elements from products or feedstocks by reacting them with hydrogen. Stabilization usually involves converting unsaturated hydrocarbons such as olefins and gum-forming unstable diolefins to paraffins. Objectionable elements removed by hydrotreating include sulfur, nitrogen, oxygen, halides, and trace metals. Hydrotreating is applied to a wide range of feedstocks, from naphtha to reduced crude. When the process is employed specifically for sulfur removal it is usually called hydrodesulfurization, or HDS. To meet environmental objectives it also may be necessary to hydrogenate aromatic rings to reduce aromatic content by converting aromatics to paraffins.

Although there are about 30 hydrotreating processes available for licensing [1], most of them have essentially the same process flow for a given application. Figure 9.1 illustrates a typical hydrotreating unit.

The oil feed is mixed with hydrogen-rich gas either before or after it is preheated to the proper reactor inlet temperature. Most hydrotreating reactions are carried out below 800°F (427°C) to minimize cracking, and the feed is usually

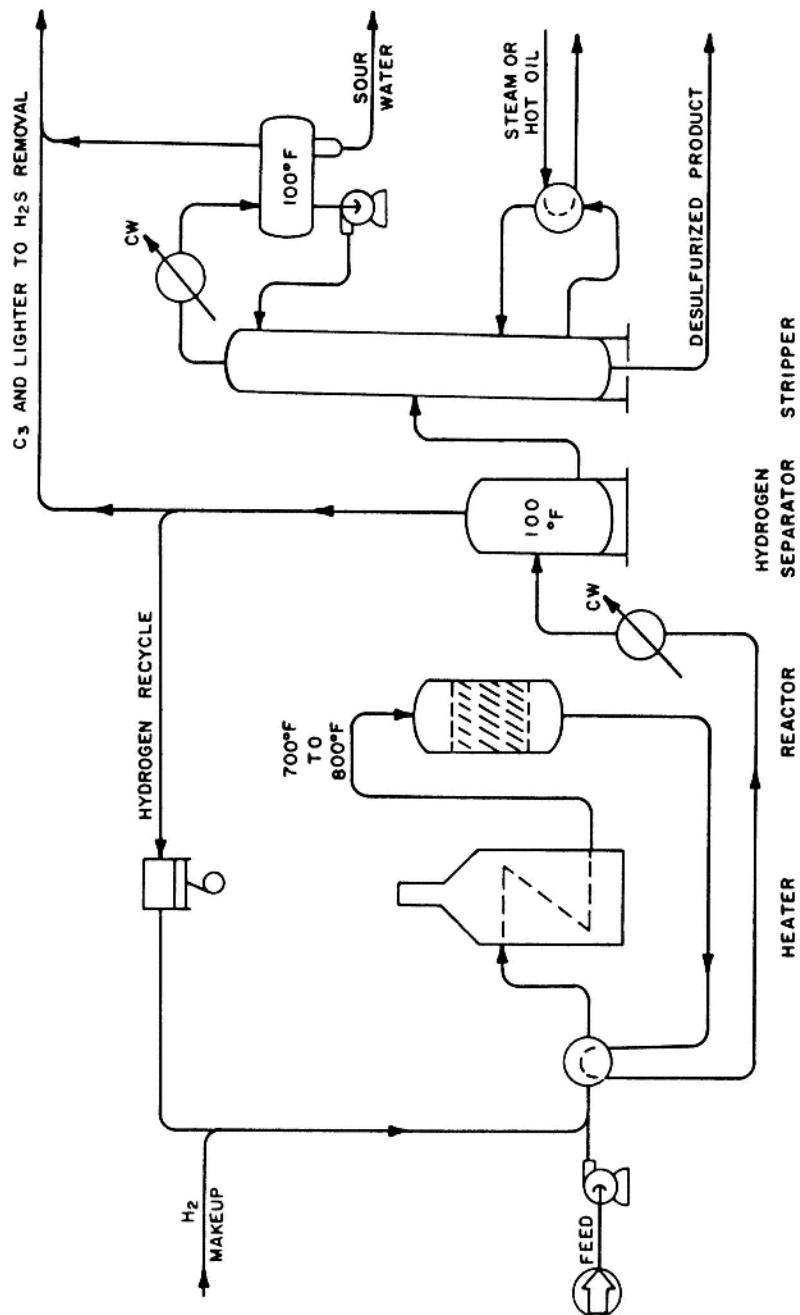


Figure 9.1 Catalytic hydrodesulfurizer.

heated to between 500 and 800°F (260–427°C). The oil feed combined with the hydrogen-rich gas enters the top of the fixed-bed reactor. In the presence of the metal-oxide catalyst, the hydrogen reacts with the oil to produce hydrogen sulfide, ammonia, saturated hydrocarbons, and free metals. The metals remain on the surface of the catalyst and other products leave the reactor with the oil–hydrogen stream. The reactor effluent is cooled before separating the oil from the hydrogen-rich gas. The oil is stripped of any remaining hydrogen sulfide and light ends in a stripper. The gas may be treated to remove hydrogen sulfide and recycled to the reactor.

9.1 HYDROTREATING CATALYSTS

Catalysts developed for hydrotreating include cobalt and molybdenum oxides on alumina, nickel oxide, nickel thiomolybdate, tungsten and nickel sulfides, and vanadium oxide [2]. The cobalt and molybdenum oxides on alumina catalysts are in most general use today because they have proven to be highly selective, easy to regenerate, and resistant to poisons. They must be activated by converting the hydrogenation metals from the oxide to the sulfide form.

If, however, the removal of nitrogen is a significant consideration, catalysts composed of nickel–cobalt–molybdenum or nickel–molybdenum compounds supported on alumina are more efficient. Nitrogen is usually more difficult to remove than sulfur from hydrocarbon streams, and any treatment which reduces excess nitrogen concentration to a satisfactory level usually will effectively remove excess sulfur. Nickel-containing catalysts generally require activation by presulfiding with carbon disulfide, mercaptans, or dimethyl sulfide before bringing up to reaction temperature; however, some refiners activate these cobalt–molybdenum catalysts by injecting the sulfiding chemical into the oil feed during startup [3]. The sulfiding reaction is highly exothermic and care must be taken to prevent excessive temperatures during activation.

Cobalt–molybdenum catalysts are selective for sulfur removal and nickel–molybdenum catalysts are selective for nitrogen removal, although both catalysts will remove both sulfur and nitrogen [4]. Nickel–molybdenum catalysts have a higher hydrogenation activity than cobalt–molybdenum which results, at the same operating conditions, in a greater saturation of aromatic rings. Simply stated, if sulfur reduction is the primary objective, then a cobalt–molybdenum catalyst will reduce the sulfur a given amount at less severe operating conditions with a lower hydrogen consumption than nickel–molybdenum catalyst. If nitrogen reduction or aromatic ring saturation is desired, nickel–molybdenum catalyst is the preferred catalyst.

The ability to adjust pore size to concentrate pores around a particular diameter has a great impact on the hydrotreating activity both at start-of-run (SOR)

and as the catalyst ages. Reactions taking place in the hydrotreating of gas oils [400–1050°F (200–566°C)] generally require a minimum pore size to overcome most diffusional restrictions. Pores that are larger than necessary lend little to improving diffusional characteristics and as the pore diameters of the catalyst increase the surface area decreases (at constant pore volume). Activity generally decreases with surface area and loss in pore volume occurs in the smallest diameter pores first. Highest activity retention is maintained if pore volume is concentrated in a very narrow range of pore diameters.

At the hydrotreating severity to reduce sulfur in LCO to 0.05 wt%, the performance of high-activity NiMo and CoMo catalysts appears to be equivalent.

Catalyst consumption varies from 0.001 to 0.007 lb/bbl (0.003 to 0.02 kg/m³) feed depending upon the severity of operation and the gravity and metals content of the feed.

9.2 AROMATICS REDUCTION

Hydrogen partial pressure is the most important parameter controlling aromatic saturation. Depending on type of feedstock, the required hydrogen partial pressure to reduce aromatic content to 10 vol% may vary as much as 40%. Several investigators [2,5] have shown that at LHSV_s of 2.0, aromatics in diesel fuel blending stocks can be reduced to <10 vol% only at pressures of 1500 psig (10.4 MPa) or greater.

Wilson, Fisher, and Kriz [16] demonstrated that at 715°F (380°C), LHSV_s of 0.75–2.0 h⁻¹, and 2450 psig (16.9 MPa), even the most difficult hydrodearomatizations can be achieved to levels of less than 10 vol% aromatics with nickel-tungsten on gamma-alumina catalysts.

Hydrogenation is an exothermic reaction and equilibrium yields are favored by low temperatures. Reaction rates increase with temperature, and hydrogenation of aromatic ring compounds is a compromise between using low reactor temperatures to achieve maximum reduction of aromatic content and a high temperature to give high reaction rates and a minimum amount of catalyst charge per barrel of feed. Maximum aromatic reduction is achieved between 700–750°F (370–400°C) [usually between 705–725°F (375–385°C)] because of the interrelation between thermodynamic equilibrium and reaction rates. Relationships between reaction temperature and pressure are shown in Figure 9.2 [18]. For a given pressure, the optimum temperature is a function of the types of aromatic compounds in the feed and space velocity.

High-pressure single-stage hydrotreating of only the front end [400–550°F (205–288°C)] of a LCO reduced hydrogen consumption and extended catalyst life. Usually this fraction originally contains about 11.1 wt% mono-aromatics and 17.5 wt% di-aromatics. Hydrogenation at 1200 psig (8.2 MPa) reduces the

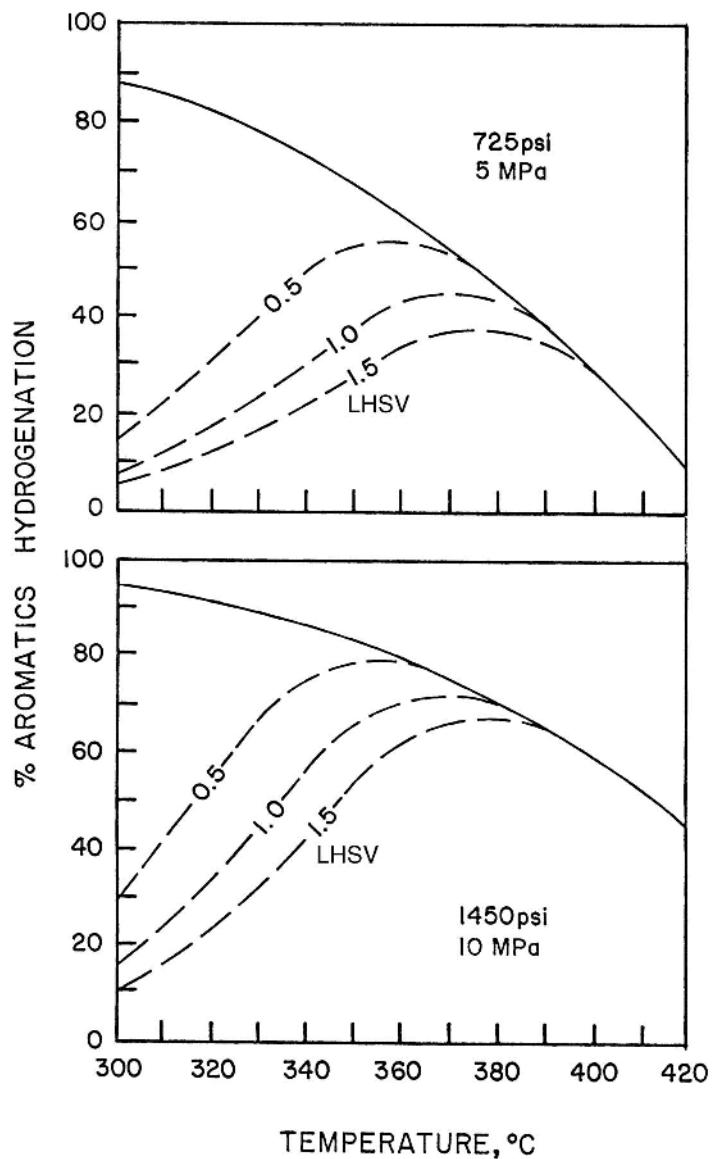


Figure 9.2 Kinetic rate and thermodynamic equilibrium effects on aromatics reduction.
(From Ref. 17.)

di-aromatic content to 0.4 wt% and increases the mono-aromatic content to 18.3 wt%. Saturation of the final aromatic ring is difficult because of the resonance stabilization of the mono-aromatic ring. Hydrogenation at 1500 psig (10.3 MPa) is required to reduce the aromatic content to 10 wt%, but only about 1/3 as much hydrogen is required as compared to reducing the aromatic content of the full-range [400–650°F (205–345°C)] LCO. This is because the back end of the LCO contains only di- and tri⁺-aromatics and the front end contains almost all of the mono-aromatics, about 1/3 of the di-aromatics, and none of the tri-aromatics in the LCO.

Hydrotreating the feed to the FCC unit reduces the sulfur contents of the FCC products but also increases the aromatic content of the LCO (probably because the percentage of mono-aromatic compounds in the feed is increased). Hydrotreating the FCC feed also makes it more difficult to reduce the aromatics content of the LCO to <20 vol%.

9.3 REACTIONS

The main hydrotreating reaction is that of desulfurization but many others take place to a degree proportional to the severity of the operation. Typical reactions are:

1. Desulfurization
 - a. Mercaptans: $\text{RSH} + \text{H}_2 \rightarrow \text{RH} + \text{H}_2\text{S}$
 - b. Sulfides: $\text{R}_2\text{S} + 2\text{H}_2 \rightarrow 2\text{RH} + \text{H}_2\text{S}$
 - c. Disulfides: $(\text{RS})_2 + 3\text{H}_2 \rightarrow 2\text{RH} + 2\text{H}_2\text{S}$
 - d. Thiophenes:

$$\begin{array}{c} \text{HC}-\text{CH} \\ || \quad || \\ \text{HC} \quad \text{CH} + 4\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{S} \\ \backslash \quad / \\ \text{S} \end{array}$$
2. Denitrogenation
 - a. Pyrrole: $\text{C}_4\text{H}_4\text{NH} + 4\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{NH}_3$
 - b. Pyridine: $\text{C}_5\text{H}_5\text{N} + 5\text{H}_2 \rightarrow \text{C}_5\text{H}_{12} + \text{NH}_3$
3. Deoxidation
 - a. Phenol: $\text{C}_6\text{H}_5\text{OH} + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{H}_2\text{O}$
 - b. Peroxides: $\text{C}_7\text{H}_{13}\text{OOH} + 3\text{H}_2 \rightarrow \text{C}_7\text{H}_{16} + 2\text{H}_2\text{O}$
4. Dehalogenation

Chlorides: $\text{RCl} + \text{H}_2 \rightarrow \text{RH} + \text{HCl}$.
5. Hydrogenation:

Pentene: $\text{C}_5\text{H}_{10} + \text{H}_2 \rightarrow \text{C}_5\text{H}_{12}$
6. Hydrocracking: $\text{C}_{10}\text{H}_{22} + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{C}_6\text{H}_{14}$

The ease of desulfurization is dependent upon the type of compound. Lower-boiling compounds are desulfurized more easily than higher-boiling ones. The difficulty of sulfur removal increases in the order paraffins, naphthenes, aromatics [5].

Nitrogen removal requires more severe operating conditions than does desulfurization. For middle distillate fractions from crude oils containing high concentrations of nitrogen compounds, more efficient nitrogen reduction is achieved by using a catalyst charge of 90% nickel–molybdenum and 10% nickel–tungsten [10].

Hydrogen consumption is about 70 scf/bbl of feed per percent sulfur, about 320 scf/bbl oil feed per percent nitrogen, and 180 scf/bbl per percent oxygen removed. Hydrogen consumption for olefin and aromatics reduction can be estimated from the stoichiometric amounts required. If operating conditions are severe enough that an appreciable amount of cracking occurs, hydrogen consumption increases rapidly. It is important to note that actual hydrogen makeup requirements are from two to ten times the amount of stoichiometric hydrogen required. This is due to the solubility loss in the oil leaving the reactor effluent separator and the saturation of olefins produced by cracking reactions.

All reactions are exothermic and, depending on the specific conditions, a temperature rise through the reactor of 5 to 20°F (3 to 11°C) is usually observed.

9.4 PROCESS VARIABLES

The principal operating variables are temperature, hydrogen partial pressure, and space velocity.

Increasing temperature and hydrogen partial pressure increases sulfur and nitrogen removal and hydrogen consumption. Increasing pressure also increases hydrogen saturation and reduces coke formation. Increasing space velocity reduces conversion, hydrogen consumption, and coke formation. Although increasing temperature improves sulfur and nitrogen removal, excessive temperatures must be avoided because of the increased coke formation. Typical ranges of process variables in hydrotreating operations are [1]:

Temperature	520–645°F	270–340°C
Pressure	100–3,000 psig	690–20,700 kPag
Hydrogen, per unit of feed		
Recycle	2,000 scf/bbl	360 m ³ /m ³
Consumption	200–800 scf/bbl	36–142 m ³ /m ³
Space velocity (LHSV)		1.5–8.0

9.5 CONSTRUCTION AND OPERATING COSTS

Hydrogen consumption for sulfur, nitrogen, and oxygen removal can be estimated from a monograph prepared by Nelson [6] or from Section 9.2. Assume hydrogen loss by solution in products is approximately one pound per barrel of feed [190 scf/bbl ($34 \text{ m}^3/\text{m}^3$)].

Construction and operating costs can be estimated from Figure 9.3 and Table 9.1.

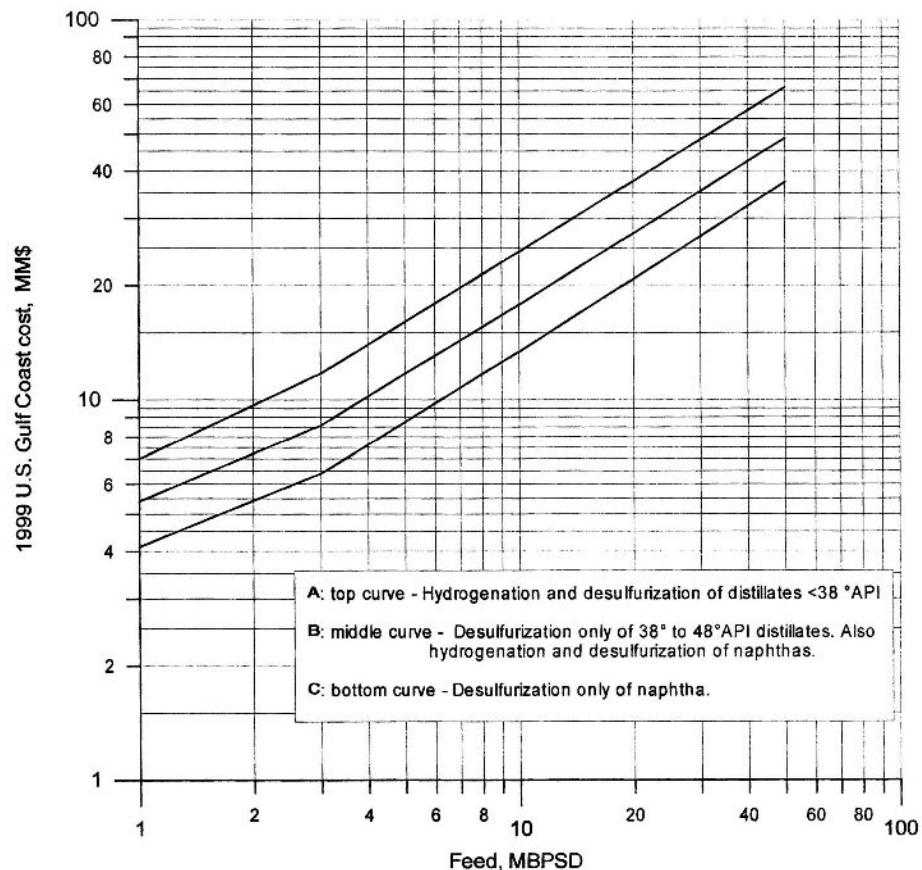


Figure 9.3 Catalytic desulfurization and hydrogenation unit investment cost: 1999 U.S. Gulf Coast. (See Table 9.1.)

Table 9.1 Catalytic Desulfurization and Hydrogenation Unit Cost Data*Costs included*

1. Product fractionation.
2. Complete preheat, reaction, and hydrogen circulation facilities.
3. Sufficient heat exchange to cool products to ambient temperature.
4. Central control system.
5. Initial catalyst charge.

Costs not included

1. Feed fractionation.
2. Makeup hydrogen generation.
3. Sulfur recovery from off-gas.
4. Cooling water, steam, and power supply.

Royalty^a

Running royalty is about \$0.03/bbl (\$0.19/m³)

Paid-up royalty is about \$30/BPD (\$189/m³/D)

Utility data (per unit feed)

	“A”	“B”	“C”
Steam, lb/bbl	10	8	6
kg/m ³	0.7	0.6	0.4
Power, kWh	6.0	3.0	2.0
Cooling water, gal crclt. (30°FΔt)	500	400	300
m ³ crclt. (17°CΔt)	1.9	1.5	1.1
Fuel (LHV), MMBtu	0.2	0.15	0.1
MMJ	211	158	105
Hydrogen makeup, scf	400–800	150–400	100–150
m ³	10–20	4–10	3–4.2
Catalyst replacement, \$/bbl	0.04	0.03	0.02
\$/m ³	0.25	0.19	0.12

^a Royalties apply to gas oils and resids. Naphtha and kerosine are royalty-free.

Note: See Fig. 9.3.

9.6 CASE-STUDY PROBLEM: HYDROTREATERS

Environmental Protection Authority standards for motor fuels require that sulfur, olefin, and aromatic contents be less than specified values. Hydrotreating is used to reduce the concentrations in finished products by processing feedstocks for units producing motor fuel blending components or by processing blending stocks to lower concentrations of the specific components (Table 9.2). Without hydrotreating, the sulfur contents of gasolines and diesel fuels from North Slope Alas-

Table 9.2 Medium Distillate Hydrotreater Material Balance

Component	vol%	BPD	°API	lb/h/BPD	lb/h	wt% S	lb/h S
<i>Feed</i>							
AGO	39.0	12,500	30.0	12.77	159,653	0.52	830
LCGO	23.5	7,587	30.0	12.78	96,967	0.93	905
Atm JET	37.8	12,200	37.5	12.21	148,906	0.24	357
H ₂ , scf/bbl		500			3,524		
Total	100.0	32,287	32.3	12.67	409,076	0.51	2,092
<i>Products</i>							
H ₂ S					2,013		1,895
C ₂ -					1,385		
C ₃	1.0	337		7.42	2,500		
iC ₄	1.9	634		8.22	5,210		
nC ₄	1.0	315		8.51	2,677		
Jet	36.3	11,956	38.5	12.14	145,194	0.05	73
Diesel	59.8	19,686	31.0	12.70	250,096	0.05	125
Total	100.0	32,927			409,076		2,092

kan crude exceed EPA specifications. By hydrotreating the fluid catalytic cracking unit feedstocks and the jet and diesel fuel blending stocks, the low sulfur specifications for gasolines, diesel, and jet fuel can be met. Two hydrotreaters will be used, one for FCC feedstocks (Tables 9.4 and 9.5) and the other for diesel and jet fuel blending stocks (Table 9.3).

There is very little in the literature on yields from hydrotreating but these operations are relatively mild and product yields from 95 to 98 vol% on feed (same boiling range as feed) can be expected with an increase of 1°API in the gravity of the heavier products. Light product (C₄-) yield distribution is assumed

Table 9.3 Medium Distillate Hydrotreater Utility Requirements

Utility	Per bbl feed	Per day	Per min
Steam, Mlb	0.01	323	
Power, MkWh	0.006	194	
Cooling water, Mgal circulated	0.5	16,144	11.21
Fuel, MMBtu	0.2	6,457	
H ₂ , Mscf	0.5	16,144	
Catalyst repl, \$	0.02	646	

Table 9.4 FCC Hydrotreater Material Balance

Component	vol%	BPD	°API	lb/h/BPD	lb/h	wt% S	lb/h S
<i>Feed</i>							
LCGO	56.7	20,500	22.2	13.42	275,119	0.95	2,614
HVGO	43.3	15,644	15.5	14.03	219,518	1.51	3,357
H ₂ , scf/bbl		500			3,974		
Total	100.0	36,144	19.3	13.69	494,637	1.20	5,928
<i>Products</i>							
H ₂ S					5,352		5,037
C ₂ -					1,193		
C ₃	0.5	199		7.42	1,476		
iC ₄	1.0	374		8.22	3,076		
nC ₄	0.5	186		8.51	1,580		
HT LVGO	55.5	20,090	23.2	13.35	268,103	0.10	261
HT HVGO	42.4	15,331	16.5	13.95	213,857	0.29	630
Total	100.0	36,180			494,637		5,928

Table 9.5 FCC Feed HT Utility Requirements

Utility	Per bbl		
	feed	Per day	Per min
Steam, Mlb	0.01	361	
Power, MkWh	0.006	217	
Cooling water, MMgal circulated	0.5	18,072	12.55
Fuel, MMBtu	0.2	7,729	
H ₂ , Mscf	0.5	18,072	
Catalyst repl, \$	0.02	723	

to be similar to that obtained from hydrocracking. R. E. Maples has published a compilation of literature data [11] which indicate a hydrotreating severity of 400 scf of hydrogen per barrel of feed is adequate for each of these hydrotreaters and a solution loss of 100 scf per barrel of feed is assumed.

PROBLEMS

1. Estimate the hydrogen consumption required to completely remove the sulfur from a hydrotreater feedstock and to reduce the nitrogen content

of the product to 15 ppm by weight. The 48.5° API naphtha feed to the unit contains 0.62% sulfur, 0.15% nitrogen, and 0.09% oxygen by weight.

2. The hydrogen required for hydrotreating in a refinery is usually obtained from catalytic reforming operations. Calculate the minimum barrels per day of reformer feed required to provide 120% of the hydrogen necessary to completely desulfurize 1000 bbl/day of naphtha having the following properties:

^o API	55.0
S, as mercaptans (RSH), wt%	0.5
S, as sulfides (R ₂ S), wt%	0.5
S, total, wt%	1.0

The reformer feed has the following properties:

Component	vol%	gal/lb mol
C ₆ naphthenes	20.0	13.1
C ₇ naphthenes	10.0	15.4
C ₈ naphthenes	10.0	18.3
Paraffins	50.0	18.5
Aromatics	10.0	13.0

Make the following simplifying assumptions:

1. Conversion of naphthenes is 90% for each type.
2. C₆ naphthenes convert only to benzene, C₇ naphthenes convert only to toluene, and C₈ naphthenes convert only to xylene.
3. Aromatics and paraffins in the reformer feed do not react.

Express the actual hydrogen consumption in the hydrotreater and the hydrogen yield from the reformer as scf/bbl of feed.

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10

Catalytic Reforming and Isomerization

The demand of today's automobiles for high-octane gasolines has stimulated the use of catalytic reforming. Catalytic reformate furnishes approximately 30–40% of the U.S. gasoline requirements but, with the implementation of restrictions on the aromatic contents of gasolines, can be expected to decrease.

In catalytic reforming, the change in the boiling point of the stock passed through the unit is relatively small as the hydrocarbon molecular structures are rearranged to form higher-octane aromatics with only a minor amount of cracking. Thus catalytic reforming primarily increases the octane of motor gasoline rather than increasing its yield; in fact, there is a decrease in yield because of hydrocracking reactions which take place in the reforming operation.

The typical feedstocks to catalytic reformers are heavy straight-run (HSR) gasolines and naphthas [180–375°F (82–190°C)] and heavy hydrocracker naphthas. These are composed of the four major hydrocarbon groups: paraffins, olefins, naphthenes, and aromatics (PONA). Typical feedstocks and reformer products have the following PONA analyses (vol %):

Component	Feed	Product
Paraffins	30–70	30–50
Olefins	0–2	0–2
Naphthenes	20–60	0–3
Aromatics	7–20	45–60

The paraffins and naphthenes undergo two types of reactions in being converted to higher octane components: cyclization and isomerization. The ease and probability of either of these occurring increases with the number of carbon atoms

in the molecules and it is for this reason that only the HSR gasoline is used for reformer feed. The LSR gasoline [C_5 -180°F (C_5 -82°C)] is largely composed of lower-molecular-weight paraffins that tend to crack to butane and lighter fractions and it is not economical to process this stream in a catalytic reformer. Hydrocarbons boiling above 400°F (204°C) are easily hydrocracked and cause an excessive carbon laydown on the catalyst.

10.1 REACTIONS

As in any series of complex chemical reactions, reactions occur which produce undesirable products in addition to those desired. Reaction conditions have to be chosen that favor the desired reactions and inhibit the undesired ones. Desirable reactions in a catalytic reformer all lead to the formation of aromatics and isoparaffins as follows:

1. Paraffins are isomerized and to some extent converted to naphthenes. The naphthenes are subsequently converted to aromatics.
2. Olefins are saturated to form paraffins which then react as in (1).
3. Naphthenes are converted to aromatics.
4. Aromatics are left essentially unchanged.

Reactions leading to the formation of undesirable products include:

1. Dealkylation of side chains on naphthenes and aromatics to form butane and lighter paraffins
2. Cracking of paraffins and naphthenes to form butane and lighter paraffins

As the catalyst ages, it is necessary to change the process operating conditions to maintain the reaction severity and to suppress undesired reactions (Table 10.1)

There are four major reactions that take place during reforming. They are: (1) dehydrogenation of naphthenes to aromatics, (2) dehydrocyclization of paraffins to aromatics, (3) isomerization, and (4) hydrocracking. The first two of these reactions involve dehydrogenation and will be discussed together.

Dehydrogenation Reactions

The dehydrogenation reactions are highly endothermic and cause a decrease in temperature as the reaction progresses. In addition, the dehydrogenation reactions have the highest reaction rates of the reforming reactions which necessitates the use of the interheaters between catalyst beds to keep the mixture at sufficiently high temperatures for the reactions to proceed at practical rates (see Figure 10.1).

Table 10.1 Some Basic Relationships in Catalytic Reforming

Reaction	Reaction rate	Heat effect	Effect of high pressure	Effect of high temperature	Effect of high space velocity	Effect on hydrogen production	Effect on RVP	Effect on density	Effect on volumetric yield	Effect on octane
Hydrocracking	Slowest	Exothermic	Aids	Aids	Hinders	Absorb	Increase	Decrease	Varies	Increase
Isomerization	Rapid	Mildly exothermic	None	Aids	Hinders	None	Increase	Slight decrease	Slight increase	Increase
Cyclization	Slow	Mildly exothermic	Hinders	Aids	Hinders	Evolves	Decrease	Increase	Decrease	Increase
Naphthalene isomerization	Rapid	Mildly exothermic	None	Aids	Hinders	None	Decrease	Slight increase	Slight increase	Slight decrease
Naphthalene dehydrogenation	Very fast	Quite endothermic	Hinders	Aids	Hinders	Evolves	Decrease	Increase	Decrease	Increase

Source: Ref. 7.

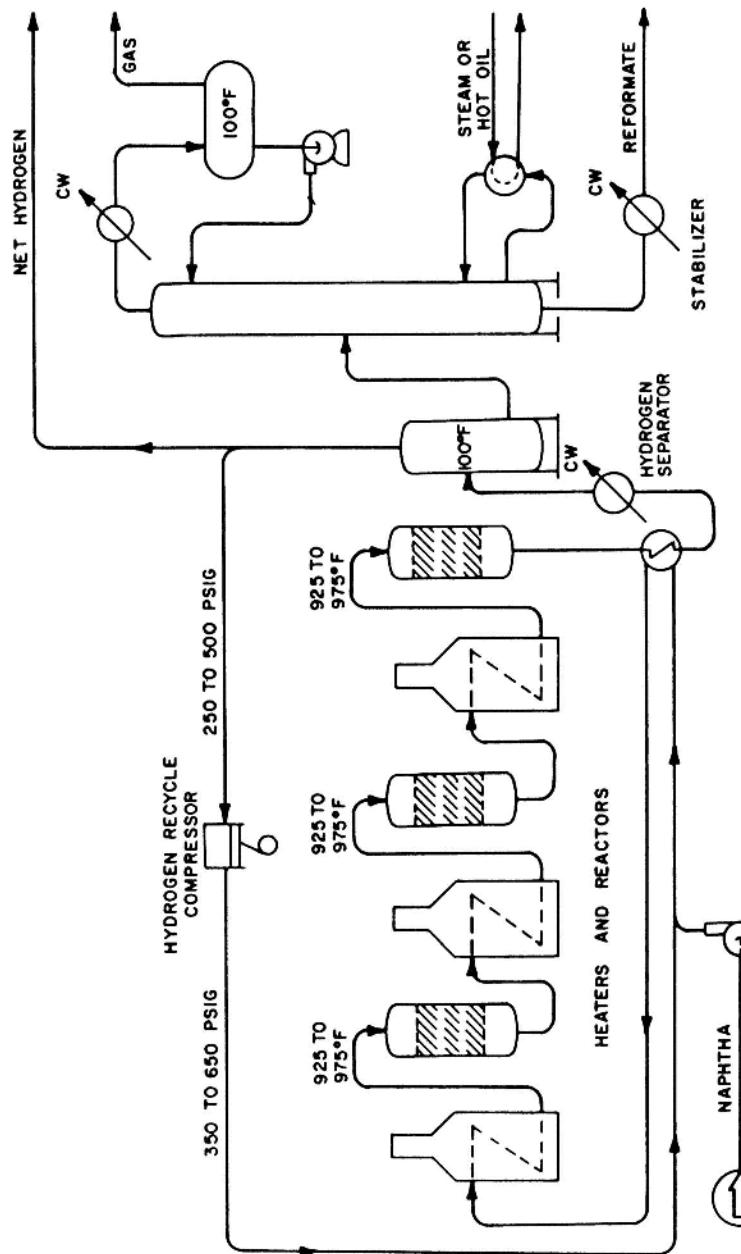
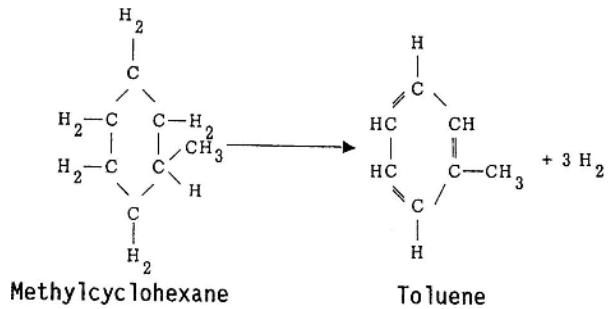


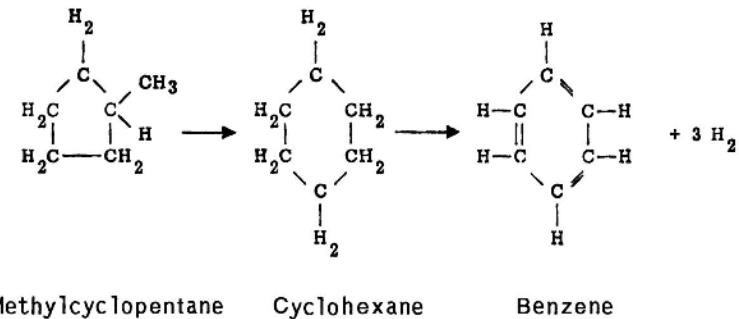
Figure 10.1 Catalytic reforming, semiregenerative process.

The major dehydrogenation reactions are:

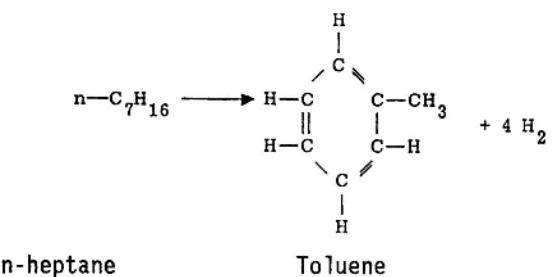
1. Dehydrogenation of alkylcyclohexanes to aromatics:



2. Dehydroisomerization of alkylcyclopentanes to aromatics:



3. Dehydrocyclization of paraffins to aromatics:



The dehydrogenation of cyclohexane derivatives is a much faster reaction than either the dehydroisomerization of alkylcyclopentanes or the dehydrocyclization of paraffins, however, all three reactions take place simultaneously and are necessary to obtain the aromatic concentration needed in the reformate product to give the octane improvement needed.

Aromatics have a higher liquid density than paraffins or naphthenes with the same number of carbon atoms, so 1 volume of paraffins produces only 0.77 volumes of aromatics, and 1 volume of naphthenes about 0.87 volume. In addition, conversion to aromatics increases the gasoline end point because the boiling points of aromatics are higher than the boiling points of paraffins and naphthenes with the corresponding number of carbons.

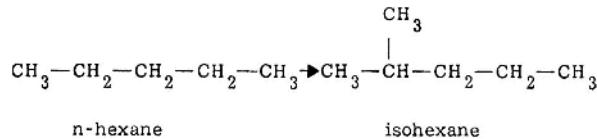
The yield of aromatics is increased by:

1. High temperature (increases reaction rate but adversely affects chemical equilibrium)
2. Low pressure (shifts chemical equilibrium “to the right”)
3. Low space velocity (promotes approach to equilibrium)
4. Low hydrogen-to-hydrocarbon mole ratios (shifts chemical equilibrium “to the right,” however, a sufficient hydrogen partial pressure must be maintained to avoid excessive coke formation)

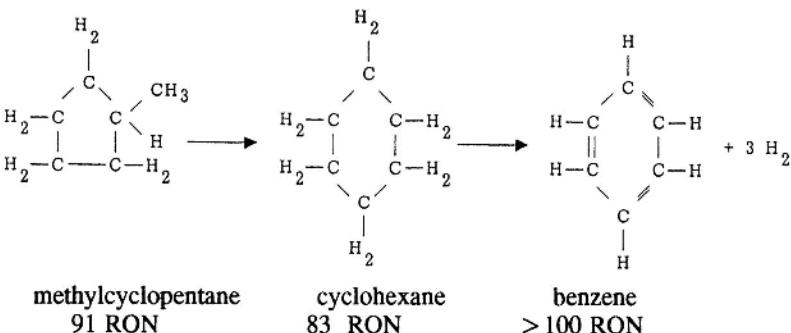
Isomerization Reactions

Isomerization of paraffins and cyclopentanes usually results in a lower octane product than does conversion to aromatics. However, there is a substantial increase over that of the un-isomerized materials. These are fairly rapid reactions with small heat effects.

1. Isomerization of normal paraffins to isoparaffins:



2. Isomerization of alkylcyclopentanes to cyclohexanes, plus subsequent conversion to benzene:



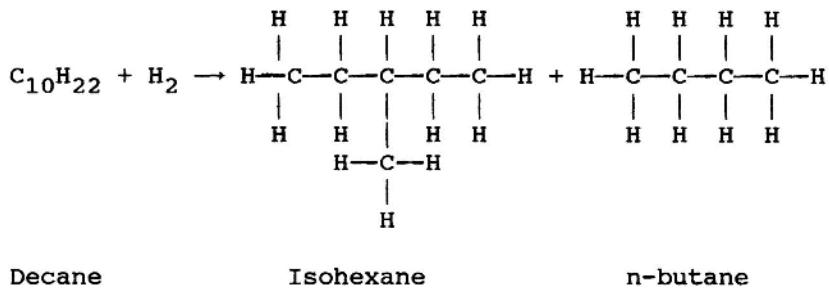
Isomerization yield is increased by:

1. High temperature (which increases reaction rate)
2. Low space velocity
3. Low pressure

There is no isomerization effect due to the hydrogen-to-hydrocarbon mole ratios, but high hydrogen-to-hydrocarbon ratios reduce the hydrocarbon partial pressure and thus favor the formation of isomers.

Hydrocracking Reactions

The hydrocracking reactions are exothermic and result in the production of lighter liquid and gas products. They are relatively slow reactions and therefore most of the hydrocracking occurs in the last section of the reactor. The major hydrocracking reactions involve the cracking and saturation of paraffins.



The concentration of paraffins in the charge stock determines the extent of the hydrocracking reaction, but the relative fraction of isomers produced in any molecular weight group is independent of the charge stock.

Hydrocracking yields are increased by:

1. High temperature
2. High pressure
3. Low space velocity

In order to obtain high product quality and yields, it is necessary to carefully control the hydrocracking and aromatization reactions. Reactor temperatures are carefully monitored to observe the extent of each of these reactions.

Low pressure reforming is generally used for aromatics production and the following generalizations hold for feedstocks in the 155–345°F (68–175°C) TBP boiling range:

1. On a mole basis, naphthalene conversion to aromatics is about 98% with the number of carbon atoms in the precursor being retained in the product as follows:

Methylcyclopentane produces benzene.
Cyclohexane produces benzene.
Dimethylcyclopentane produces toluene.
Dimethylcyclohexane produces xylene.
Cycloheptane produces toluene.
Methylcycloheptane produces xylene.

2. For paraffins the following number of moles of aromatics are produced from one mole of paraffins having the indicated number of carbon atoms:

1 mole P_6 yields 0.05 moles A_6 .
1 mole P_7 yields 0.10 moles A_7 .
1 mole P_8 yields 0.25 moles A_8 .
1 mole P_9 yields 0.45 moles A_9 .
1 mole P_{10} yields 0.45 moles A_{10} .

10.2 FEED PREPARATION

The active material in most catalytic reforming catalysts is platinum. Certain metals, hydrogen sulfide, ammonia, and organic nitrogen and sulfur compounds will deactivate the catalyst [10]. Feed pretreating, in the form of hydrotreating, is usually employed to remove these materials. The hydrotreater employs a cobalt-molybdenum catalyst to convert organic sulfur and nitrogen compounds to hydrogen sulfide and ammonia, which then are removed from the system with the unreacted hydrogen. The metals in the feed are retained by the hydrotreater catalyst. Hydrogen needed for the hydrotreater is obtained from the catalytic reformer. If the boiling range of the charge stock must be changed, the feed is redistilled before being charged to the catalytic reformer.

10.3 CATALYTIC REFORMING PROCESSES

There are several major reforming processes in use today. These include the Platforming process licensed by UOP LLC (Photo 4, Appendix E), Powerforming (Exxon) (Photo 5, Appendix E), Ultraforming (Amoco), Catalytic Reforming (Engelhard), Magnaforming (ARCO), Reforming (Institut Francais du Petrole [IFP]), and Rheniforming (Chevron). There are several other processes in use at

some refineries but these are limited to a few installations and are not of general interest.

Reforming processes are classified as continuous, cyclic, or semiregenerative depending upon the frequency of catalyst regeneration. The equipment for the continuous process is designed to permit the removal and replacement of catalyst during normal operation. As a result, the catalyst can be regenerated continuously and maintained at a high activity. As increased coke laydown and thermodynamic equilibrium yields of reformate are both favored by low pressure operation, the ability to maintain high catalyst activities and selectivities by continuous catalyst regeneration is the major advantage of the continuous type of unit. This advantage has to be evaluated with respect to the higher capital costs and possible lower operating costs due to lower hydrogen recycle rates and pressures needed to keep coke laydown at an acceptable level.

The semiregenerative unit is at the other end of the spectrum and has the advantage of minimum capital costs. Regeneration requires the unit to be taken off-stream. Depending upon severity of operation, regeneration is required at intervals of 3 to 24 months. High hydrogen recycle rates and operating pressures are utilized to minimize coke laydown and consequent loss of catalyst activity.

The cyclic process is a compromise between these extremes and is characterized by having a swing reactor in addition to those on-stream in which the catalyst can be regenerated without shutting the unit down. When the activity of the catalyst in one of the on-stream reactors drops below the desired level, this reactor is isolated from the system and replaced by the swing reactor. The catalyst in the replaced reactor is then regenerated by admitting hot air into the reactor to burn the carbon off the catalyst. After regeneration it is used to replace the next reactor needing regeneration.

The reforming process can be obtained as a continuous or semiregenerative operation and other processes as either continuous, cyclic, or semiregenerative. The reforming semiregenerative reforming process is typical of fixed-bed reactor reforming operations and will be described here.

The semiregenerative process is shown in the simplified process flow diagram given in Figure 10.1 [6]. The pretreated feed and recycle hydrogen are heated to 925 to 975°F (498–524°C) before entering the first reactor. In the first reactor, the major reaction is the dehydrogenation of naphthenes to aromatics and, as this is strongly endothermic, a large drop in temperature occurs. To maintain the reaction rate, the gases are reheated before being passed over the catalyst in the second reactor. As the charge proceeds through the reactors, the reaction rates decrease and the reactors become larger, and the reheat needed becomes less. Usually three or four reactors are sufficient to provide the desired degree of reaction and heaters are needed before each reactor to bring the mixture up to reaction temperature. In practice, either separate heaters can be used or one heater can contain several separate coils. A typical gas composition leaving each

of the reactors in a four reactor system, with a HSR naphtha feed of 180–380°F; severity, 99 RON; and pressure, 163 psi (1124 kPa) is as follows [2]:

	Feed	1	2	3
P	60	59	50	29
N	29	8	6	5
A	11	33	45	87
Total	100	100	96	87

Note: Reactor outlet, mol/100 mol feed.

The reaction mixture from the last reactor is cooled and the liquid products condensed. The hydrogen-rich gases are separated from the liquid phase in a drum separator, and the liquid from the separator is sent to a fractionator to be debutanized.

The hydrogen-rich gas stream is split into a hydrogen recycle stream and a net hydrogen by-product which is used in hydrotreating or hydrocracking operations or as fuel.

The reformer operating pressure and the hydrogen/feed ratio are compromises among obtaining maximum yields, long operating times between regeneration, and stable operation. It is usually necessary to operate at pressures from 50 to 350 psig (345–2415 kPa) and at hydrogen charge ratios of 3–8 mol H₂/mol feed (2800–7600 scf/bbl). Liquid hourly space velocities in the area of 1 to 3 are in general use.

The original reforming process is classified as a semiregenerative type because catalyst regeneration is infrequent and runs of 6 to 24 months between regeneration are common. In the cyclic processes, regeneration is typically performed on a 24- or 48-hour cycle, and a spare reactor is provided so that regeneration can be accomplished while the unit is still on-stream. Because of these extra facilities, the cyclic processes are more expensive but offer the advantages of low pressure operation and higher yields of reformate at the same severity.

Example Problem

Calculate the length of time between regeneration of catalyst in a reformer operating at the following conditions:

Liquid hourly space velocity (LHSV) = 3.0 v/hr/v
 Feed rate = 5000 BPSD
 Feed gravity = 55.0° API

Catalyst bulk density = 50 lb/ft³
Hydrogen-to-feed ratio = 8000 scf/bbl
Number of reactors = 3

Catalyst deactivates after processing 90 barrels of feed per pound of catalyst. If the catalyst bed is 6 ft deep in each reactor, what are the reactor inside diameters? Assume an equal volume of catalyst in each reactor.

Solution:

Time between regenerations:

$$\begin{aligned}5000 \text{ BPD} &= 1170 \text{ ft}^3/\text{hr} \\ \text{Total catalyst} &= 1170/3 = 390 \text{ ft}^3 \\ (390 \text{ ft}^3) (50 \text{ lb}/\text{ft}^3) &= 19,500 \text{ lb} \\ (19,500 \text{ lb}) (90 \text{ bbl/lb})/5,000 \text{ bbl/day} &= 351 \text{ days}\end{aligned}$$

Inside diameter:

$$\begin{aligned}\text{Volume of catalyst per reactor} &= 390/3 = 130 \text{ ft}^3 \\ \text{Inside area} &= (130 \text{ ft}^3)/(6 \text{ ft}) = 21.67 \text{ ft}^2 \\ \text{Inside diameter} &= 5.25 \text{ ft}\end{aligned}$$

The continuous catalytic reforming process unit can consist of either a stacked design (UOP LLC), in which the reactors are stacked on top of each other, or of side-by-side reactors (IFP). In both cases the sequence of flow of the reactants is similar to that shown for the semiregenerative system in Figure 10.1.

In the stacked design (CCR Platforming™ Unit), freshly regenerated catalyst is introduced in the top of the upper reactor between two concentric perforated cylinders (made from Johnson screens) and flows by gravity from top to bottom. The reactants are introduced on the outside of the outer cylinder and flow radially through the catalyst to the center of the inner cylinder (see Fig. 10.2). Partially aged catalyst is removed from the bottom of the lowest reactor and sent to an external regenerator where the carbon is burned from the catalyst, and the catalyst is reduced and acidified before being returned to the upper reactor [12].

The IFP system is similar to that of UOP LLC except that catalyst removed from all of the reactors, except the last, is transported by hydrogen lifts to the top of the next reactor in the series [5]. The catalyst removed from the last reactor is conveyed by nitrogen to the regenerator section.

10.4 REFORMING CATALYST

All of the reforming catalyst in general use today contains platinum supported on an alumina base. In most cases rhenium is combined with platinum to form

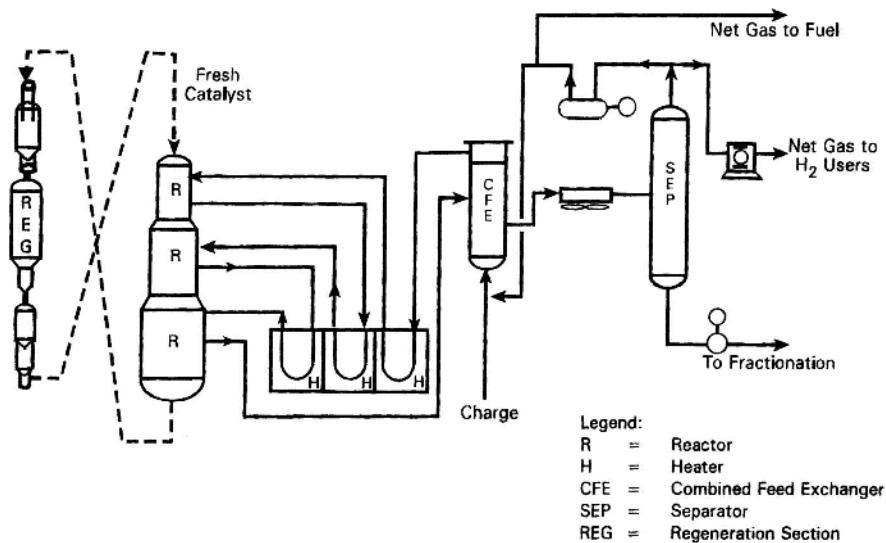


Figure 10.2 Continuous catalyst regeneration (CCR Platforming™) catalytic reformer.
(Courtesy of UOP LLC.)

a more stable catalyst which permits operation at lower pressures. Platinum is thought to serve as a catalytic site for hydrogenation and dehydrogenation reactions and chlorinated alumina provides an acid site for isomerization, cyclization, and hydrocracking reactions [10]. Reforming catalyst activity is a function of surface area, pore volume, and active platinum and chlorine content. Catalyst activity is reduced during operation by coke deposition and chloride loss. In a high pressure process, up to 200 barrels of charge can be processed per pound of catalyst before regeneration is needed. The activity of the catalyst can be restored by high temperature oxidation of the carbon followed by chlorination. This type of process is referred to as semiregenerative and is able to operate for 6- to 24-month periods between regenerations. The activity of the catalyst decreases during the on-stream period and the reaction temperature is increased as the catalyst ages to maintain the desired operating severity. Normally the catalyst can be regenerated in situ at least three times before it has to be replaced and returned to the manufacturer for reclamation.

Catalyst for fixed-bed reactors is extruded into cylinders 1/32 to 1/16 in. (0.8 to 1.6 mm) diameter with lengths about 3/16 in. (5 mm). The catalyst for

continuous units is spherical with diameters approximately 1/32 to 1/16 in. (0.8 to 1.6 mm).

10.5 REACTOR DESIGN

Fixed-bed reactors used for semiregenerative and cyclic catalytic reforming vary in size and mechanical details, but all have basic features as shown in Figure 10.3. Very similar reactors are used for hydrotreating, isomerization, and hydro-cracking.

The reactors have an internal refractory lining which is provided to insulate the shell from the high reaction temperatures and thus reduce the required metal thickness. Metal parts exposed to the high temperature hydrogen atmosphere are constructed from steel containing at least 5% chromium and 0.5% molybdenum to resist hydrogen embrittlement. Proper distribution of the inlet vapor is necessary to make maximum use of the available catalyst volume. Some reactor designs provide for radial vapor flow rather than the simpler straight-through type shown here. The important feature of vapor distribution is to provide maximum contact time with minimum pressure drop.

Temperature measurement at a minimum of three elevations in the catalyst bed is considered essential to determine catalyst activity and as an aid in coke burn-off operations.

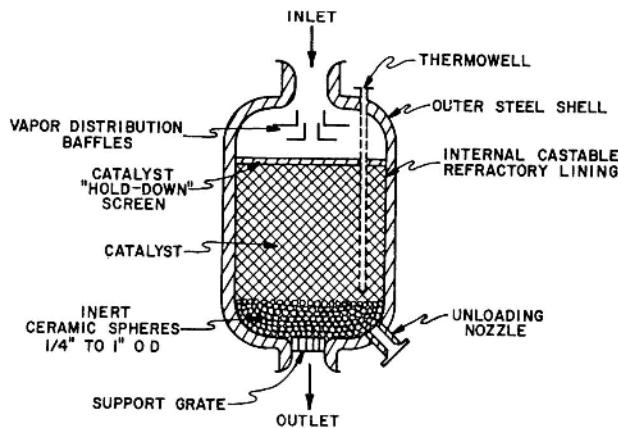


Figure 10.3 Typical fixed-bed downflow catalytic reformer.

The catalyst pellets are generally supported on a bed of ceramic spheres about 12 to 16 in. (30 to 40 cm) deep. The spheres vary in size from about 1 in. (25 mm) on the bottom to about 0.35 in. (9 mm) on the top.

10.6 YIELDS AND COSTS

Catalytic reforming yields can be estimated using Figures 10.4 through 10.7. These simplified yield correlations are approximations only and are not specific for any catalyst, operating parameters, or process configuration. Actual yields are functions of reactor pressure, catalyst type and activity, and feed quality. Capital and operating costs can be obtained from Figure 10.8 and its accompanying descriptive material (Table 10.2).

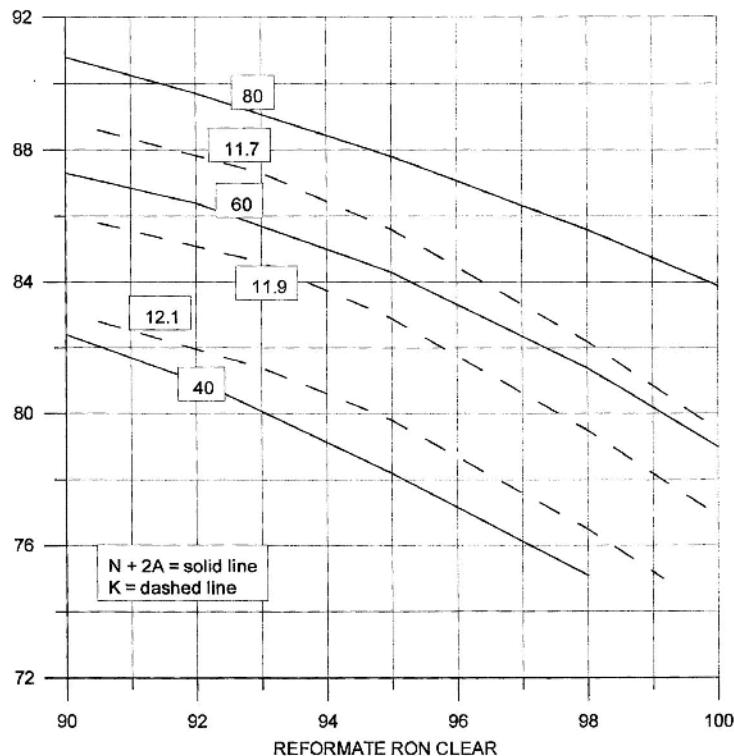


Figure 10.4 Catalytic reforming yield correlations.

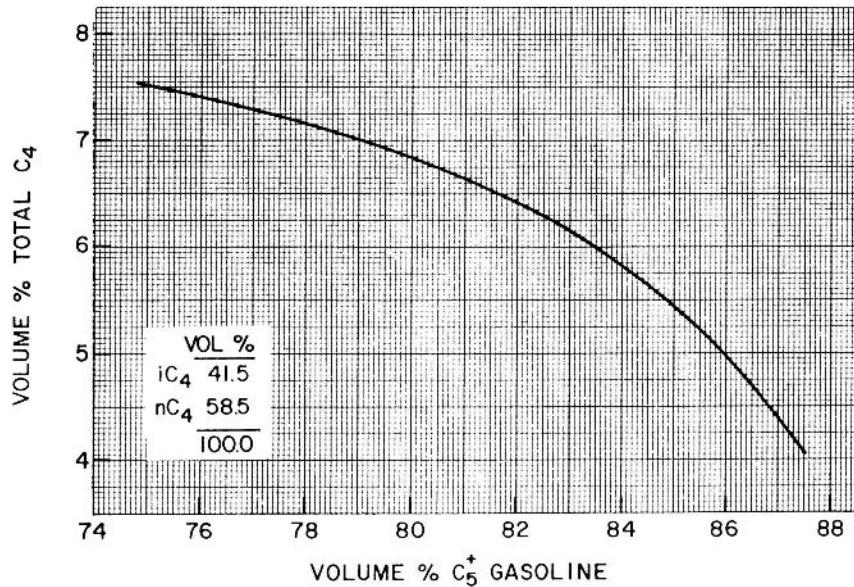


Figure 10.5 Catalytic reforming yield correlations.

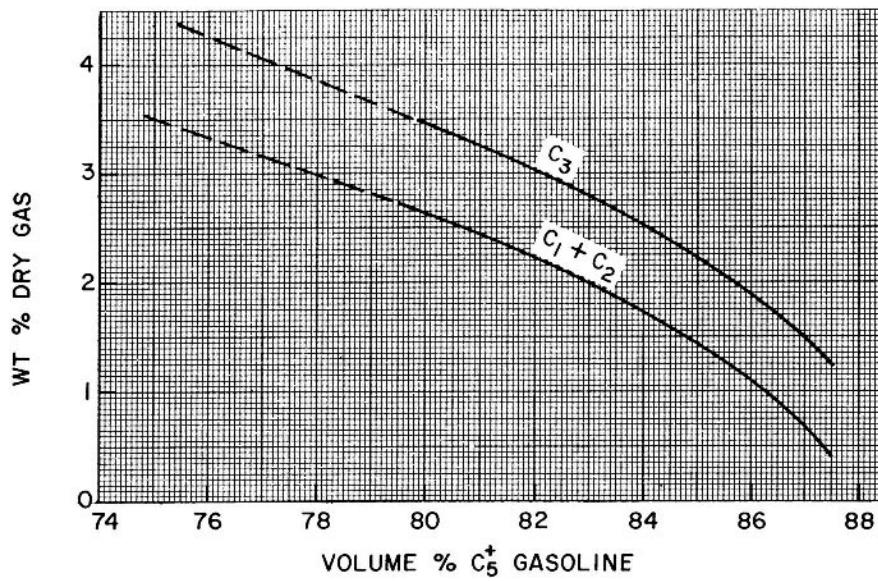


Figure 10.6 Catalytic reforming yield correlations.

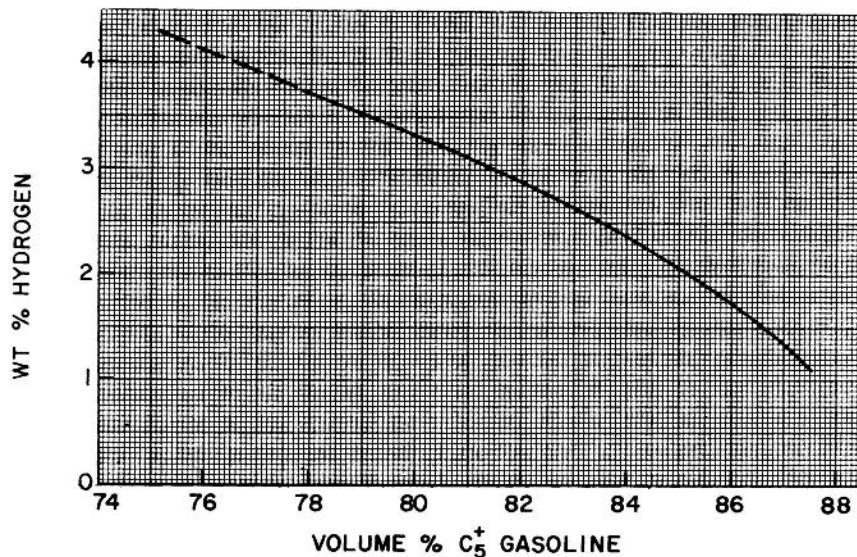


Figure 10.7 Catalytic reforming yield correlations.

10.7 ISOMERIZATION

The octane numbers of the LSR naphtha [C_5 -180°F (C_5 -82°C)] can be improved by the use of an isomerization process to convert normal paraffins to their isomers. This results in significant octane increases as n-pentane has an unleaded (clear) RON of 61.7 and isopentane has a rating of 92.3. In once-through isomerization where the normal and iso compounds come essentially to thermodynamic equilibrium, the unleaded RON of LSR naphtha can be increased from 70 to about 82–84. If the normal components are recycled, the resulting research octane numbers will be about 87–93 RONC.

Reaction temperatures of about 200–400°F (95–205°C) are preferred to higher temperatures because the equilibrium conversion to isomers is enhanced at the lower temperatures. At these relatively low temperatures a very active catalyst is necessary to provide a reasonable reaction rate. The available catalysts used for isomerization contain platinum on various bases. Some types of catalysts require the continuous addition of very small amounts of organic chlorides to maintain high catalyst activities. This is converted to hydrogen chloride in the reactor, and consequently the feed to these units must be free of water and other oxygen sources in order to avoid catalyst deactivation and potential corrosion problems. A second type of catalyst uses a molecular sieve base and is reported

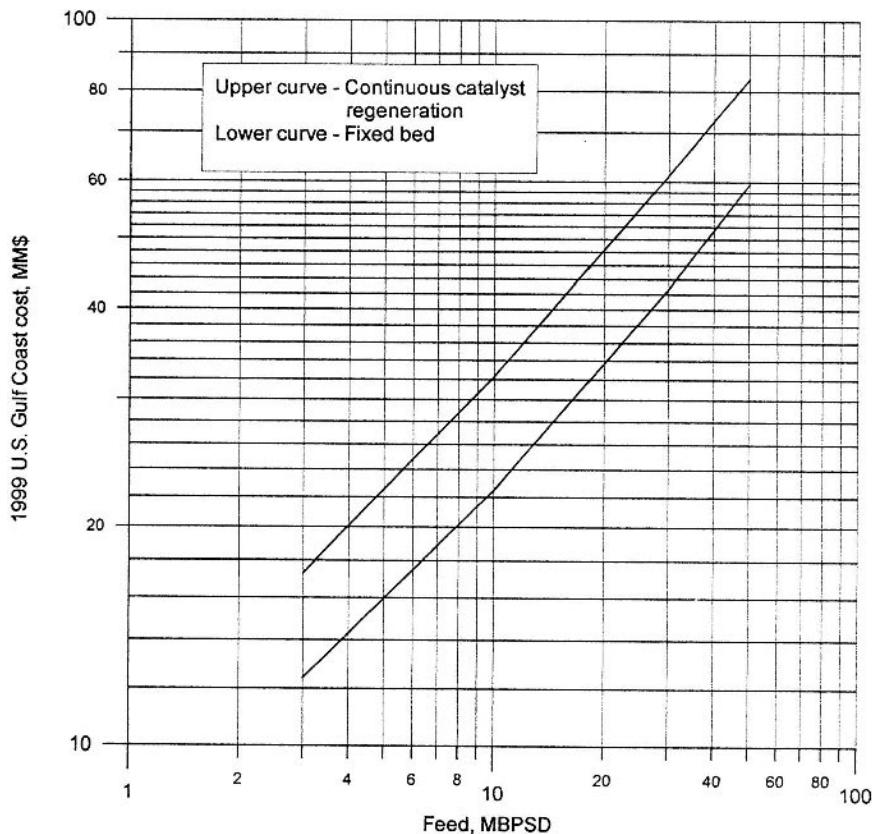


Figure 10.8 Catalytic reforming unit investment cost: 1999 U.S. Gulf Coast. (See Table 10.2.)

to tolerate feeds saturated with water at ambient temperature [8]. A third type of catalyst contains platinum supported on a novel metal oxide base. This catalyst has 150°F (83°C) higher activity than conventional zeolic isomerization catalysts and can be regenerated. Catalyst life is usually three years or more with all of these catalysts.

An atmosphere of hydrogen is used to minimize carbon deposits on the catalyst but hydrogen consumption is negligible [7].

The composition of the reactor products can closely approach chemical equilibrium. The actual product distribution is dependent upon the type and age of the catalyst, the space velocity, and the reactor temperature. The pentane fraction of the reactor product is about 75 to 80 wt% iso-pentane, and the hexane fraction is about 86 to 90 wt% hexane isomers [4].

Table 10.2 Catalytic Reforming Unit Cost Data*Costs included*

1. All battery limit facilities required for producing 102 RON unleaded reformate from a HSR naphtha sulfur-free feed
2. Product stabilizer
3. All necessary control and instrumentation
4. Preheat and product cooling facilities to accept feed and release products at ambient temperatures

Costs not included

1. Cooling water, steam, and power supply
2. Initial catalyst charge
3. Royalty
4. Feed fractionation or desulfurization

Catalyst charge

Initial catalyst charge cost is approximately \$200/BPD of feed.

Royalties

Running royalty is about \$0.05 to \$0.10/bbl.
Paid-up royalty is about \$50 to \$100/BPD.

Utility data (per bbl feed)

Steam, ^a lb	30
Power, kWh	3
Cooling water, gal	400
Fuel gas (LHV), MMBtu	0.3
Catalyst replacement, \$	0.10

^a With some configurations, a net steam production is realized.

Note: See Fig. 10.8.

Following is a simplified conversion summary for a typical LSR cut. The values are on a relative weight basis and do not account for the weight loss resulting from hydrocracking to molecules lighter than pentane.

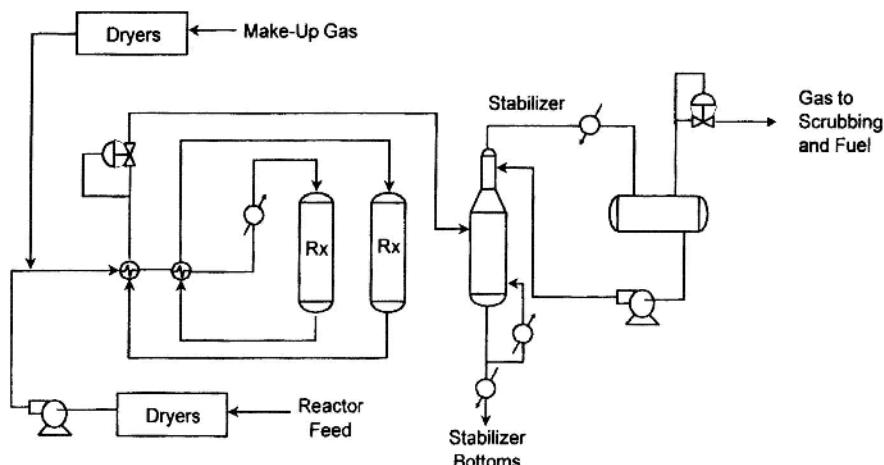
LSR component	Feed weight	Product weight	RONC (unleaded)
Isopentane	22	41	92
Normal pentane	33	12	62
2,2-Dimethylbutane	1	15	96
2,3-Dimethylbutane	2	5	84
2-Methylpentane	12	15	74
3-Methylpentane	10	7	74
Normal hexane	20	5	26
Total	100	100	

If the normal pentane in the reactor product is separated and recycled the product RON can be increased by about 3 numbers (83 to 86 RONC) [1]. If both normal pentane and normal hexane are recycled the product clear RON can be improved to about 87 to 90. Separation of the normals from the isomers can be accomplished by fractionation or by vapor phase adsorption of the normals on a molecular sieve bed. The adsorption process is well developed in several large units [8].

Some hydrocracking occurs during the reactions resulting in a loss of gasoline and the production of light gas. The amount of gas formed varies with the catalyst type and age and is sometimes a significant economic factor. The light gas produced is typically in the range of 1.0 to 4.0 wt% of the hydrocarbon feed to the reactor. For preliminary estimates the composition of the gas produced can be assumed to be 95 wt% methane and 5 wt% ethane.

For refineries that do not have hydrocracking facilities to supply isobutane for alkylation unit feed, the necessary isobutane can be made from n-butane by isomerization. The process is very similar to that of LSR gasoline isomerization but a feed deisobutanizer is used to concentrate the n-butane in the reactor charge. The reactor product is about 58 to 62 wt% isobutane.

A representative flow scheme for an isomerization unit is shown in Figure 10.9. Typical operating conditions are [4,7]:



H-O-T = Hydrogen-Once-Through

Figure 10.9 H-O-T Penex™ isomerization unit. (Reprinted courtesy of UOP LLC.)

Reactor temperature	200–400°F	95–205°C
Pressure	250–500 psig	1725–3450 kP
Hydrogen/HC mole ratio	0.05:1	
Single-pass LHSV	1–2 v/hr/v	
Liquid product yield	>98 wt%	

10.8 CAPITAL AND OPERATING COSTS

The capital construction and operating costs for an isomerization unit can be estimated from Figure 10.10 and Table 10.3.

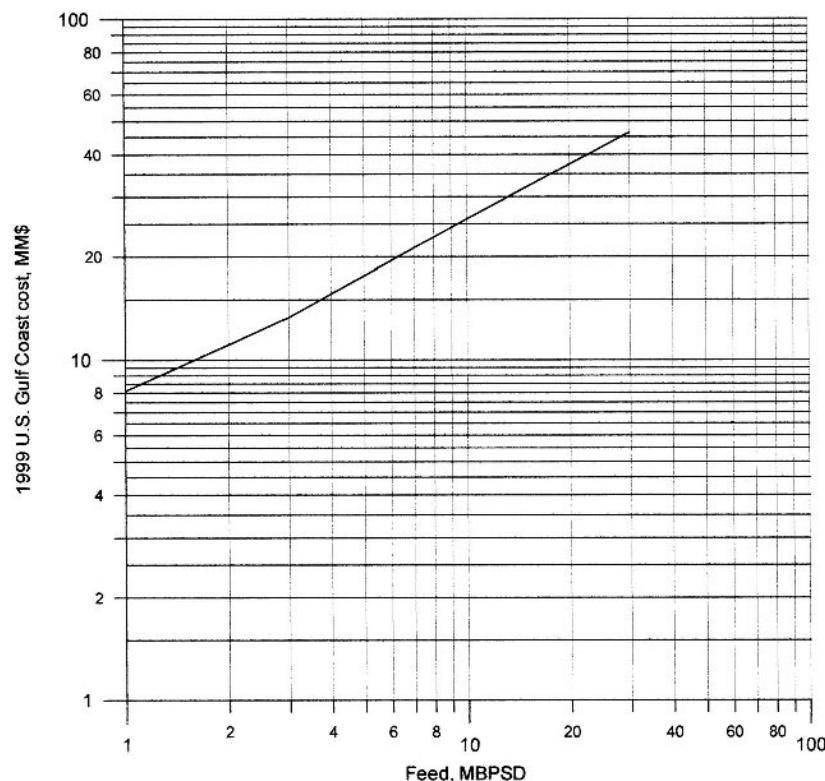


Figure 10.10 Paraffin isomerization units (platinum catalyst type) investment cost: 1999 U.S. Gulf Coast. (See Table 10.3.)

Table 10.3 Paraffin Isomerization with Platinum Catalysts Cost Data*Costs included*

1. Feed drying
2. Drying of hydrogen makeup
3. Complete preheat, reaction, and hydrogen circulation facilities
4. Product stabilization
5. Sufficient heat exchange to cool products to ambient temperatures
6. Central controls
7. Paid-up royalty

Costs not included

1. Hydrogen source
2. Cooling water, steam, and power supply
3. Feed desulfurization
4. Initial catalyst charge, about \$100/BPD of reactor feed

Royalties

Paid-up royalty is about \$90 to \$160/BPD.

Utility data (per bbl "fresh" feed)

Power, kWh	1.0
Cooling water, gal (30°F)	600–1000
Fuel (LHV), MMBtu	0.20
Catalyst replacement, \$	0.05
Hydrogen makeup, scf	40

Note: See Fig. 10.10.

10.9 ISOMERIZATION YIELDS

Yields vary with feedstock properties and operating severity. A typical product yield is given in Table 10.4 for a 13 number improvement in both RON and MON clear for a 12 psi RVP C₅–C₇ isomerate product.

Table 10.4 Isomerization Yields

Component	vol% on feed
C ₃	0.5
iC ₄	1.5
nC ₄	1.0
C ₅ –C ₇	102.0

10.10 CASE-STUDY PROBLEM: NAPHTHA HYDROTREATER, CATALYTIC REFORMER, AND ISOMERIZATION UNIT

In this case, the feed to the catalytic reformer consists of the heavy straight-run (HSR) gasoline (190 to 380°F) from the crude unit and the coker gasoline. In practice the coker gasoline would probably be separated into a C₅-180°F fraction, which would not be reformed, and a 180 to 380°F fraction which would be used as reformer feed. As sufficient information is not available to estimate the quantities and properties of these fractions, it is necessary for the purposes of this calculation to send all of the coker gasoline to the reformer. The C₅-180°F fraction will undergo little octane improvement but its gasoline quality will be helped by saturation of the olefins. The required severity of reforming is not known until after the gasoline blending calculations are made. Therefore it is necessary to assume a value for the first time through. A severity of 94 RON clear is used for this calculation. The following procedure is used:

1. Calculate the characterization factor (K_w) of the feed.
2. Determine C₅₊ gasoline volume yield from Figure 10.3.
3. Determine weight or volume yields of H₂, C₁ + C₂, C₃, iC₄, and nC₄ from Figures 10.4, 10.5, and 10.6.
4. Calculate weight yield of all product streams except C₅₊ gasoline.
5. Determine weight yield of C₅₊ gasoline by difference.
6. Calculate API gravity of C₅₊ gasoline.
7. Make sulfur and/or nitrogen balance if needed to determine H₂S and NH₃ made and net hydrogen produced.
8. Estimate utility requirements from Table 10.2.

The results are tabulated in Tables 10.5 for the hydrotreater and catalytic reformer and 10.6 for the isomerization unit. Table 10.7 gives chemical and utility requirement data for the processes.

PROBLEMS

1. Reactor pressure is an important process variable in catalytic reforming. A common reaction in reforming is the conversion of methylcyclopentane to benzene. Calculate the barrels of benzene formed from one barrel of methylcyclopentane at the following reactor outlet conditions: (a) 900°F, 600 psia, and (b) 900°F, 300 psia.

The hydrogen feed rate to the reactor is 10,000 scf/bbl of methylcyclopentane. Assume the reaction is a single ideal gas-phase reaction and thermodynamic equilibrium is obtained. The National Bureau of

Table 10.5 Hydrotreater and Catalytic Reformer Material Balance: 100,000 BPCD Alaska North Slope Crude Oil Basis (Severity, 94 ROM clear; $K_w = 11.7$)

Component	vol%	BPD	°API	(lb/hr)/BPD	lb/hr	wt% S	lb/hr S
<i>Feed</i>							
190–380°F HSR	69.3	12,500	48.5	11.47	143,380	0.1	140
Coker naphtha	30.7	5,540	54.6	11.09	61,420	0.65	400
Total	100.0	18,040			204,800		540
<i>Products</i>							
H ₂ wt%, total	1.7				3,480		
C ₁ + C ₂ wt%	1.0				2,050		
C ₃ , wt%	1.8	500		7.42	3,690		
iC ₄	2.0	360		8.22	2,960		
nC ₄	2.8	505		8.51	4,300		
C ₅ + reformate	86.5	15,610	39.7	12.06	188,320		
Total		16,975			204,800		
<i>Hydrogen^a</i>							
H ₂ S					574		540
H ₂ , net					3,446		

^a H₂S = 32.06 = 16.84 lb-mol/hr; H₂ in H₂S = (16.84)(2) = 34 lb/hr.

Table 10.6 Isomerization Unit Material Balance: 100,000 BPCD Alaska North Slope Crude Oil Basis (Severity, Once-Through)

Component	vol%	BPD	°API	(lb/hr)/BPD	lb/hr	wt% S	lb/hr S
<i>Feed</i>							
C ₅ -180°F	73.4	4,277	63.0	10.61	45,394	0.02	1
Coker light naphtha	26.6	1,551	65.0	10.51	6,303	0.41	64
Total	100.0	5,828			616,970		65
<i>Products</i>							
H ₂ S					69		65
C ₃ , wt%	0.5	29		7.39	215		
iC ₄	0.8	47		8.22	382		
nC ₄	2.2	128		8.51	1,092		
C ₅ + reformate	98.4	5,735	65.6	10.46	60,007		
Total		16,975			204,800		65

Table 10.7 Hydrotreater, Catalytic Reformer, and Isomerization Unit Chemical and Utility Requirements

Utility	Reformer and HT		Isomerization	
	Per barrel feed	Per day	Per barrel feed	Per day
Steam, Mlb	0.036	631		
Power, MkWh	0.005	88	0.001	6
CW, Mgal	0.9	15,786	0.8	4,662
Fuel, HMBtu	0.4	7,016	0.2	1,166
Catalyst, \$	0.12	2,105	0.05	291
H ₂ makeup, Mscf			0.04	233

Standards values for free energies of formation at 900°F are +66.09 kcal/g mol for methylcyclopentane and +50.78 kcal/g mol for benzene.

2. Determine the yield of n-butane and C₅+ gasoline when reforming 4500 BPD of HSR gasoline, K_w = 11.9, to a 92 clear RON.
3. A 180 to 380°F virgin naphtha stream with a mean average boiling point of 275°F and 50.2°API is reformed to a 96 RON clear gasoline blending stock. Make an overall material balance around the reformer for a 10,000 BPD feed rate.
4. Estimate the installed cost for a 6200 BPSD isomerization unit to increase the RON of a LSR naphtha by 13 numbers. Determine the utility requirements and estimate the direct operating costs per barrel of feed if two operators are required per shift at an hourly rate of \$17.37 per operator.
5. Estimate the direct operating cost per barrel of feed for an 8400 BPSD catalytic reformer upgrading an HSR naphtha to a 96 RON clear product. The 50.2°API naphtha feed has a MABP of 275°F. Assume the reformer requires two operators per shift at an hourly rate of \$17.37 per operator. Include royalty costs as a direct operating cost.
6. For problem 5, express the direct operating cost on a per barrel of C₅+ reformate basis and compare with the cost of producing a barrel of 90 RON clear reformate from the same feed.
7. For the reforming units in problems 5 and 6, what is the single largest operating expense per barrel? What percentage of the cost is this?
8. Draw a flow diagram for an isomerization unit which increases by 20 research numbers the octane of the feed consisting of 45 vol% n-pentane and 55 vol% n-hexane.

9. Calculate the product gas composition of a reformer operated to maximize aromatics production with the following feedstock of saturated hydrocarbons:

	vol%
C ₆ H ₁₂	10.1
C ₆ H ₁₄	18.9
C ₇ H ₁₄	12.8
C ₇ H ₁₆	21.2
C ₈ H ₁₆	17.7
C ₈ H ₁₈	19.3
Total	100.0

10. Calculate the total operating costs per gallon of reformate for producing (a) a 92 clear RON product from 10,000 BPCD of the HSR naphtha from the assigned crude oil, and (b) a 98 clear RON product. Use heating value of comparable products to obtain values of gases produced.

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11

Alkylation and Polymerization

The addition of an alkyl group to any compound is an alkylation reaction but in petroleum refining terminology the term alkylation is used for the reaction of low molecular weight olefins with an isoparaffin to form higher molecular weight isoparaffins [11]. Although this reaction is simply the reverse of cracking, the belief that paraffin hydrocarbons are chemically inert delayed its discovery until about 1935 [8]. The need for high-octane aviation fuels during World War II acted as a stimulus to the development of the alkylation process for production of isoparaffinic gasolines of high octane number.

Although alkylation can take place at high temperatures and pressures without catalysts, the only processes of commercial importance involve low-temperature alkylation conducted in the presence of either sulfuric or hydrofluoric acid. The reactions occurring in both processes are complex and the product has a rather wide boiling range. By proper choice of operating conditions, most of the product can be made to fall within the gasoline boiling range with motor octane numbers from 88 to 94 [8] and research octane numbers from 94 to 99.

11.1 ALKYLATION REACTIONS

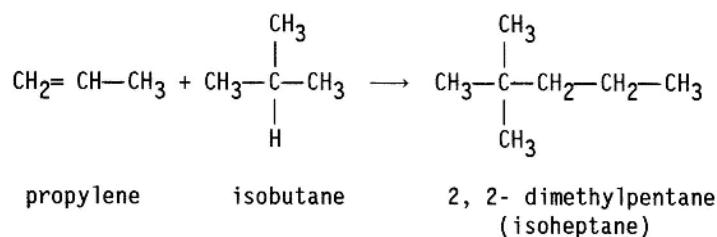
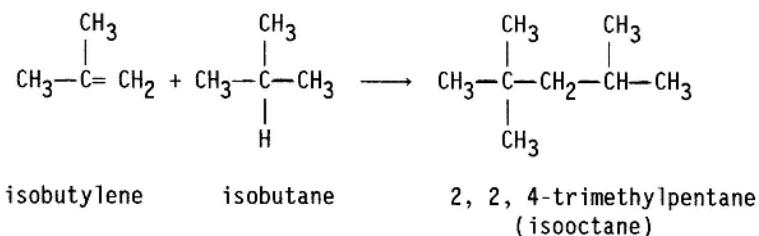
In alkylation processes using hydrofluoric or sulfuric acids as catalysts, only isoparaffins with tertiary carbon atoms, such as isobutane or isopentane, react with the olefins. In practice only isobutane is used because isopentane has a sufficiently high octane number and low vapor pressure to allow it to be effectively blended directly into finished gasolines.

The process using sulfuric acid as a catalyst is much more sensitive to temperature than the hydrofluoric acid process. With sulfuric acid it is necessary to carry out the reactions at 40 to 70°F (5 to 21°C) or lower, to minimize oxidation reduction reactions which result in the formation of tars and the evolution of sulfur dioxide. When anhydrous hydrofluoric acid is the catalyst, the temperature is usually limited to 100°F (38°C) or below [8]. In both processes, the volume

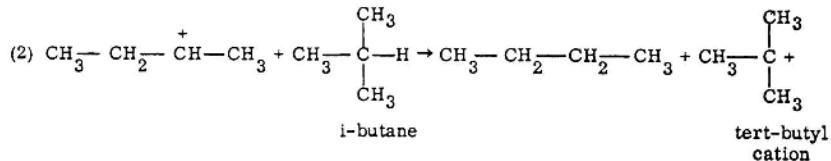
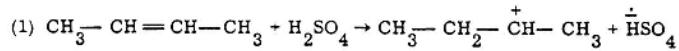
of acid employed is about equal to that of the liquid hydrocarbon charge and sufficient pressure is maintained on the system to keep the hydrocarbons and acid in the liquid state. High isoparaffin/olefin ratios (4:1 to 15:1) are used to minimize polymerization and to increase product octane. Efficient agitation to promote contact between the acid and hydrocarbon phases is essential to high product quality and yields. Contact times from 10 to 40 minutes are in general use. The yield, volatility, and octane number of the product is regulated by adjusting the temperature, acid/hydrocarbon ratio, and isoparaffin/olefin ratio. At the same operating conditions, the products from the hydrofluoric and sulfuric acid alkylation process are quite similar [3,4]. In practice, however, the plants are operated at different conditions and the products are somewhat different. The effects of variables will be discussed for each process later, but for both processes the more important variables are:

1. Reaction temperature
2. Acid strength
3. Isobutane concentration
4. Olefin space velocity

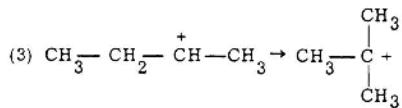
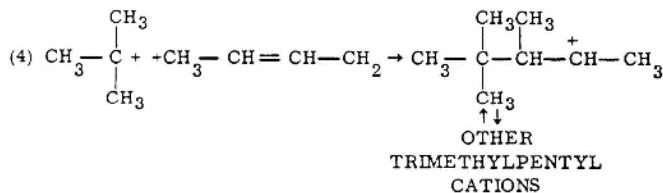
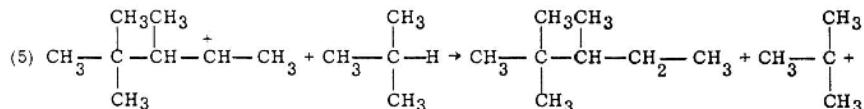
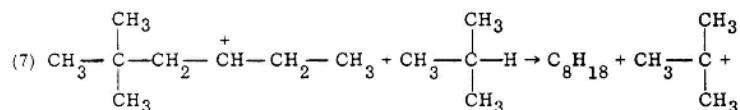
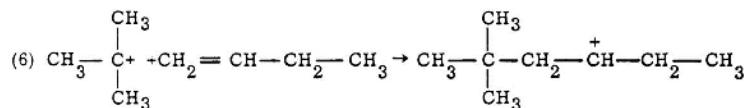
The principal reactions which occur in alkylation are the combinations of olefins with isoparaffins as follows:



Another significant reaction in propylene alkylation is the combination of propylene with isobutane to form propane plus isobutylene. The isobutylene then reacts with more isobutane to form 2,2,4-trimethylpentane (isoctane). The first step involving the formation of propane is referred to as a hydrogen transfer reaction.

Initiation to form tert-butyl cation:

sec-butyl ion may isomerize instead of forming cation as in reaction (2):

Reaction of tert-butyl cations with 2-butene:Reaction of trimethylpentyl cations:Formation of dimethylhexanes:

The formation of a new tert-butyl cation continues the chain.

Figure 11.1 Alkylation chemistry.

Research on catalyst modifiers is being conducted to promote this step since it produces a higher octane alkylate than is obtained by formation of isoheptanes.

A number of theories have been advanced to explain the mechanisms of catalytic alkylation and these are discussed in detail by Gruse and Stevens [8]. The one most widely accepted involves the formation of carbonium ions by transfer of protons from the acid catalyst to olefin molecules, followed by combination with isobutane to produce tertiary-butyl cations. The tertiary-butyl ion reacts with 2-butene to form C₈ carbonium ions capable of reacting with isobutane to form C₈ paraffins and tertiary-butyl ions. These tertiary-butyl ions then react with other 2-butene molecules to continue the chain. Figure 11.1 illustrates the above sequence using sulfuric acid, 2-butene, and isobutane as the example reaction. The alkylation reaction is highly exothermic, with the liberation of 124,000 to 140,000 Btu per barrel of isobutane reacting [13].

11.2 PROCESS VARIABLES

The most important process variables are reaction temperature, acid strength, isobutane concentration, and olefin space velocity. Changes in these variables affect both product quality and yield.

Reaction temperature has a greater effect in sulfuric acid processes than in those using hydrofluoric acid. Low temperatures mean higher quality and the effect of changing sulfuric acid reactor temperature from 25 to 55°F (−4 to 13°C) is to decrease product octane from one to three numbers depending upon the efficiency of mixing in the reactor. In hydrofluoric acid alkylation, increasing the reactor temperature from 60 to 125°F (16 to 52°C) degrades the alkylate quality about three octane numbers [16].

In sulfuric acid alkylation, low temperatures cause the acid viscosity to become so great that good mixing of the reactants and subsequent separation of the emulsion is difficult. At temperatures above 70°F (21°C), polymerization of the olefins becomes significant and yields are decreased. For these reasons the normal sulfuric acid reactor temperature is from 40 to 50°F (5 to 10°C) with a maximum of 70°F (21°C) and a minimum of 30°F (−1°C).

For hydrofluoric acid alkylation, temperature is less significant and reactor temperatures are usually in the range of 70 to 100°F (21 to 38°C).

Acid strength has varying effects on alkylate quality depending on the effectiveness of reactor mixing and the water content of the acid. In sulfuric acid alkylation, the best quality and highest yields are obtained with acid strengths of 93 to 95% by weight of acid, 1 to 2% water, and the remainder hydrocarbon diluents. The water concentration in the acid lowers its catalytic activity about 3 to 5 times as much as hydrocarbon diluents, thus an 88% acid containing 5% water is a much less effective catalyst than the same strength acid containing 2%

water. The poorer the mixing in a reactor, the higher the acid strength necessary to keep acid dilution down [16]. Increasing acid strength from 89 to 93% by weight increases alkylate quality by one to two octane numbers.

In hydrofluoric acid alkylation the highest octane number alkylate is attained in the 86 to 90% by weight acidity range. Commercial operations usually have acid concentrations between 83 and 92% hydrofluoric acid and contain less than 1% water.

Isobutane concentration is generally expressed in terms of isobutane/olefin ratio. High isobutane/olefin ratios increase octane number and yield, and reduce side reactions and acid consumption. In industrial practice the isobutane/olefin ratio on reactor charge varies from 5:1 to 15:1. In reactors employing internal circulation to augment the reactor feed ratio, internal ratios from 100:1 to 1000:1 are realized. Olefin space velocity is defined as the volume of olefin charged per hour divided by the volume of acid in the reactor. Lowering the olefin space velocity reduces the amount of high-boiling hydrocarbons produced, increases the product octane, and lowers acid consumption. Olefin space velocity is one way of expressing reaction time; another is by using contact time. Contact time is defined as the residence time of the fresh feed and externally recycled isobutane in the reactor. Contact time for hydrofluoric acid alkylation ranges from 5 to 25 minutes and for sulfuric acid alkylation from 5 to 40 minutes [9]. Although the relationship is only approximate, Mrstik, Smith, and Pinkerton [13] developed a correlating factor, F, which is useful in predicting trends in alkylate quality where operating variables are changed.

$$F = \frac{I_E(I/O)_F}{100(SV)_O}$$

where

I_E = isobutane in reactor effluent, liquid volume %

$(I/O)_F$ = volumetric isobutane/olefin ratio in feed

$(SV)_O$ = olefin space velocity, v/hr/v

The higher the value of F, the better the alkylate quality. Normal values of F range from 10 to 40.

11.3 ALKYLATION FEEDSTOCKS

Olefins and isobutane are used as alkylation unit feedstocks. The chief sources of olefins are catalytic cracking and coking operations. Butenes and propene are the most common olefins used, but pentenes (amylanes) are included in some

cases. Some refineries include pentenes in alkylation unit feed to lower the FCC gasoline vapor pressure and reduce the bromine number in the final gasoline blend. Alkylation of pentenes is also considered as a way to reduce the C₅ olefin content of final gasoline blends and reduce its effects on ozone reduction and visual pollution in the atmosphere. Olefins can be produced by dehydrogenation of paraffins, and isobutane is cracked commercially to provide alkylation unit feed. Hydrocrackers and catalytic crackers produce a great deal of the isobutane used in alkylation but it is also obtained from catalytic reformers, crude distillation, and natural gas processing. In some cases, normal butane is isomerized to produce additional isobutane for alkylation unit feed.

11.4 ALKYLATION PRODUCTS

In addition to the alkylate stream, the products leaving the alkylation unit include the propane and normal butane that enter with the saturated and unsaturated feed streams as well as a small quantity of tar produced by polymerization reactions.

The product streams leaving an alkylation unit are:

1. LPG grade propane liquid
2. Normal butane liquid
3. C₅+ alkylate
4. Tar

Table 11.1 Range of Operating Variables in Alkylation

	HF	H ₂ SO ₄
Isobutane concentrations		
vol% in reaction zone	30–80	40–80
External ratio to olefins	3–12	3–12
Internal ratio to olefins	—	50–1000
Olefin concentration		
Total HC contact time, min	8–20	20–30
Olefin space velocity, v/hr/v	—	0.1–0.6
Reactor temperature		
°F	60–115	35–60
°C	16–46	2–16
Reactor acid conc., wt%	80–95	88–95
Acid in emulsion, vol%	25–80	40–60

Source: Ref. 18.

Table 11.2 Theoretical Yields and Isobutane Requirements Based on Olefin Reacting

	Alkylate vol%	Isobutane vol%
Ethylene	188	139
Propene	181	128
Butenes (mixed)	172	112
Pentenes (mixed)	165	96

Source: Ref. 22.

Only about 0.1% by volume of olefin feed is converted into tar. This is not truly a tar but a thick dark brown oil containing complex mixtures of conjugated cyclopentadienes with side chains [22].

Typical alkylation operating conditions are shown in Table 11.1 and theoretical yields of alkylates and isobutane requirements based on olefin reacted are given in Table 11.2.

11.5 CATALYSTS

Concentrated sulfuric and hydrofluoric acids are the only catalysts used commercially today for the production of high octane alkylate gasoline but other catalysts are used to produce ethylbenzene, cumene, and long-chain (C_{12} to C_{16}) alkylated benzenes [22].

As discussed in Section 11.1, the desirable reactions are the formation of C_8 carbonium ions and the subsequent formation of alkylate. The main undesirable reaction is polymerization of olefins. Only strong acids can catalyze the alkylation reaction but weaker acids can cause polymerization to take place. Therefore, the acid strengths must be kept above 88% by weight H_2SO_4 or HF in order to prevent excessive polymerization. Sulfuric acid containing free SO_3 also causes undesired side reactions and concentrations greater than 99.3% H_2SO_4 are not generally used [22].

Isobutane is soluble in the acid phase only to the extent of about 0.1% by weight in sulfuric acid and about 3% in hydrofluoric acid. Olefins are more soluble in the acid phase and a slight amount of polymerization of the olefins is desirable as the polymerization products dissolve in the acid and increase the solubility of isobutane in the acid phase.

If the concentration of the acid becomes less than 88%, some of the acid must be removed and replaced with stronger acid. In hydrofluoric acid units, the

acid removed is redistilled and the polymerization products removed as a thick, dark “acid soluble oil” (ASO). The concentrated HF is recycled in the unit and the net consumption is about 0.3 lb per barrel of alkylate produced [20]. Unit inventory of hydrofluoric acid is about 25–40 lb acid per BPD of feed [15].

The sulfuric acid removed usually is regenerated in a sulfuric acid plant which is generally not a part of the alkylation unit. The acid consumption typically ranges from 13 to 30 lb per barrel of alkylate produced. Makeup acid is usually 98.5 to 99.3 wt% H_2SO_4 .

11.6 HYDROFLUORIC ACID PROCESSES [10,17,18]

There are two commercial alkylation processes using hydrofluoric acid as the catalyst. They are designed and licensed by Phillips Petroleum Company and UOP. Typical operating conditions are given in Tables 11.3 and 11.4.

The basic flow scheme is the same for both the Phillips and the UOP processes (Fig. 11.2). See also Photo 12, Appendix E.

Both the olefin and isobutane feeds are dehydrated by passing the feedstocks through a solid bed desiccant unit. Good dehydration is essential to minimize potential corrosion of process equipment which results from addition of water to hydrofluoric acid.

After dehydration the olefin and isobutane feeds are mixed with hydrofluoric acid at sufficient pressure to maintain all components in the liquid phase. The reaction mixture is allowed to settle into two liquid layers. The acid has a higher density than the hydrocarbon mixture and is withdrawn from the bottom of the settler and passed through a cooler to remove the heat gained from the exothermic reaction. The acid is then recycled and mixed with more fresh feed, thus completing the acid circuit.

A small slip-stream of acid is withdrawn from the settler and fed to an acid rerun column to remove dissolved water and polymerized hydrocarbons. The acid rerun column contains about five trays and operates at 150 psig (1034 kPa) [3].

Table 11.3 HF Alkylation Yields, Product Octanes, and Isobutane Requirements

	vol/vol olefin		Clear octane no.	
	Isobutane	Alkylate	Research	Motor
Propylene	1.33	1.77	93	91
Butylenes	1.16	1.75	96	94

Table 11.4 HF Alkylate Properties

API Gravity, °API	71.4	
RVP, psi (kPa)	4.5	(31)
ASTM distillation		
	°F	°C
IBP	110	43
5%	155	68
10%	172	78
20%	190	88
50%	217	103
70%	222	105
90%	245	119
EP	370	188

The overhead product from the rerun column is clear hydrofluoric acid which is condensed and returned to the system.

The bottom product from the rerun column is a mixture of tar and an HF–water azeotrope. These components are separated in a tar settler (not shown on the flow diagram). The tar is used for fuel and the HF–water mixture is neutralized with lime or caustic. This rerun operation is necessary to maintain the activity of the hydrofluoric acid catalyst.

The hydrocarbon layer removed from the top of the acid settler is a mixture of propane, isobutane, normal butane, and alkylate along with small amounts of hydrofluoric acid. These components are separated by fractionation and the isobutane is recycled to the feed. Propane and normal butane products are passed through caustic treaters to remove trace quantities and hydrofluoric acid.

Although the flow sheet (Fig. 11.2) shows the fractionation of propane, isobutane, normal butane, and alkylate to require three separate fractionators, many alkylation plants have a single tower where propane is taken off overhead, a partially purified isobutane recycle is withdrawn as a liquid several trays above the feed tray, a normal butane product is taken off as a vapor several trays below the feed tray and the alkylate is removed from the bottom.

The design of the acid settler–cooler–reactor section is critical to good conversion in a hydrofluoric acid alkylation system. Different reactor system designs have been made over the years by both UOP and Phillips. Many of the reactor systems designed by UOP are similar to a horizontal shell and tube heat exchanger with cooling water flowing inside the tubes to maintain the reaction temperatures at the desired level. Good mixing is attained in the reactor by using a recirculating pump to force the mixture through the reactor at a rate about eight to ten times the mixed hydrocarbon feed rate to the reactor.

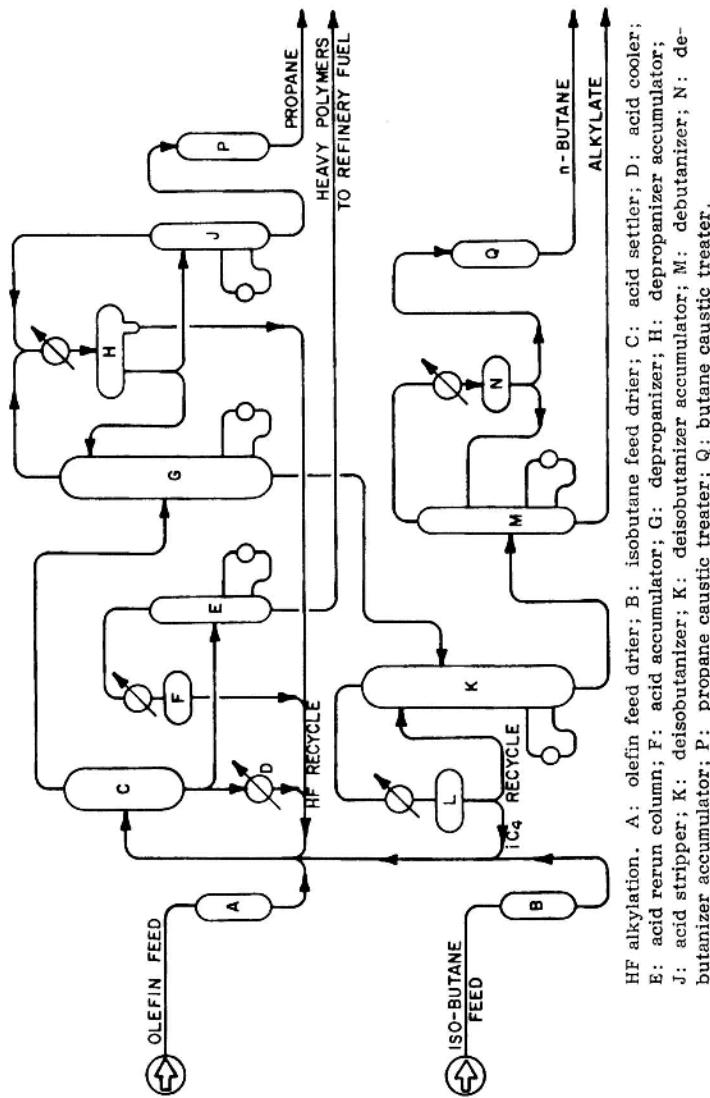


Figure 11.2 Phillips hydrofluoric acid alkylation unit.

HF alkylation. A: olefin feed drier; B: iso-butane feed drier; C: acid rerun column; D: acid cooler; E: acid stripper; F: depropanizer; G: deisobutanizer accumulator; H: debutanizer; J: debutanizer accumulator; K: deisobutanizer; L: debutanizer; M: debutanizer; N: debutanizer; P: depropanizer; Q: butane caustic treater.

Reactor systems designed by Phillips usually have been similar to that illustrated in Figure 11.3. Acid circulation in this system is by gravity differential and thus a relatively expensive acid circulation pump is not necessary.

In portions of the process system where it is possible to have HF–water mixtures, the process equipment is fabricated from Monel metal or Monel-clad steel. The other parts of the system are carbon steel.

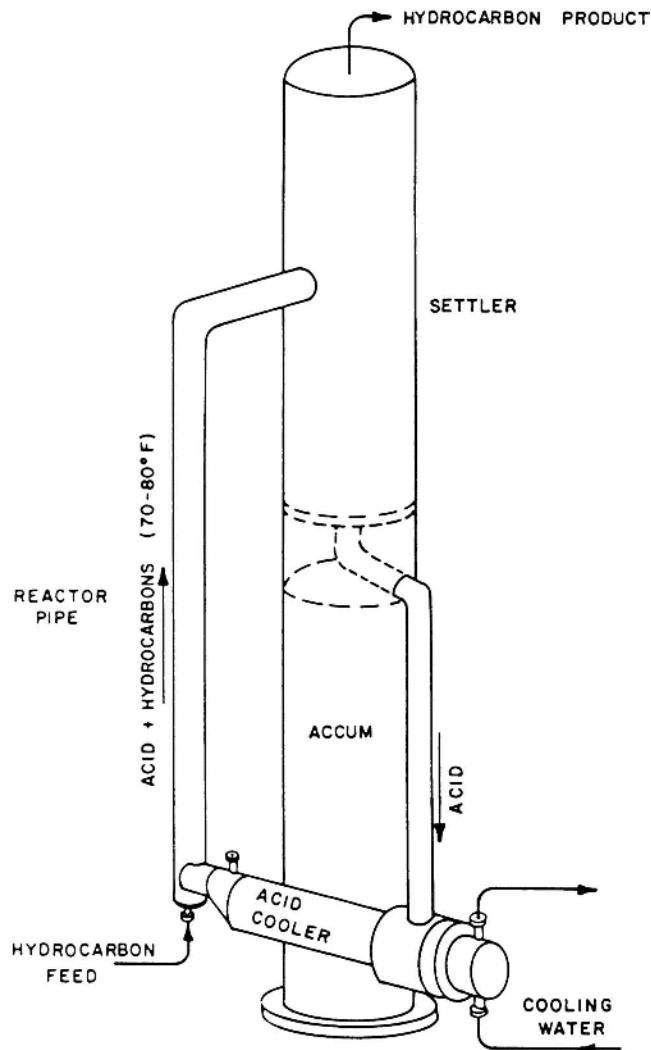


Figure 11.3 Phillips HF reactor.

Special precautions are taken to protect maintenance and operating personnel from injury by accidental contact with acid. These precautions include special seals on acid-containing equipment such as pumps and valve stems; rubber safety jackets, pants, gloves, and boots which must be worn by personnel entering an acid area; safety eyeglasses; caustic tubs for washing all hand tools; safety showers; special acid drain systems; and many others.

Careful attention to engineering design details and extensive operator training combined with the above precautions are necessary to provide safe operations for hydrofluoric acid alkylation units.

11.7 SULFURIC ACID ALKYLATION PROCESSES

The major alkylation processes using sulfuric acid as a catalyst are the autorefrigeration process, licensed by Exxon Research and Engineering (similar to a process previously licensed by the M. W. Kellogg Company), and the effluent refrigeration process, licensed by Stratford Engineering Corporation. There are also some older units using time-tank reactors but no new units of this type have been constructed recently.

The major differences between the autorefrigeration and effluent refrigeration processes are in the reactor designs and the point in the process at which propane and isobutane are evaporated to induce cooling and provide the process refrigeration required. The process flow diagram for the autorefrigeration process is shown in Figure 11.4.

The autorefrigeration process uses a multistage cascade reactor with mixers in each stage to emulsify the hydrocarbon–acid mixture. Olefin feed or a mixture of olefin feed and isobutane feed is introduced into the mixing compartments and enough mixing energy is introduced to obtain sufficient contacting of the acid catalyst with the hydrocarbon reactants to obtain good reaction selectivity. The reaction is held at a pressure of approximately 10 psig (69 kPag) in order to maintain the temperature at about 40°F (5°C). In the Stratco, or similar type of reactor system, pressure is kept high enough [45–60 psig (310–420 kPag)] to prevent vaporization of the hydrocarbons [12]. In the Exxon process, acid and isobutane enter the first stage of the reactor and pass in series through the remaining stages. The olefin hydrocarbon feed is split and injected into each of the stages. Exxon mixes the olefin feed with the recycle isobutane and introduces the mixture into the individual reactor sections to be contacted with the catalyst (Photo 13, Appendix E).

The gases vaporized to remove the heats of reaction and mixing energy are compressed and liquefied. A portion of this liquid is vaporized in an economizer to cool the olefin hydrocarbon feed before it is sent to the reactor. The vapors are returned for recompression. The remainder of the liquefied hydrocar-

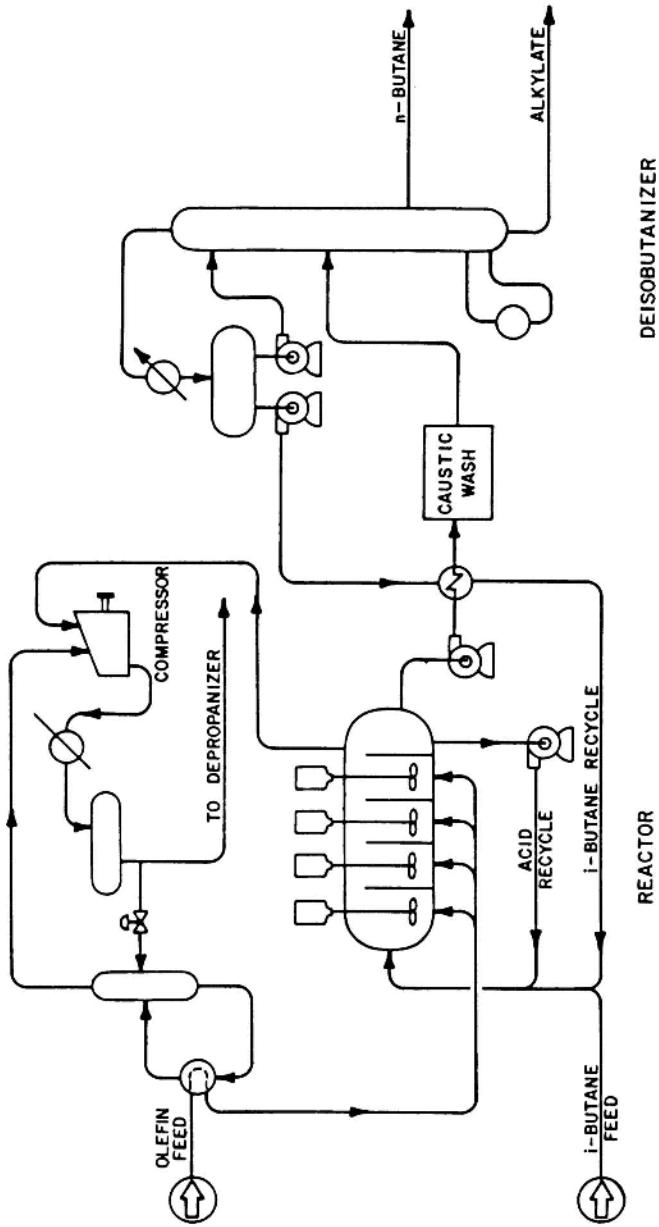


Figure 11.4 Autorefrigeration sulfuric acid alkylation unit.

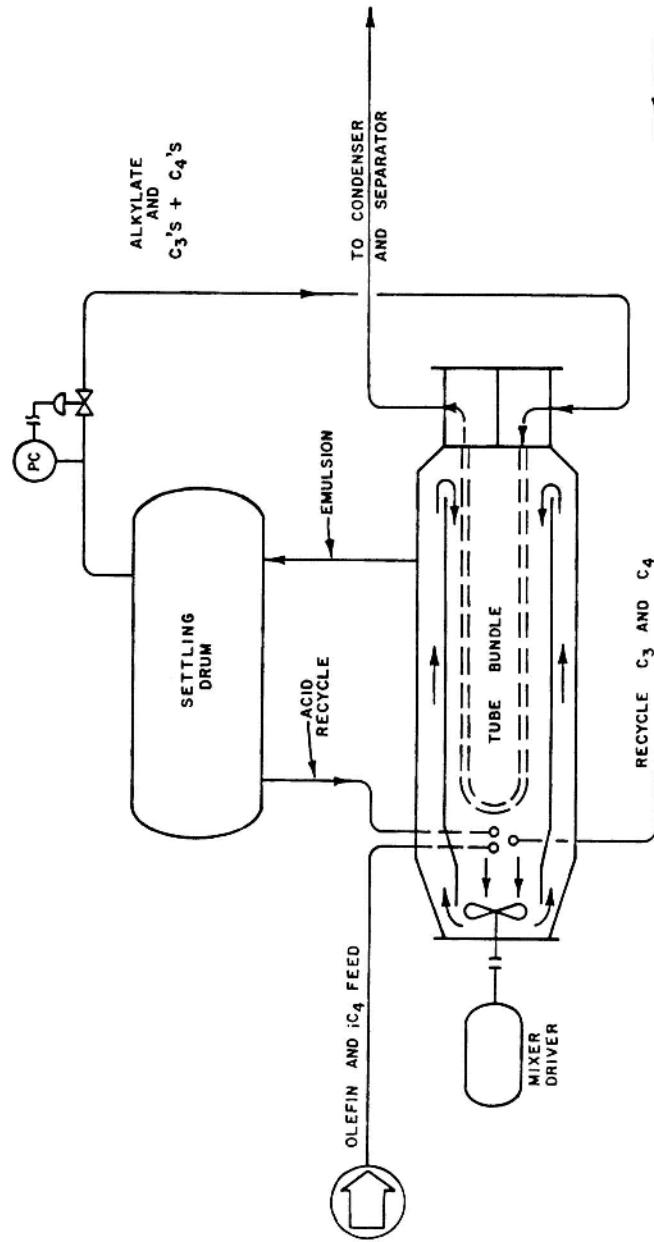


Figure 11.5 Stratco contactor.

bon is sent to a depropanizer column for removal of the excess propane which accumulates in the system. The liquid isobutane from the bottom of the depropanizer is pumped to the first stage of the reactor.

The acid–hydrocarbon emulsion from the last reactor stage is separated into acid and hydrocarbon phases in a settler. The acid is removed from the system for reclamation, and the hydrocarbon phase is pumped through a caustic wash followed by a water wash (or a fresh acid wash followed by either caustic or alkaline water washes) to eliminate trace amounts of acid and then sent to a deisobutanizer [14]. The deisobutanizer separates the hydrocarbon feed stream into isobutane (which is returned to the reactor), n-butane, and alkylate product.

The effluent refrigeration process (Stratco) uses a single-stage reactor in which the temperature is maintained by cooling coils (Fig. 11.5). The reactor contains an impeller that emulsifies the acid–hydrocarbon mixture and recirculates it in the reactor. Average residence time in the reactor is on the order of 20 to 25 minutes.

Emulsion removed from the reactor is sent to a settler for phase separation. The acid is recirculated and the pressure of the hydrocarbon phase is lowered to flash vaporize a portion of the stream and reduce the liquid temperature to about 30°F (-1°C) [2]. The cold liquid is used as coolant in the reactor tube bundle.

The flashed gases are compressed and liquefied, then sent to the depropanizer where LPG grade propane and recycle isobutane are separated. The hydrocarbon liquid from the reactor tube bundle is separated into isobutane, n-butane, and alkylate streams in the deisobutanizer column. The isobutane is recycled and n-butane and alkylate are product streams.

A separate distillation column can be used to separate the n-butane from the mixture or it can be removed as a sidestream from the deisobutanizing column. The choice is a matter of economics because including a separate column to remove the n-butane increases the capital and operating costs. Separating n-butane as a sidestream from the deisobutanizing can be restricted because the pentane content is usually too high to meet butane sales specifications. The side-stream n-butane can be used for gasoline blending [12].

Typical product yields and qualities are:

Item	Propylene	Butylene	Pentylene
True alkylate, LV% on olefin	171–178	170–178	197–220
iC4 consumed, LV% on olefin	119–132	110–117	96–133
Acid consumed (98.5 wt%), lb/bbl TA	34–42	13–25	25–42
RVP, psi	3.8	2.6	4.0
MONC	88–90	92–94	88–93
RONC	89–92	94–98	90–92

Source: Exxon Research and Engineering Co. and Stratco, Inc.

11.8 COMPARISON OF PROCESSES

The most desirable alkylation process for a given refinery is governed by economics. In particular the location of the refinery with respect to acid supply and disposal is very important. If the refinery is at a distance from either sulfuric acid suppliers or purchasers of spent sulfuric acid, the cost of transportation of fresh acid and/or the cost of disposing of the large quantities of spent acid can render the use of sulfuric acid economically unattractive. Only a small amount of makeup hydrofluoric acid is required for the HF process, as facilities are provided to regenerate the spent hydrofluoric acid. As a result, the cost of transporting hydrofluoric acid from a remote supplier is not a major cost. L. F. Albright, in a series of articles on alkylation processes, summarized the comparison of the processes [1–5]. The following discussion highlights the main issues.

The important question for a refinery is which alkylation process is best for the production of the desired product. Many factors are important, including total operating expenses; initial capital costs; alkylate quality; flexibility of operation; reactants available; yields and conversion of reactants; maintenance problems; safety; experience with a given process; and patents, licensing arrangements, and possible royalties.

Advocates of the hydrofluoric acid process argue that both capital and total operating costs are less than those of sulfuric acid processes for the following reasons:

1. Smaller and simpler reactor designs are feasible.
2. Cooling water can be used instead of refrigeration.
3. Smaller settling devices are needed for emulsions.
4. Essentially complete regeneration of the hydrofluoric acid catalyst occurs. Hence, hydrofluoric acid consumption and costs are very low. Disposal of spent acid is not necessary.
5. There is increased flexibility of operation relative to temperature, external ratio of isobutane to olefin, etc.
6. There is decreased need for turbulence or agitation when acid and hydrocarbon streams are combined.

Advocates of sulfuric acid processes counter the above arguments for hydrofluoric acid processes with the following:

1. Additional equipment is needed for the hydrofluoric acid process to recover or neutralize the hydrofluoric acid in various streams. Such equipment includes the hydrofluoric acid stripper tower, hydrofluoric acid regeneration tower, and neutralization facilities for the several product streams. With sulfuric acid, the entire effluent hydrocarbon stream is neutralized.

2. Equipment is required to dry the feed streams to a few ppm water in hydrofluoric acid processes. Drying is beneficial but typically not required in sulfuric acid processes. Normally only feed coalesers are used to remove the free water that drops out of the chilled feed.
3. Additional equipment at increased cost is required for safety in a hydrofluoric acid unit. In some hydrofluoric acid plants, a closed cooling water system is required as a safety measure in the event of hydrofluoric acid leakage into the system. Maintenance costs and the amount of safety equipment in hydrofluoric acid processes are greater.
4. Capital costs for hydrofluoric acid processes are slightly more than sulfuric acid processes when the cost of hydrofluoric acid mitigation equipment is included.
5. Isobutane in hydrofluoric acid processes is not fully used for production of alkylate, since self-alkylation occurs to a higher extent when hydrofluoric acid is used as a catalyst.
6. There are greater limitations on obtaining alkylates with high octane numbers with hydrofluoric acid processes. This is particularly true if isobutylene is removed from the feed by an upstream MTBE or ETBE unit.
7. Safety and environmental restrictions limit the use of hydrofluoric systems in highly populated areas [23].

11.9 ALKYLATION YIELDS AND COSTS

Typical alkylation yields based on percent of olefin in fresh feed are given in Table 11.5. These do not take into account effects of temperature and are based on isobutane olefin ratios of 10:1 for propylene, 6:1 for butylenes, and 10:1 for amylenes.

Cost curves for construction of alkylation units are shown in Figure 11.6. The costs are average costs and include the items given in Table 11.6. Power and chemical consumption are also given in Table 11.6.

11.10 POLYMERIZATION

Propene and butenes can be polymerized to form a high-octane product boiling in the gasoline boiling range. The product is an olefin having unleaded octane numbers of 97 RON and 83 MON. The polymerization process was widely used in the 1930s and 1940s to convert low-boiling olefins into gasoline blending stocks but was supplanted by the alkylation process after World War II. The mandated reduction in use of lead in gasoline and the increasing proportion of

Table 11.5 Typical Alkylation Yields Based on Percent Olefin in Fresh Feed

	Propylene				Butylene				Amylene			
	MW	lb/gal	vol%	wt%	MW	lb/gal	vol%	wt%	MW	lb/gal	vol%	wt%
<i>Feeds</i>												
Olefin	42.0	4.38	100.00	100.00	56.0	5.00	100.00	100.00	70.1	5.46	100.00	100.00
Isobutane	58.1	4.69	160.00	171.32	124.07	58.1	4.69	120.00	112.56	108.76	58.1	4.69
Total			260.00	271.32	224.07			220.00	212.56	208.76		
<i>Products</i>												
Propane	44.0	4.26	29.80	29.05	27.70	—	—	—	—	—	—	—
n-Butane	—	—	—	—	—	58.1	4.88	12.71	12.40	12.00	—	—
Pentane	72.1	5.21	7.17	8.53	4.98	72.1	5.21	6.80	7.08	5.50	72.1	5.25
Depent rerun	112.6	5.84	159.40	212.56	79.27	112.6	5.84	151.10	176.56	88.03	110.9	5.86
alkylate											145.60	156.19
Alkyl bottoms	165.0	6.31	12.60	18.18	4.61	165	6.31	11.90	15.02	5.12	230	6.67
Tar, 20° API	360	7.78	1.70	3.00	0.35	360	7.78	0.96	1.50	0.23	360	7.78
Total			210.67	271.32	16.91			183.47	212.56	110.88		
(Total feeds)/ (total products)			1.234	1.000	1.917			1.199	1.000	1.883		
										1.158	1.000	1.668

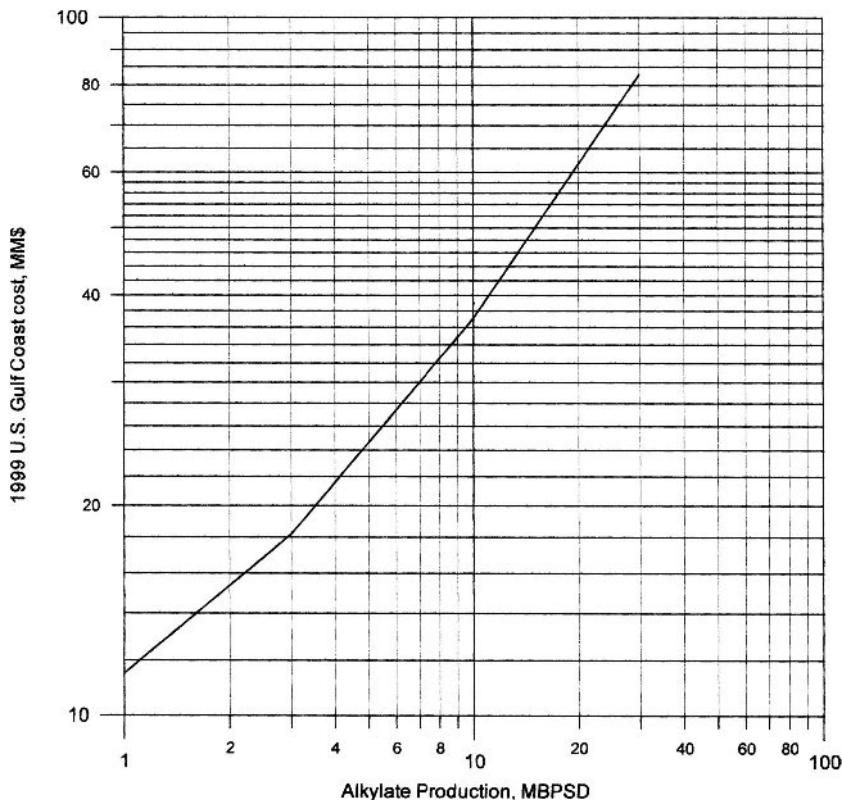


Figure 11.6 Alkylation unit investment cost: 1999 U.S. Gulf Coast. (See Table 11.6.)

the market demand for unleaded gasolines created a need for low-cost processes to produce high-octane gasoline blending components. Polymerization produces about 0.7 barrels of polymer gasoline per barrel of olefin feed as compared with about 1.5 barrels of alkylate by alkylation, and the product has a high octane sensitivity, but capital and operating costs are much lower than for alkylation. As a result, polymerization processes are being added to some refineries.

Typical polymerization reactions are shown in Table 11.7 but while iC_4H_8 reacts to give primarily diisobutylene, propene gives mostly trimers and dimers with only about 10% conversion to dimer [21].

The most widely used catalyst is phosphoric acid on an inert support. This can be in the form of phosphoric acid mixed with kieselguhr (a natural clay) or a film of liquid phosphoric acid on crushed quartz. Sulfur in the feed poisons the catalyst and any basic materials neutralize the acid and increase catalyst con-

Table 11.6 Alkylation Unit Cost Data*Costs included*

1. All facilities required for producing alkylate from a feedstream of isobutane and C₃ to C₅ unsaturates in proper proportions.
2. All necessary controllers and instrumentation.
3. All BL process facilities.
4. Feed treating (molecular sieve unit to remove moisture in feed).

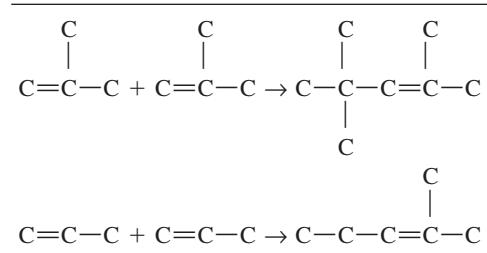
Costs not included

1. Cooling water, steam and power supply.
2. Feed and product storage.

	HF	H ₂ SO ₄
<i>Royalty</i>		
\$/bbl TA ^a	0.03	0–0.04
<i>Utility data (per bbl TA^a)</i>		
Steam, lb	200	200
Power, kWh	3.7	4.6
Cooling water, gal crclt.	3,700	3,300
<i>Chemicals (per bbl TA^a)</i>		
Acid, lb	0.3	30
Caustic, lb	0.2	0.2

^a Total alkylate (C₅ + alkylate).

Note: See Fig. 11.6.

Table 11.7 Polymerization Reactions

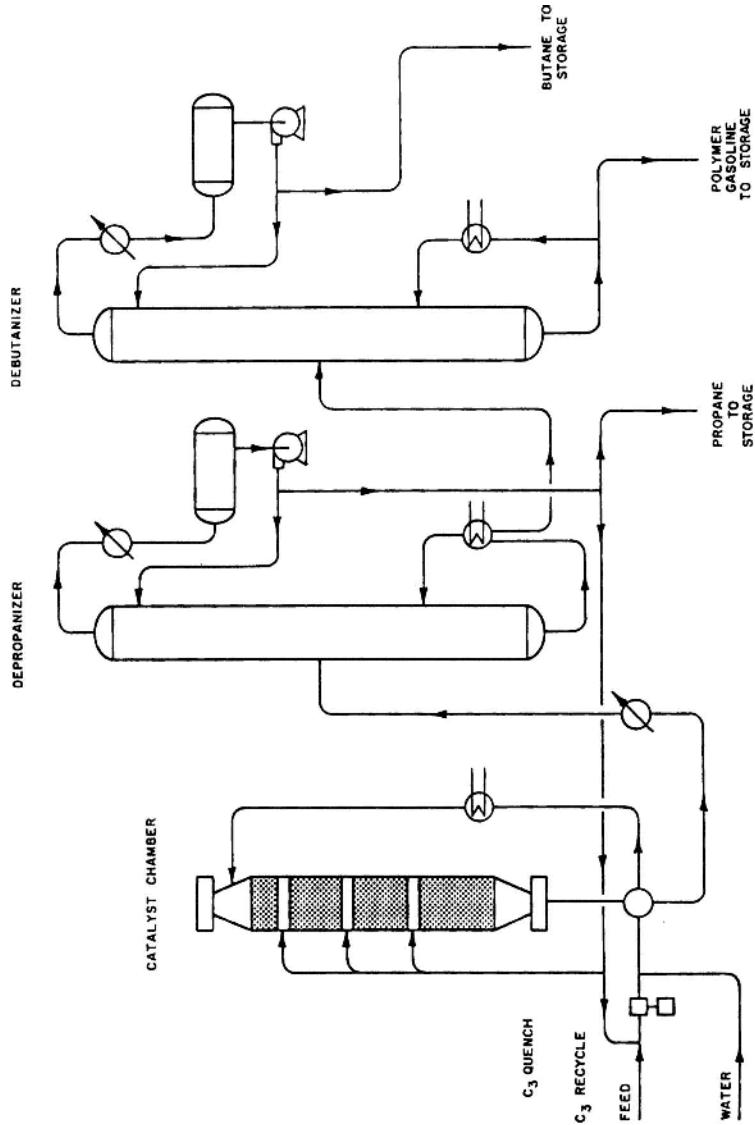


Figure 11.7 UOP solid phosphoric acid polymerization unit. (From Ref. 21.)

Table 11.8 Polymerization Operating Conditions

Temperature ^a	300–425°F (175–235°C)
Pressure	400–1,500 psi (2,760–10,340 kPa)
Space velocity	0.3 gal/lb (2.5 l/kg-hr)

^a Usually 200–220°C.

Note: Higher pressures mean lower temperatures.

sumption. Oxygen dissolved in the feed adversely affects the reactions and must be removed. Normal catalyst consumption rates are in the range of one pound of catalyst per 100 to 200 gallons of polymer produced (830 to 1660 l/kg).

The feed, consisting of propane and butane as well as propene and butene, is contacted with an amine solution to remove hydrogen sulfide and caustic washed to remove mercaptans. It is then scrubbed with water to remove any caustic or amines and then dried by passing through a silica gel or molecular sieve bed. Finally, a small amount of water (350–400 ppm) is added to promote ionization of the acid before the olefin feed steam is heated to about 400°F (204°C) and passed over the catalyst bed. Reactor pressures are about 500 psig (3450 kPa).

The polymerization reaction is highly exothermic and temperature is controlled either by injecting a cold propane quench or by generating steam. The propane and butane in the feed act as diluents and a heat sink to help control the rate of reaction and the rate of heat release. Propane is also recycled to help control the temperature.

After leaving the reactor the product is fractionated to separate the butane and lighter material from the polymer gasoline. Gasoline boiling range polymer production is normally 90–97 wt% on olefin feed or about 0.7 barrel of polymer per barrel of olefin feed. A simplified process flow diagram for the UOP unit is shown in Figure 11.7 [19] and ranges of reaction conditions given in Table 11.8 [21].

Insitut Francais du Petrole licenses a process to produce dimate (isohexene) from propene using a homogeneous aluminum alkyl catalyst which is not recovered. The process requires a feed stream that is better than 99% propane and propene because C₂s and C₄s poison the catalyst. Dienes and triple bonded hydrocarbons can create problems and in some cases it is necessary to selectively hydrogenate the feed to eliminate these compounds. The major advantage of this process is the low capital cost because it operates at low pressures. A simplified process flow diagram is given in Figure 11.8 [6] and feed impurity limits in Table 11.9.

Product properties and yields are shown in Table 11.10 for alkylate, polymer, and dimer blending stocks. Table 11.11 shows polymerization unit costs.

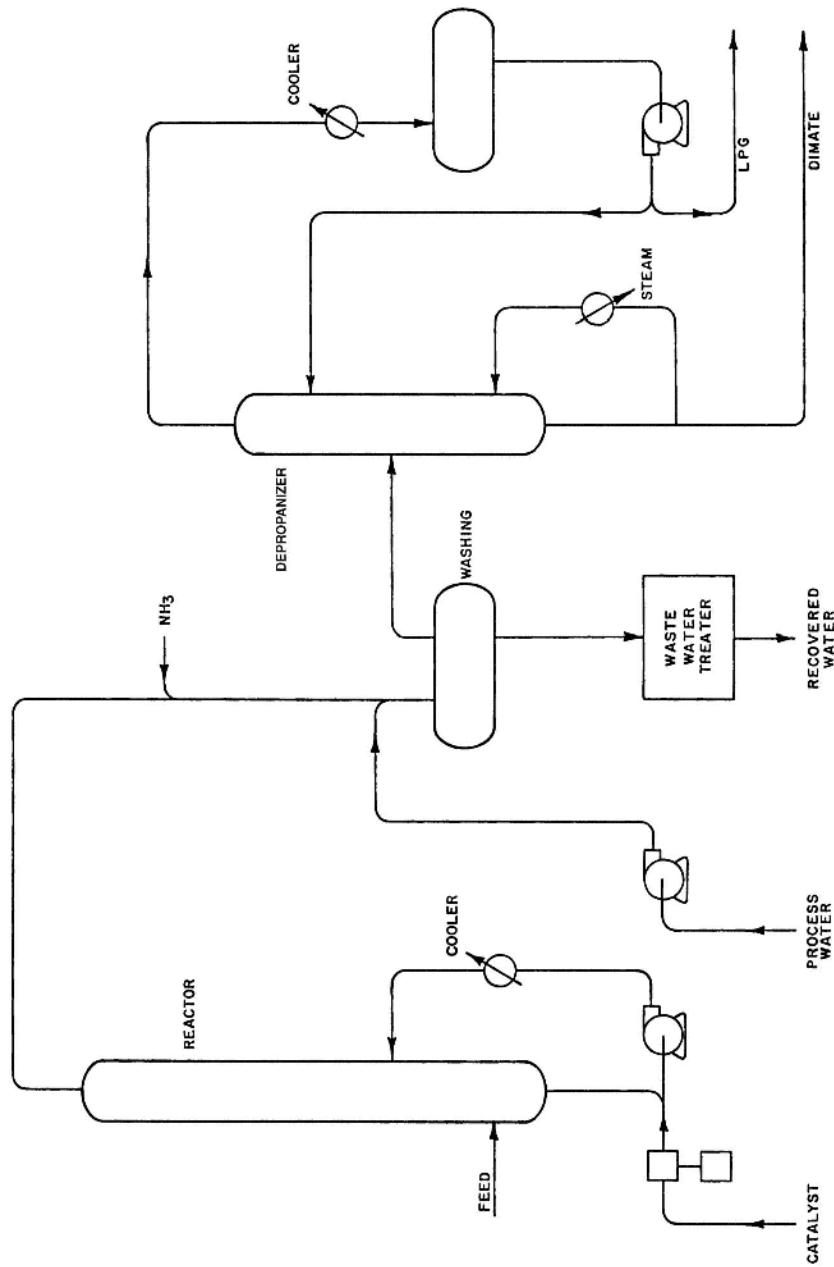


Figure 11.8 DIMERSOL polymerization unit. (From Ref. 6.)

Table 11.9 Dimersol Feed Impurities

Component	ppm
H ₂ O	3
Acetylene	15
Sulfur	5
Propadiene	1
Butadiene	10

Source: Ref. 6.

Table 11.10 Volume Yields Per bbl Mixed Olefin Feed

	Alkylate	Polymer	Dimate
C ₅ + gasoline	1.55	0.68	0.68
RON	94	97	97
MON	91	83	82

Table 11.11 Polymerization Unit Cost Data

Investment cost

1999 U.S. Gulf Coast

500 BPI

\$1,750,000

2000 BPD

\$5,000,000

Costs included

Costs are for reactor section only but include preheat heat exchange and product cooling.

Utility data (per bbl polymer)

Fuel, MM Btu	0.036
MMkJ	0.038
Cooling water, gal crclt., 30°F Δt	290
m ³ crclt., 17°C Δt	1.1

Table 11.12 HF Alkylation Unit Material Balance

Component	BPD	°API	lb/h/BPD	lb/h
<i>Feed</i>				
iC ₄ =	3,129		8.22	25,716
C ₄	3,559		8.76	31,180
C ₃	0			0
Total	6,688			56,896
<i>Products</i>				
C ₄ =	952		8.76	8,341
nC ₄	331		8.51	2,820
C ₅ + alkylate	4,117	77.9	9.86	40,584
Alkylate bottoms	310			4,683
Tar	25			468
Total	5,735			56,896

11.11 CASE-STUDY PROBLEM: ALKYLATION AND POLYMERIZATION

Tables 11.12 and 11.13 give the alkylation and polymerization units material balances and Table 11.14 shows the alkylation and polymerization units chemical and utility requirements.

There is not sufficient isobutane available for alkylating both the butylenes and propylenes. Therefore, butylenes will be alkylated up to the amount of isobutane available and the remaining butylenes plus the propylenes will be polymerized.

Table 11.13 Polymerization Unit Material Balance

Component	BPD	°API	lb/h/BPD	lb/h
<i>Feed</i>				
C ₃ =	2,094			15,475
C ₄ =	952			8,341
Total	3,046			23,816
C ₅ + polymer	2,071	47.9	11.50	23,816

Table 11.14 Alkylation and Polymerization Units Chemical and Utility Requirements

	Alkylation		Isomerization	
	Per/B TA	Per day	Per/B poly	Per day
Steam, Mlb	0.011	45	0.036	75
Power, MkWh	0.0037	15		
Cooling water, Mgal	3.7	15,231	0.29	601
Fuel, MMBtu	1.04	4,281	0.036	75
HF acid, lb	0.3	1,235		
Caustic, lb	0.2	823		
Catalyst, \$			0.84	1,740

PROBLEMS

1. A refinery has available 2700 BPCD of butylene and 2350 BPCD of isobutane for possible alkylation unit feed. How many barrels of alkylate can be made from these feedstocks? What will be the production of other products?
2. An unsaturated feed stream consisting of 1750 BPCD of butylene and 1550 BPCD of propylene is fed to an alkylation unit. How many BPCD of isobutane will be required for the unit? How much alkylate will be made?
3. Make an overall material balance for an alkylation unit with feed rates of 1710 BPCD of propylene, 3320 BPCD of butylene, 1550 BPCD of amylene, and 9570 BPCD of isobutane.
4. Estimate the 2002 construction costs for building the alkylation unit of problem 3 and the chemical and utility requirements (a) if sulfuric acid catalyst is used and (b) if hydrofluoric acid catalyst is used.
5. Using the construction costs and chemical and utility requirements of problem 4, what are the costs per barrel of alkylate produced for direct operation, including royalties but not labor, and depreciation. Assume 16-year straight-line depreciation, with dismantling costs equal to salvage value. Compare total costs per barrel of alkylate for hydrofluoric and sulfuric acid processes.
6. Compare the operating costs per barrel of alkylate produced from a 4000 BPSD sulfuric acid alkylation plant and a 4000 BPSD hydrofluoric acid alkylation plant. Obtain chemical costs from the latest issue of *Chemical Marketing Reporter*. Use the following utility costs: steam, \$3.15/Mlb; electric power, \$0.05/kWh; cooling water:

makeup, \$0.45/M gal, circulating, see p. 355; fuel, \$2.25/MM Btu; labor costs, \$950/day.

7. A refinery has 5560 BPSD of isobutane available for alkylation. There are also 2110 BPSD of propylene, 2200 BPSD of butylene, and 1400 BPSD of amylene available. What combination of feedstocks to the alkylation unit will maximize alkylate production?
8. Estimate the 1978 construction costs for building an alkylation unit to feed 2400 BPSD of propylene, 4000 BPSD of butylene, and 8350 BPSD of isobutane.
9. Assuming 16-year straight-line depreciation and dismantling costs to equal salvage value; calculate the operating costs, including depreciation and running royalties, but not labor, per barrel of alkylate produced for hydrofluoric and sulfuric acid plants producing 10,000 BPSD of alkylate.
10. For problem 6, compare the daily operating costs for a 4000 BPSD feed rate hydrofluoric acid plant when producing alkylate from 98% propylene feedstock with that when using a 97.5% butylene feedstock.
11. Make an overall volume and weight material balance for an alkylation unit with feed rates of 1550 BPCD of propylene, 3520 BPCD of butylene, 1800 BPCD of amylene and 9510 BPCD of isobutane.
12. For an alkylation plant with a 97.2% on-stream factor producing 9000 BPCD of alkylate gasoline having clear octane numbers of 95.9 MON and 97.3 RON, estimate its 2004 U.S. Gulf Coast construction cost and its annual chemical and utility requirements.
13. Make an overall weight and volume material balance for an alkylation unit with a feedrate of 2500 BPCD of butylene and 2800 BPCD of isobutane.
14. A refinery has 8000 BPSD of isobutane available for alkylation. There are also 2120 BPSD of propylene, 3985 BPSD of butylene, and 1880 BPSD of amylene available. What is the maximum yield of pentane-free alkylate that can be produced?

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12

Product Blending

Increased operating flexibility and profits result when refinery operations produce basic intermediate streams that can be blended to produce a variety of on-specification finished products. For example, naphthas can be blended into either gasoline or jet fuel, depending upon the product demand. Aside from lubricating oils, the major refinery products produced by blending are gasolines, jet fuels, heating oils, and diesel fuels. The objective of product blending is to allocate the available blending components in such a way as to meet product demands and specifications at the least cost and to produce incremental products which maximize overall profit. The volumes of products sold, even by a medium-sized refiner, are so large that savings of a fraction of a cent per gallon will produce a substantial increase in profit over the period of one year. For example, if a refiner sells about one billion gallons of gasoline per year (about 65,000 BPCD; several refiners sell more than that in the United States), a saving of one one-hundredth of a cent per gallon results in an additional profit of \$100,000 per year.

Today most refineries use computer-controlled in-line blending for blending gasolines and other high-volume products. Inventories of blending stocks, together with cost and physical property data are maintained in the computer. When a certain volume of a given quality product is specified, the computer uses linear programming models to optimize the blending operations to select the blending components to produce the required volume of the specified product at the lowest cost.

To ensure that the blended streams meet the desired specifications, stream analyzers, measuring, for example, boiling point, specific gravity, RVP, and research and motor octane, are installed to provide feedback control of additives and blending streams.

Blending components to meet all critical specifications most economically is a trial-and-error procedure which is easy to handle with the use of a computer. The large number of variables makes it probable there will be a number of equivalent solutions that give the approximate equivalent total overall cost or profit.

Optimization programs permit the computer to provide the optimum blend to minimize cost and maximize profit. Both linear and geometric programming techniques are used. Geometric programming is preferred if sufficient data are available to define the equations because components blend nonlinearly and values are functions of the quantities of the components and their characteristics.

The same basic techniques are used for calculating the blending components for any of the blended refinery products. Gasoline is the largest volume refinery product and will be used as an example to help clarify the procedures.

For purposes of preliminary cost evaluation studies, calculations generally are not made on the percent distilled specifications at intermediate percentages, even though these are important with respect to such operating characteristics as warm-up, acceleration, and economy. The allowable blending stocks are those with boiling ranges within the product specifications [e.g., C₄-380°F (C₄-193°C)] and the control criteria are to meet Reid vapor pressure (RVP) and octane requirements.

12.1 REID VAPOR PRESSURE

The desired RVP of a gasoline is obtained by blending n-butane with C₅-380°F (C₅-193°C) naphtha. The amount of n-butane required to give the needed RVP is calculated by:

$$M_t(RVP)_t = \sum_{i=1}^n M_i(RVP)_i \quad (1)$$

where

- M_t = total moles blended product
- (RVP)_t = specification RVP for product, psi
- M_i = moles of component i
- (RVP)_i = RVP of component i, psi or kPa

Example 1

Base Stock	BPD	lb/hr	MW	mol/hr	mol%	RVP	PVP
LSR gasoline	4,000	39,320	86	457	21.0	11.1	2.32
Reformate	6,000	69,900	115	617	28.4	2.8	0.80
Alkylate	3,000	30,690	104	295	13.4	4.6	0.62
FCC gasoline	8,000	87,520	108	810	37.2	4.4	1.64
Total	21,000			2,179	100.0		

Blend for a 10 psi RVP (n-butane: MW = 58, RVP = 52).

Butane requirement:

$$\begin{aligned}
 (2,179)(5.38) + M(52.0) &= (2,179 + M)(10) \\
 11,723 + 52.0M &= 21,790 + 10.0M \\
 42.0M &= 10,067 \\
 M &= 240 \text{ moles nC}_4 \text{ required}
 \end{aligned}$$

	BPD	lb/hr	MW	mol/hr
n-Butane	1,640	13,920	58	240

$$\text{Total 10 psi RVP gasoline} = 21,000 + 1,640 = 22,640 \text{ BPD}$$

Blending property data for many refinery streams are given in Table 12.1.

The theoretical method for blending to the desired Reid vapor pressure requires that the average molecular weight of each of the streams be known. Although there are accepted ways of estimating the average molecular weight of a refinery stream from boiling point, gravity, and characterization factor, a more convenient way is to use the empirical method developed by Chevron Research Company. Vapor pressure blending indices (VPBI) have been compiled as a function of the RVP of the blending streams and are given in Table 12.2. The Reid vapor pressure of the blend is closely approximated by the sum of all the products of the volume fraction (v) times the VPBI for each component. In equation form:

$$RVP_{\text{blend}} = \sum v_i (\text{VPBI})_i \quad (2)$$

In the case where the volume of the butane to be blended for a given RVP is desired:

$$A(\text{VPBI})_a + B(\text{BPBI})_b + \dots + W(\text{VPBI})_w = (Y + W)(\text{VPBI})_m \quad (3)$$

where

A = bbl of component a , etc.

W = bbl of n-butane (w)

$Y = A + B + C + \dots$ (all components except n-butane)

$(\text{VPBI})_m$ = VPBI corresponding to the desired RVP of the mixture

w = subscript indicating n-butane

Table 12.1 Blending Component Values for Gasoline Blending Streams

No.	Component	RVP, psi	MON	RON	°API
1.	iC ₄	71.0	92.0	93.0	
2.	nC ₄	52.0	92.0	93.0	
3.	iC ₅	19.4	90.8	93.2	
4.	nC ₅	14.7	72.4	71.5	
5.	iC ₆	6.4	78.4	79.2	
6.	LSR gasoline (C ₅ -180°F)	11.1	61.6	66.4	78.6
7.	LSR gasoline isomerized once-through	13.5	81.1	83.0	80.4
8.	HSR gasoline	1.0	58.7	62.3	48.2
9.	Light hydrocrackate	12.9	82.4	82.8	79.0
10.	Hydrocrackate, C ₅ -C ₆	15.5	85.5	89.2	86.4
11.	Hydrocrackate, C ₆ -190°F	3.9	73.7	75.5	85.0
12.	Hydrocrackate, 190–250°F	1.7	75.6	79.0	55.5
13.	Heavy hydrocrackate	1.1	67.3	67.6	49.0
14.	Coker gasoline	3.6	60.2	67.2	57.2
15.	Light thermal gasoline	9.9	73.2	80.3	74.0
16.	C ₆ ⁺ light thermal gasoline	1.1	68.1	76.8	55.1
17.	FCC gasoline, 200–300°F	1.4	77.1	92.1	49.5
18.	Hydrog. light FCC gasoline, C ₅ ⁺	13.9	80.9	83.2	51.5
19.	Hydrog. C ₅ -200°F FCC gasoline	14.1	81.7	91.2	58.1
20.	Hydrog. light FCC gasoline, C ₆ ⁺	5.0	74.0	86.3	49.3
21.	Hydrog. C ₅ ⁺ FCC gasoline	13.1	80.7	91.0	54.8
22.	Hydrog. 300–400°F FCC gasoline	0.5	81.3	90.2	48.5
23.	Reformate, 94 RON	2.8	84.4	94.0	45.8
24.	Reformate, 98 RON	2.2	86.5	98.0	43.1
25.	Reformate, 100 RON	3.2	88.2	100.0	41.2
26.	Aromatic concentrate	1.1	94.0	107.0	
27.	Alkylate, C ₃ ⁼	5.7	87.3	90.8	
28.	Alkylate, C ₄ ⁼	4.6	95.9	97.3	70.3
29.	Alkylate, C ₃ ⁼ , C ₄ ⁼	5.0	93.0	94.5	
30.	Alkylate, C ₅ ⁼	1.0	88.8	89.7	
31.	Polymer	8.7	84.0	96.9	59.5

Table 12.2 Reid Vapor Blending Index Numbers for Gasoline and Turbine Fuels

Vapor Pressure, psi	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.00	0.05	0.13	0.22	0.31	0.42	0.52	0.64	0.75	0.87
1	1.00	1.12	1.25	1.38	1.52	1.66	1.79	1.94	2.08	2.23
2	2.37	2.52	2.67	2.83	2.98	3.14	3.30	3.46	3.62	3.78
3	3.94	4.11	4.28	4.44	4.61	4.78	4.95	5.13	5.30	5.48
4	5.65	5.83	6.01	6.19	6.37	6.55	6.73	6.92	7.10	7.29
5	7.47	7.66	7.85	8.04	8.23	8.42	8.61	8.80	9.00	9.19
6	9.39	9.58	9.78	9.98	10.2	10.4	10.6	10.8	11.0	11.2
7	11.4	11.6	11.8	12.0	12.2	12.4	12.6	12.8	13.0	13.2
8	13.4	13.7	13.9	14.1	14.3	14.5	14.7	14.9	15.2	15.4
9	15.6	15.8	16.0	16.2	16.4	16.7	16.9	17.1	17.3	17.6
10	17.8	18.0	18.2	18.4	18.7	18.9	19.1	19.4	19.6	19.8
11	20.0	20.3	20.5	20.7	20.9	21.2	21.4	21.6	21.9	22.1
12	22.3	22.6	22.8	23.0	23.3	23.5	23.7	24.0	24.2	24.4
13	24.7	24.9	25.2	25.4	25.6	25.9	26.1	26.4	26.6	26.8
14	27.1	27.3	27.6	27.8	28.0	28.3	28.5	28.8	29.0	29.3
15	29.5	29.8	30.0	30.2	30.5	30.8	31.0	31.2	31.5	31.8
16	32.0	32.2	32.5	32.8	33.0	33.2	33.5	33.8	34.0	34.3
17	34.5	34.8	35.0	35.3	35.5	35.8	36.0	36.3	36.6	36.8
18	37.1	37.3	37.6	37.8	38.1	38.4	38.6	38.9	39.1	39.4
19	39.7	39.9	40.2	40.4	40.7	41.0	41.2	41.5	41.8	42.0
20	42.3	42.6	42.8	43.1	43.4	43.6	43.9	44.2	44.4	44.7
21	45.0	45.2	45.5	45.8	46.0	46.3	46.6	46.8	47.1	47.4
22	47.6	47.9	48.2	48.4	48.7	49.0	49.3	49.5	49.8	50.1
23	50.4	50.6	50.9	51.2	51.5	51.7	52.0	52.3	52.6	52.8
24	53.1	53.4	53.7	54.0	54.2	54.5	54.8	55.1	55.3	55.6
25	55.9	56.2	56.5	56.7	57.0	57.3	57.5	57.9	58.1	58.4
26	58.7	59.0	59.3	59.6	59.8	60.1	60.4	60.7	61.0	61.3
27	61.5	61.8	62.1	62.4	62.7	63.0	63.3	63.5	63.8	64.1
28	64.4	64.7	65.0	65.3	65.6	65.8	66.1	66.4	66.7	67.0
29	67.3	67.6	67.9	68.2	68.4	68.8	69.0	69.3	69.6	69.9
30	70.2									
40	101									
(nC ₄)	51.6	138								
(iC ₄)	72.2	210								
(C ₅)	190	705								
Example: Calculate the vapor pressure of a gasoline blend as follows:										
Component Volume Fraction Vapor Pressure, psi Vapor Pressure Blending Index No. Volume Fraction x VPBI										
n-Butane 0.050 51.6 138 6.90 Light Straight Run 0.450 6.75 10.9 4.90 Heavy Refined 0.500 1.00 1.00 0.50 Total 1.000 7.4 12.3 12.30										

From the brochure, "31.0°API Iranian Heavy Crude Oil," by arrangement with Chevron Research Company. Copyright © 1971 by Chevron Oil Trading Company.

Source: Ref. 5.

Example 2

Component	BPCD	RVP	VPBI	vol X VPBI
n-Butane	W	51.6	138.0	138W
LSR gasoline	4,000	11.1	20.3	81,200
Reformate	6,000	2.8	3.62	21,720
Alkylate	3,000	4.6	6.73	20,190
FCC gasoline	8,000	4.4	6.37	50,960
Total	21,000 + W			174,070 + 138W

For 10 psi RVP, $(VPBI)_m = 17.8$

$$17.8(21,000 + W) = 174,070 + 138W$$

$$(138 - 17.8)W = 373,800 - 174,070$$

$$120.2W = 199,730$$

$$W = 1,660 \text{ bbl n-butane required}$$

$$\text{Total 10 psi RVP gasoline} = 21,000 + 1,660 = 22,660 \text{ BPCD}$$

Although this differs slightly from the result obtained in Example 1, they agree well within the limits required for normal refinery operation.

12.2 OCTANE BLENDING

Octane numbers are blended on a volumetric basis using the blending octane numbers of the components. True octane numbers do not blend linearly and it is necessary to use blending octane numbers in making calculations. Blending octane numbers are based upon experience and are those numbers which, when added on a volumetric average basis, will give the true octane of the blend. True octane is defined as the octane number obtained using a CFR test engine.

The formula used for calculations is:

$$B_t ON_t = \sum_{i=1}^n (B_i ON_i) \quad (4)$$

where

B_t = total gasoline blended, bbl

ON_t = desired octane of blend

B_i = bbl of component i

ON_i = blending octane number of component i

12.3 BLENDING FOR OTHER PROPERTIES

There are several methods of estimating the physical properties of a blend from the properties of the blending stocks. One of the most convenient methods of estimating properties that do not blend linearly is to substitute for the value of the inspection to be blended another value which has the property of blending approximately linear. Such values are called blending factors or blending index numbers. The Chevron Research Company has compiled factors or index numbers for vapor pressures, viscosities, flash points, and aniline points. These are tabulated in Tables 12.2, 12.3, 12.4, and 12.5, respectively. This material is copyrighted and reproduced with permission of the Chevron Research Company. Table 12.6 shows the blending values of octane improvers.

Examples are given in each table of the use of blending index numbers. Since it is more complicated than the others, viscosity blending is more fully discussed below.

In blending some products, viscosity is one of the specifications that must be met. Viscosity is not an additive property and it is necessary to use special techniques to estimate the viscosity of a mixture from the viscosities of its components. The method most commonly accepted is the use of special charts developed by and obtainable from ASTM.

Blending of viscosities may be calculated conveniently by using viscosity factors from Table 12.3. It is usually true to a satisfactory approximation that the viscosity factor (VF) of the blend will be the sum of all the products of the volume fraction times the viscosity factor for each component. In equation form:

$$VF_{blend} = \sum (V_i \times VF_i) \quad (5)$$

Table 12.3 shows an example calculation.

Blending of kinematic viscosities (centistokes) may be done at any temperature, but the viscosities of all components of the blend must be expressed at the same temperature. Blending of Saybolt Universal viscosities also may be done at any temperature and interchangeably with kinematic viscosities at the same temperature. Therefore, Table 12.3 may be used to convert viscosities expressed in centistokes to Saybolt Universal seconds (SUS) and vice versa.

Viscosity factors also are given in Table 12.3 for viscosities expressed in Saybolt Furol seconds (SFS). It is important that Saybolt Furol viscosities be blended only at 122°F (50°C). If SFS viscosities are at any other temperature, they must be converted to centistokes or SUS before blending.

Viscosity factors for SFS at 122°F (50°C) may be used interchangeably with viscosity factors for SUS at 130°F (54.4°C) and with centistokes at 130°F (54.4°C). Thus, Table 12.3 may be used also to convert viscosities in SFS at 122°F (50°C) to either kinematic or Saybolt Universal viscosities at 130°F (54.4°C).

Table 12.3 Viscosity Blending Index Numbers

FACTORS FOR VOLUME BLENDING OF VISCOSITIES AT CONSTANT TEMPERATURE CORRESPONDING TO VALUES OF KINEMATIC VISCOSITY										
WEIGHTNESSES										
	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.5	0.009	0.006	0.013	0.019	0.025	0.030	0.036	0.041	0.046	0.051
0.6	0.056	0.061	0.065	0.069	0.074	0.078	0.082	0.086	0.089	0.093
0.7	0.097	0.100	0.104	0.107	0.110	0.114	0.117	0.120	0.123	0.126
0.8	0.128	0.131	0.134	0.137	0.139	0.142	0.145	0.147	0.149	0.152
0.9	0.154	0.156	0.159	0.161	0.163	0.165	0.167	0.169	0.172	0.174
EST										
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1	0.166	0.194	0.210	0.224	0.236	0.247	0.257	0.266	0.274	0.283
2	0.290	0.307	0.303	0.309	0.314	0.320	0.325	0.330	0.334	0.338
3	0.342	0.349	0.350	0.353	0.355	0.356	0.358	0.360	0.364	0.372
4	0.375	0.379	0.380	0.383	0.385	0.387	0.390	0.393	0.396	0.396
5	0.395	0.400	0.402	0.404	0.406	0.408	0.410	0.411	0.413	0.414
6	0.412	0.415	0.415	0.415	0.415	0.415	0.415	0.415	0.415	0.415
7	0.431	0.432	0.433	0.434	0.435	0.436	0.437	0.438	0.440	0.443
8	0.447	0.448	0.449	0.450	0.451	0.452	0.453	0.454	0.455	0.456
9	0.453	0.454	0.455	0.456	0.456	0.457	0.458	0.459	0.460	0.461
EST										
	0	1	2	3	4	5	6	7	8	9
10	0.462	0.470	0.477	0.483	0.489	0.494	0.499	0.503	0.508	0.511
20	0.515	0.524	0.525	0.525	0.528	0.530	0.532	0.534	0.535	0.536
30	0.540	0.542	0.543	0.543	0.544	0.545	0.545	0.545	0.545	0.545
40	0.561	0.562	0.564	0.566	0.567	0.568	0.569	0.570	0.571	0.571
50	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
60	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
70	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
80	0.601	0.602	0.603	0.603	0.603	0.603	0.603	0.603	0.603	0.603
90	0.603	0.603	0.603	0.603	0.603	0.603	0.603	0.603	0.603	0.603
EST										
	0	10	20	30	40	50	60	70	80	90
100	0.513	0.518	0.523	0.527	0.531	0.534	0.537	0.541	0.545	0.549
200	0.567	0.569	0.570	0.570	0.571	0.572	0.573	0.574	0.575	0.576
300	0.567	0.569	0.570	0.571	0.571	0.571	0.571	0.571	0.571	0.571
400	0.560	0.561	0.562	0.563	0.564	0.565	0.566	0.567	0.568	0.568
500	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
600	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
700	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
800	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
900	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569	0.569
EST										
	0	100	200	300	400	500	600	700	800	900
1,000	0.717	0.721	0.724	0.727	0.730	0.733	0.735	0.737	0.739	0.741
2,000	0.713	0.715	0.717	0.718	0.720	0.721	0.724	0.725	0.726	0.727
3,000	0.757	0.758	0.759	0.761	0.762	0.764	0.765	0.767	0.768	0.769
4,000	0.767	0.768	0.769	0.770	0.771	0.772	0.773	0.773	0.774	0.774
5,000	0.770	0.770	0.770	0.771	0.771	0.771	0.771	0.771	0.771	0.771
6,000	0.770	0.770	0.770	0.771	0.771	0.771	0.771	0.771	0.771	0.771
7,000	0.785	0.786	0.786	0.787	0.787	0.787	0.788	0.789	0.790	0.790
8,000	0.790	0.790	0.790	0.791	0.791	0.791	0.792	0.792	0.793	0.793
9,000	0.793	0.794	0.794	0.794	0.795	0.795	0.795	0.795	0.795	0.795
EST										
	0	100	200	300	400	500	600	700	800	900
10,000	0.799	0.799	0.802	0.804	0.805	0.808	0.810	0.812	0.815	0.815
20,000	0.817	0.817	0.818	0.818	0.819	0.820	0.821	0.822	0.823	0.823
30,000	0.828	0.829	0.830	0.831	0.832	0.833	0.834	0.835	0.836	0.836
40,000	0.836	0.837	0.838	0.838	0.839	0.840	0.841	0.841	0.842	0.842
50,000	0.842	0.843	0.843	0.844	0.844	0.845	0.845	0.846	0.846	0.846
60,000	0.847	0.848	0.848	0.848	0.849	0.849	0.850	0.850	0.851	0.851
70,000	0.851	0.851	0.851	0.851	0.851	0.851	0.851	0.851	0.851	0.851
80,000	0.856	0.856	0.856	0.856	0.856	0.856	0.856	0.856	0.856	0.856
EST										
	0	100,000	200,000	300,000	400,000	500,000	600,000	700,000	800,000	900,000
1,000,000	0.860	0.860	0.861	0.861	0.861	0.861	0.861	0.861	0.861	0.861
2,000,000	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877	0.877
3,000,000	0.887	0.887	0.887	0.887	0.887	0.887	0.887	0.887	0.887	0.887
4,000,000	0.894	0.894	0.894	0.894	0.894	0.894	0.894	0.894	0.894	0.894
5,000,000	0.897	0.897	0.897	0.897	0.897	0.897	0.897	0.897	0.897	0.897
6,000,000	0.903	0.903	0.903	0.903	0.903	0.903	0.903	0.903	0.903	0.903
7,000,000	0.906	0.906	0.906	0.906	0.906	0.906	0.906	0.906	0.906	0.906
8,000,000	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909
9,000,000	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912
EST										
	0	10,000	20,000	30,000	40,000	50,000	60,000	70,000	80,000	90,000
100,000,000	0.860	0.860	0.861	0.861	0.861	0.861	0.861	0.861	0.861	0.861
200,000,000	0.873	0.873	0.873	0.873	0.873	0.873	0.873	0.873	0.873	0.873
300,000,000	0.887	0.887	0.887	0.887	0.887	0.887	0.887	0.887	0.887	0.887
400,000,000	0.894	0.894	0.894	0.894	0.894	0.894	0.894	0.894	0.894	0.894
500,000,000	0.897	0.897	0.897	0.897	0.897	0.897	0.897	0.897	0.897	0.897
600,000,000	0.903	0.903	0.903	0.903	0.903	0.903	0.903	0.903	0.903	0.903
700,000,000	0.906	0.906	0.906	0.906	0.906	0.906	0.906	0.906	0.906	0.906
800,000,000	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909	0.909
900,000,000	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912
EST										
	0	100	200	300	400	500	600	700	800	900
1,000,000	0.722	0.725	0.726	0.727	0.728	0.729	0.730	0.731	0.732	0.733
2,000,000	0.725	0.725	0.727	0.727	0.727	0.727	0.727	0.727	0.727	0.727
3,000,000	0.729	0.729	0.731	0.731	0.731	0.731	0.731	0.731	0.731	0.731
4,000,000	0.732	0.732	0.733	0.733	0.733	0.733	0.733	0.733	0.733	0.733
5,000,000	0.734	0.734	0.734	0.734	0.734	0.734	0.734	0.734	0.734	0.734
6,000,000	0.735	0.735	0.735	0.735	0.735	0.735	0.735	0.735	0.735	0.735
7,000,000	0.736	0.736	0.736	0.736	0.736	0.736	0.736	0.736	0.736	0.736
8,000,000	0.737	0.737	0.737	0.737	0.737	0.737	0.737	0.737	0.737	0.737
9,000,000	0.738	0.738	0.738	0.738	0.738	0.738	0.738	0.738	0.738	0.738
EST										
	0	100	200	300	400	500	600	700	800	900
1,000,000	0.778	0.785	0.792	0.798	0.804	0.811	0.817	0.823	0.829	0.835
2,000,000	0.782	0.785	0.791	0.797	0.803	0.809	0.815	0.821	0.827	0.833
3,000,000	0.787	0.787	0.791	0.797	0.801	0.806	0.811	0.816	0.821	0.826
4,000,000	0.791	0.791	0.794	0.798	0.801	0.806	0.811	0.816	0.821	0.826
5,000,000	0.794	0.794	0.797	0.800	0.802	0.806	0.811	0.816	0.821	0.826
6,000,000	0.796	0.796	0.798	0.800	0.802	0.806	0.811	0.816	0.821	0.826
7,000,000	0.798	0.798	0.800	0.802	0.804	0.807	0.811	0.816	0.821	0.826
8,000,000	0.800	0.800	0.802	0.804	0.806	0.808	0.811	0.816	0.821	0.826
9,000,000	0.801	0.801	0.803	0.805	0.807	0.809	0.811	0.816	0.821	0.826
EST										
	0	100	200	300	400	500	600	700		

Table 12.4 Flash Point Blending Index Numbers

May be used to blend flash temperatures determined in any apparatus but, preferably, not to blend closed cup with open cup determinations.

Flash Point, °F	0	10	20	30	40	50	60	70	80	90
0	168,000	157,000	147,000	137,000	128,000	120,000	112,000	105,000	98,600	92,400
10	86,600	81,200	76,100	71,400	67,000	62,900	59,000	55,400	52,100	49,000
20	46,000	43,300	40,700	38,300	36,100	34,000	32,000	30,100	28,400	26,800
30	25,200	23,800	22,400	21,200	20,000	18,900	17,800	16,800	15,900	15,000
40	14,200	13,500	12,700	12,000	11,400	10,800	10,200	9,680	9,170	8,690
50	8,240	7,810	7,410	7,030	6,670	6,330	6,010	5,700	5,420	5,150
60	4,890	4,650	4,420	4,200	4,000	3,800	3,620	3,441	3,280	3,120
70	2,970	2,830	2,700	2,570	2,450	2,330	2,230	2,120	2,020	1,930
80	1,840	1,760	1,680	1,600	1,530	1,460	1,400	1,340	1,280	1,220
90	1,170	1,120	1,070	1,020	978	935	896	857	821	786
100	753	722	692	652	635	609	584	560	537	515
110	495	475	456	438	420	404	388	372	358	344
120	331	318	305	294	283	272	261	252	242	233
130	224	216	208	200	193	186	179	172	166	160
140	154	149	144	138	134	129	124	120	116	112
150	108	104	101	97.1	93.8	90.6	87.5	84.6	81.7	79.0
160	76.3	73.8	71.4	69.0	66.7	64.5	62.4	60.4	58.4	56.5
170	54.7	52.9	51.3	49.6	48.0	46.5	45.1	43.6	42.3	40.9
180	39.7	38.4	37.3	36.1	35.0	33.9	32.9	31.9	30.9	30.0
190	29.1	28.2	27.4	26.6	25.8	25.0	24.3	23.6	22.9	22.2
200	21.6	20.9	20.3	19.7	19.2	18.6	18.1	17.6	17.1	16.6
210	16.1	15.7	15.2	14.8	14.4	14.0	13.6	13.3	12.9	12.5
220	12.2	11.9	11.6	11.2	10.9	10.6	10.4	10.1	9.82	9.56
230	9.31	9.07	8.83	8.60	8.37	8.16	7.95	7.74	7.55	7.35
240	7.16	6.98	6.80	6.63	6.47	6.30	6.15	5.99	5.84	5.70
250	5.56	5.42	5.29	5.16	5.03	4.91	4.79	4.68	4.56	4.45
260	4.35	4.24	4.14	4.04	3.95	3.86	3.76	3.68	3.59	3.51
270	3.43	3.35	3.27	3.19	3.12	3.05	2.98	2.91	2.85	2.78
280	2.72	2.66	2.60	2.54	2.48	2.43	2.37	2.32	2.27	2.22
290	2.17	2.12	2.08	2.03	1.99	1.95	1.90	1.86	1.82	1.79
Flash Point, °F	0	10	20	30	40	50	60	70	80	90
300	1.75	1.41	1.15	0.943	0.777	0.643	0.535	0.448	0.376	0.317
400	0.269	0.229	0.196	0.168	0.145	0.125	0.108	0.094	0.082	0.072
500	0.063	0.056	0.049	0.044	0.039	0.035	0.031	0.028	0.025	0.022

Example:	Component	Volume	Flash Point, °F	Volume X		
				Blending Index	Blending Index	Total
	A	0.80	100	753	226	
	B	0.10	90	1,170	117	
	C	0.60	130	224	134	
	Total	1.00	111	477	477	

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Source: Refs. 4 and 5.

A similar method has been developed by Reid and Allen of Chevron Research Company for the estimation of "wax" pour points of distillate blends [4]. Pour point indices for distillate stocks are given in Table 12.7. The pour point index of the blend is the sum of the products of the volume fraction times the pour point blending index (PPBI) for each component, or

$$\text{PPBI}_{\text{blend}} = \sum V_i \text{PPBI}_i \quad (6)$$

Table 12.5 Aniline Point Blending Index Numbers

Aniline Point, °F	0	-1	-2	-3	-4	-5	-6	-7	-8	-9
-10	20.0	17.4	14.9	12.6	10.3	8.10	6.06	4.17	2.46	1.00
0	49.1	46.0	42.6	39.8	36.8	33.8	30.9	28.1	25.3	22.6
Aniline Point, °F	0	1	2	3	4	5	6	7	8	9
0	49.1	52.4	55.6	58.9	62.3	65.7	69.1	72.6	76.1	79.6
10	83.2	86.8	90.5	94.2	97.9	102	105	109	113	117
20	121	125	129	133	137	141	145	149	153	157
30	162	166	170	174	179	183	187	192	196	200
40	205	209	214	218	223	227	232	237	241	246
50	250	255	260	264	269	274	279	283	288	293
60	298	303	308	312	317	322	327	332	337	342
70	347	352	357	362	367	372	377	382	388	393
80	398	403	408	414	419	424	429	435	440	445
90	451	456	461	467	472	477	483	488	494	491
100	505	510	516	521	527	532	538	543	549	554
110	560	566	571	577	582	588	594	599	605	611
120	617	622	628	634	640	645	651	657	663	669
130	674	680	686	692	698	704	710	716	722	727
140	733	739	745	751	757	763	769	775	781	788
150	794	800	806	812	818	824	830	836	842	849
160	855	861	867	873	880	886	892	898	904	911
170	917	923	930	936	942	948	955	961	967	974
180	980	986	993	999	1,006	1,012	1,019	1,025	1,031	1,038
190	1,044	1,050	1,057	1,064	1,070	1,077	1,083	1,090	1,096	1,103
200	1,110	1,116	1,122	1,129	1,136	1,142	1,149	1,156	1,162	1,169
210	1,176	1,182	1,189	1,196	1,202	1,209	1,216	1,222	1,229	1,236
220	1,242	1,249	1,255	1,262	1,269	1,276	1,283	1,290	1,330	1,337
230	1,310	1,317	1,324	1,331	1,337	1,344	1,351	1,358	1,365	1,372
240	1,379	1,386	1,392	1,400	1,406	1,413	1,420	1,427	1,434	1,441
Mixed Aniline Point, °F	0	1	2	3	4	5	6	7	8	9
0	-736	-730	-723	-716	-709	-703	-696	-689	-682	-675
10	-668	-660	-653	-646	-639	-631	-623	-616	-608	-600
20	-593	-584	-577	-569	-561	-552	-544	-536	-528	-519
30	-511	-503	-494	-486	-477	-468	-460	-451	-442	-433
40	-425	-416	-407	-398	-389	-380	-371	-361	-352	-343
50	-334	-324	-315	-306	-296	-287	-277	-267	-258	-248
60	-239	-229	-219	-210	-200	-190	-180	-170	-160	-150
70	-140	-130	-120	-110	-100	-89.6	-79.4	-69.2	-58.9	-48.6
80	-38.3	-27.9	-17.5	-7.05	3.39	13.9	24.4	35.0	45.5	56.1
90	66.8	77.4	88.1	98.8	110	120	131	142	153	164
100	175	186	197	208	219	230	241	252	263	274
110	285	297	308	319	330	342	353	364	376	387
120	399	410	422	433	445	456	468	479	491	503
130	514	526	538	550	561	573	585	597	609	620
140	632	644	656	668	680	692	704	716	728	741
Example:	Component	Volume	Aniline Point, °F			Index	Volume X Index			
	A B	0.8 0.2		70 40 (Mixed)		347 -425		278 -85		
	Total	1.0		37 (Or 102 Mixed)		193		193		

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Source: Ref. 5.

Table 12.6 Blending Values of Octane Improvers

Compound	Blending octane			
	RVP, psi	RON	MON	(R + M)/2
Methanol	40	135	105	120
Ethanol	11	132	106	119
tert-Butanol (TBA)	6	106	89	98
MTBE	9	118	101	110
ETBE	4	118	102	110
TAME	1.5	111	98	105
TEL	—	10,000	13,000	

Source: Refs. 1 and 2.

The viscosity of a blend can also be estimated by API Procedure 11A4.3, given on pages 11–35 of the *API Technical Data Book-Petroleum Refining*.

12.4 CASE-STUDY PROBLEM: GASOLINE BLENDING

The requirements are to produce a 50/50 split of premium and regular gasoline lines having 91 and 87 posted octane numbers, respectively, and Reid vapor pressures of 10.2 psi (70.3 kPa).

For this split between regular and premium, the pool octane number (PON) needed is 89.0. The available basic blending stocks are then selected for blending. This is a trial-and-error process at this stage. After selecting the stocks, the quantity of n-butane required to give the desired vapor pressure is calculated first because the n-butane contributes significantly to the octane of the finished product.

The gasoline blending streams available from the various units are:

Base stock	BPCD	MON	RON
Isomerate	5,735	81.1	83.0
Reformate	14,749	86.9	98.5
FCC C ₅ gasoline	20,117	76.8	92.3
Lt hydrocrackate	814	82.4	82.8
Alkylate	4,117	95.9	97.3
Polymer	2,071	84.0	96.9
Total:	47,603		

Table 12.7 Pour Point Blending Indices for Distillate Stocks

ASTM 50%	Temp 300	350	375	400	425	450	475	500	525	550	575	600	625	650	675	700
Pour Point	133	131	129	128	127	125	123	120	118	115	113	110	108	105	103	100
70	133	131	129	128	127	125	123	120	118	115	113	110	108	105	103	100
65	114	111	109	107	105	103	101	98	96	94	91	88	85	82	79	76
60	99	94	92	90	87	85	82	80	77	74	72	69	67	64	62	60
55	88	88	79	77	75	73	71	68	66	63	61	58	56	53	50	48
50	72	68	66	63	61	59	56	54	52	49	47	44	42	39	35	33
45	60	56	54	52	50	48	46	44	42	40	38	36	34	32	30	28
40	52	48	46	44	42	40	38	36	34	32	30	28	26	24	22	21
35	44	41	39	37	35	33	32	30	28	26	24	23	21	19	18	16
30	37	34	32	31	29	27	26	24	23	21	19	18	16	15	14	13
25	32	29	27	26	24	23	21	20	18	17	15	14	13	12	11	10
20	27	24	23	21	20	18	17	16	15	14	12	11	10	9.1	8.3	7.5
15	23	20	19	18	17	16	14	13	12	11	9.8	8.8	8.0	7.1	6.3	5.6
10	20	17	16	15	14	13	12	11	9.7	8.8	7.9	7.1	6.3	5.6	5.0	4.5
5	17	15	14	13	12	11	10	9.6	8.7	7.9	7.1	6.3	5.6	5.0	4.4	3.8
0	14	12	11	10	9.6	8.7	7.9	7.1	6.3	5.6	5.0	4.5	3.8	3.4	3.0	2.7
-5	12	10	9.5	8.7	8.0	7.2	6.5	5.8	5.1	4.5	3.9	3.4	3.0	2.7	2.4	2.1
-10	10	8.8	8.0	7.3	6.6	5.9	5.3	4.7	4.1	3.6	3.2	2.8	2.5	2.2	1.9	1.6
-15	8.8	7.4	6.8	6.1	5.5	4.9	4.4	3.9	3.4	3.0	2.6	2.2	1.9	1.7	1.4	1.2
-20	7.5	6.3	5.7	5.1	4.6	4.1	3.6	3.2	2.8	2.4	2.1	1.8	1.5	1.3	1.1	0.94
-25	6.4	5.3	4.7	4.2	3.7	3.3	2.9	2.5	2.2	1.9	1.7	1.4	1.2	1.0	0.90	0.72
-30	5.5	4.5	4.0	3.6	3.2	2.8	2.4	2.1	1.8	1.5	1.3	1.1	0.96	0.80	0.67	0.56
-35	4.6	3.7	3.3	2.9	2.6	2.3	2.0	1.7	1.4	1.2	1.0	0.90	0.75	0.62	0.51	0.43
-40	4.0	3.2	2.8	2.5	2.2	1.9	1.6	1.4	1.2	1.0	0.86	0.73	0.62	0.51	0.41	0.33
-45	3.3	2.7	2.4	2.1	1.8	1.5	1.3	1.1	0.98	0.82	0.68	0.58	0.48	0.38	0.31	0.25
-50	2.8	2.3	2.0	1.7	1.5	1.3	1.1	0.93	0.78	0.66	0.56	0.47	0.38	0.31	0.25	0.20
-55	2.5	1.9	1.7	1.4	1.2	1.1	0.90	0.77	0.65	0.55	0.46	0.37	0.30	0.24	0.19	0.15
-60	2.1	1.6	1.4	1.2	1.0	0.87	0.74	0.62	0.52	0.43	0.36	0.30	0.24	0.19	0.14	0.10
-65	1.8	1.4	1.2	1.0	0.85	0.72	0.60	0.50	0.41	0.34	0.28	0.23	0.18	0.14	0.10	0.07
-70	1.5	1.1	0.99	0.84	0.71	0.60	0.50	0.42	0.36	0.30	0.25	0.20	0.15	0.11	0.08	0.05

By arrangement with Chevron Research Company.

Source: Ref. 5.

For the first round of calculations, the blending stocks selected for the premium gasoline should total approximately the volume fraction of premium gasoline times the total blending stocks. The following stocks are used:

Component	Volume	RVP	VPBI	vol(VPBI)
n-Butane	W	51.6	138.0	138W
Isomerate	5,735	13.5	25.9	148,395
Reformate	14,749	2.2	2.7	39,517
FCC gasoline	20,117	4.4	6.4	128,199
Light hydrocrackate	814	12.9	24.4	19,895
Alkylate	4,117	4.6	6.7	27,732
Polymer	2,071	8.7	14.9	30,950
Total	47,603 + W			

$$18.2(47,603 + W) = 394,688 + 138W$$

$$866,375 + 18.2W = 394,688 + 138W$$

$$119.8W = 471,687$$

$$W = 3,937 \text{ bbl C4}$$

Total volume of 10.2 psi RVP premium gasoline = 51,540 BPCD

Octane Calculations for Pool Gasoline

Component	BPCD	Vol frac.	MON	Σ MON	RON	Σ RON
n-Butane	3,937	0.077	92.0	7.05	93.0	7.12
Isomerate	5,735	0.111	81.1	9.02	83.0	9.23
Reformate	14,749	0.286	86.9	24.85	98.5	28.18
FCC C ₅ + gasoline	20,117	0.390	76.8	29.97	92.3	36.02
Light hydrocrackate	814	0.016	82.4	1.30	82.8	1.31
Alkylate	4,117	0.080	95.9	7.66	97.3	7.77
Polymer	2,071	0.040	84.0	3.38	96.9	3.89
Total	51,540	1.000		83.23		95.53

$$\text{Pool octane } [(MON + RON)/2] = 88.38 \text{ PON}$$

This is not acceptable, as the octane requirement for pool gasoline is 89 PON. There are several ways of correcting this. Among the possibilities are:

1. Increase severity of reforming to produce a 98.8 or 100 RON clear reformate. (This does not appear to be attractive because the aromatics content of the gasoline would increase and the volume would decrease.)
2. Use an octane blending agent, such as MTBE or ETBE, to improve the pool octane.

Recalculating pool gasoline RVP and PON after adding sufficient MTBE to increase the PON to 89.0, gives the following:

Component	Volume	RVP	VPBI	vol(VPBI)
n-Butane	W	51.6	138.0	138W
Isomerate	5,735	13.5	25.9	148,395
Reformate	14,749	2.2	2.7	39,517
FCC C ₅ + naphtha	20,117	4.4	6.4	128,119
Light hydrocrackate	814	12.9	24.4	19,895
Alkylate	4,117	4.6	6.7	27,732
Polymer	2,071	8.7	14.9	30,950
MTBE	1,593	9.0	15.6	24,832
Total	49,195 + W			419,520 + 138W

$$419,520 + 138W = 18.2(49,195 + W)$$

$$119.8W = 895,349 - 419,520 = 475,829$$

$$W = 3,984 \text{ bbl}$$

Total pool 10.2 psi RVP, 89.0 PON gasoline = 53,179 BPCD

12.5 CASE-STUDY PROBLEM: DIESEL AND JET FUEL BLENDING

In order to meet sulfur specifications for diesel fuel, the basic blending streams, atmospheric gas oil and light coker gas oil (LCGO), are hydrotreated to remove sulfur and to improve cetane number by saturation of olefinic compounds in the LCGO. The hydrotreater is operated to reduce the diesel fuel sulfur to <0.05 wt% (<500 ppm). This hydrotreated product plus a small amount of alkylate bottoms is blended into diesel fuel. This diesel fuel blend also can be used for

No. 2 home heating oil by putting heating oil additives into the base stock rather than using diesel fuel additives.

Laboratory tests are necessary to determine aromatics content of diesel fuel oil and these are not available to students. Therefore, an alternative specification of a cetane index ≥ 45.0 is used.

Diesel Fuel and Home Heating Oil Blend

Component	BPCD	°API	C.I.	lb/h/BPD	lb/h	wt% S	lb/h S
HT diesel	19,686	31.0	47.6	12.70	250,096	0.05	125
Alkylate btms.	310	5.3	5.9	15.02	4,683	0.00	0
Total	19,996	30.5	46.9		254,780	0.05	125

If additional diesel fuel or No. 2 fuel oil production is needed, FCC LGO can be diverted from hydrocracker feed or the hydrocracker can be operated to produce diesel fuel rather than to maximize jet fuel production.

Jet fuel is blended from hydrotreated kerosine from the atmospheric distillation unit, the heavy naphtha fraction (350–400°F) from the atmospheric distillation unit, and the jet fuel fraction (400–525°F) from the hydrocracker.

Jet fuel sulfur specifications are assumed to be the same as those for highway diesel fuel oil.

Jet Fuel Blend

Component	BPCD	°API	lb/h/BPD	lb/h	wt% S	lb/h S
HC jet	8,441	32.2	12.61	106,439	0.00	0
Atm. kero.	11,956	38.5	12.14	145,194	0.05	73
HSR naphtha	4,332	42.5	11.85	51,354	0.11	56
Total	24,729			302,987		129

The relative quantities of diesel fuel and jet fuel can be varied over a reasonable range by changing the cut points and relative quantities of the side-cut and bottoms streams from the middle distillate hydrotreater.

PROBLEMS

1. Using values from Table 12.1, 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 C₅ FCC gasoline to produce a 9.0 psi Reid vapor pressure. What are the research and motor octane numbers of the blend?

2. For the blend of components in problem 1, what would be the posted octane number of the 9.0 psi RVP gasoline if 10 vol% MTBE was added to the gasoline mixture?
3. Calculate the amount of butane needed to produce a 12.5 psi RVP for a mixture of 2730 barrels of LSR gasoline, 2490 barrels of 94 RON reformat, 6100 barrels of heavy hydrocrackate, and 3600 barrels of C₅ + FCC gasoline. How much ETBE must be added to produce a 90 RON product?
4. What is the flash point of a mixture of 2500 barrels of oil with a flashpoint of 120°F, 3750 barrels with a flashpoint of 35°F, and 5000 barrels with a 150°F flashpoint?
5. Calculate the pour point of the following mixture:

Component	Barrels	ASTM 50% temp., °F	Pour point, °F
A	5,200	575	10
B	3,000	425	50
C	6,500	500	65
D	3,250	550	45

6. What is the viscosity of a blend of 2000 barrels of oil with a viscosity of 75.5 cSt at 130°F, 3000 barrels with 225 cSt at 130°F, and 5000 barrels with 6500 cSt at 130°F?
7. Calculate the octane numbers of the final blend and amount of butane needed for producing a 9.5 psi RVP gasoline from 5100 BPSD of LSR gasoline, 3000 BPSD light hydrocrackate, 4250 BPSD alkylate, 10,280 BPSD heavy hydrocrackate, 14,500 BPSD FCC C₅+ gasoline, 14,200 BPSD of 96 RON reformat, and 2500 BPSD of polymer gasoline.
8. Recommend the best method for increasing the clear posted octane number of the pool gasoline in problem 7 by 3 numbers. Estimate the cost involved. Assume any necessary processing units are available and have the necessary capacity.
9. Calculate the number of barrels of n-butane that have to be added to a mixture of 1000 barrels of light thermal gasoline, 1000 barrels of

polymer gasoline, and 1000 barrels of C₄ = alkylate to produce a gasoline product having 10.0 psi Reid vapor pressure.

10. What is the posted octane number and Reid vapor pressure of the gasoline product of problem 3?
11. Calculate the clear octane numbers (RON and MON) and the amount of butane needed for a 12.0 psi RVP gasoline produced from the following:

	BPSD
LSR naphtha	4,200
Light hydrocrackate	1,800
C ₅ + alkylate	4,500
Heavy hydrocrackate	9,150
Reformate (94 RON)	11,500
C ₅ + FCC gasoline	15,600

12. Recommend the best method (lowest capital cost) for increasing the posted octane number of the pool gasoline in problem 11 by 5.5 octane numbers. Estimate the size of the unit and its 1994 construction cost.

NOTES

1. H. L. Hoffman, Hydrocarbon Proc. 59(2), 57–59 (1980).
2. J. L. Keller, Hydrocarbon Proc. 58(5), 127–138 (1979).
3. E. B. Reid and H. I. Allen, Petrol. Refiner 30(5), 93–95 (1951).
4. R. O. Wickey and D. H. Chittenden, Petrol. Refiner 42(6), 157–158 (1963).
5. 31.0°API Iranian Heavy Crude Oil, Chevron Oil Trading Company, 1971.

ADDITIONAL READING

6. Oil Gas J. 88(25), 42–50 (1990).

13

Supporting Processes

There are a number of processes which are not directly involved in the production of hydrocarbon fuels but serve in a supporting role. These include the hydrogen unit, to produce hydrogen for hydrocracking and hydrotreating; the gas processing unit, which separates the low-boiling hydrocarbons; the acid gas treating unit, which removes hydrogen sulfide and other acid gases from the hydrocarbon gas stream; the sulfur recovery unit; and effluent water-treating systems.

13.1 HYDROGEN PRODUCTION AND PURIFICATION

Many refineries produce sufficient quantities of hydrogen for hydrotreating from their naphtha-fed platinum catalyst reforming operations. Some of the more modern plants with extensive hydrotreating and hydrocracking operations, however, require more hydrogen than is produced by their catalytic reforming units. This supplemental hydrogen requirement can be provided by one of two processes: partial oxidation of heavy hydrocarbons such as fuel oil, or steam reforming of light ends such as methane (natural gas), ethane, or propane [6,7]. The steam reforming process employs catalysts, but it should not be confused with the catalytic reforming of naphtha for octane improvement. Relative hydrogen production costs by the two processes are primarily a function of feedstock cost. Steam reforming of methane usually produces hydrogen at a lower cost than partial oxidation of fuel oil. For this reason steam reforming is more widely used in North America than partial oxidation for hydrogen production.

Steam reforming for hydrogen production is accomplished in four steps:

1. *Reforming.* This involves the catalytic reaction of methane with steam at temperatures in the range of 1400 to 1500°F (760–816°C), according to the following equation:



This reaction is endothermic and is carried out by passing the gas through catalyst-filled tubes in a furnace. The catalyst usually is in the form of hollow cylindrical rings ranging up to 3/4 inch in diameter. It consists of 25 to 40% nickel oxide deposited on a low-silica refractory base.

2. *Shift conversion.* More steam is added to convert the CO from step 1 to an equivalent amount of hydrogen by the following reaction:



This is an exothermic reaction and is conducted in a fixed-bed catalytic reactor at about 650°F (343°C). Multiple catalyst beds in one reactor with external cooling between beds are commonly employed to prevent the temperature from getting too high, as this would adversely affect the equilibrium conversion. The catalyst used is a mixture of chromium and iron oxide.

3. *Gas purification.* The third step is removal of carbon dioxide by absorption in a circulating amine or hot potassium carbonate solution. Several other treating solutions are in use. The treating solution contacts the hydrogen and carbon dioxide gas in an absorber containing about 24 trays, or the equivalent amount of packing. Carbon dioxide is absorbed in the solution, which is then sent to a still for regeneration.

4. *Methanation.* In this step, the remaining small quantities of carbon monoxide and carbon dioxide are converted to methane by the following reactions:



This step is also conducted in a fixed-bed catalytic reactor at temperatures of about 700 to 800°F (427°C). Both reactions are exothermic and, if the feed concentration of CO and CO₂ is more than 3%, it is necessary to recycle some of the cooled exit gas to dissipate the heat of reaction. The catalyst contains 10 to 20% nickel on a refractory base.

The preceding description is somewhat idealized, since the actual reactions are more complicated than those shown. The actual process conditions of temperature, pressure, and steam/carbon ratios are a compromise of several factors.

Figure 13.1 is a simplified flow diagram for steam reforming production of hydrogen. Investment and operating costs can be estimated from Figure 13.2 and Table 13.1.

Partial oxidation of fuel oils is accomplished by burning the fuel at high pressures (800 to 1300 psig) with an amount of pure oxygen which is limited to that required to convert the fuel oil to carbon monoxide and hydrogen. Enough water (steam) is added to shift the carbon monoxide to hydrogen in a catalytic

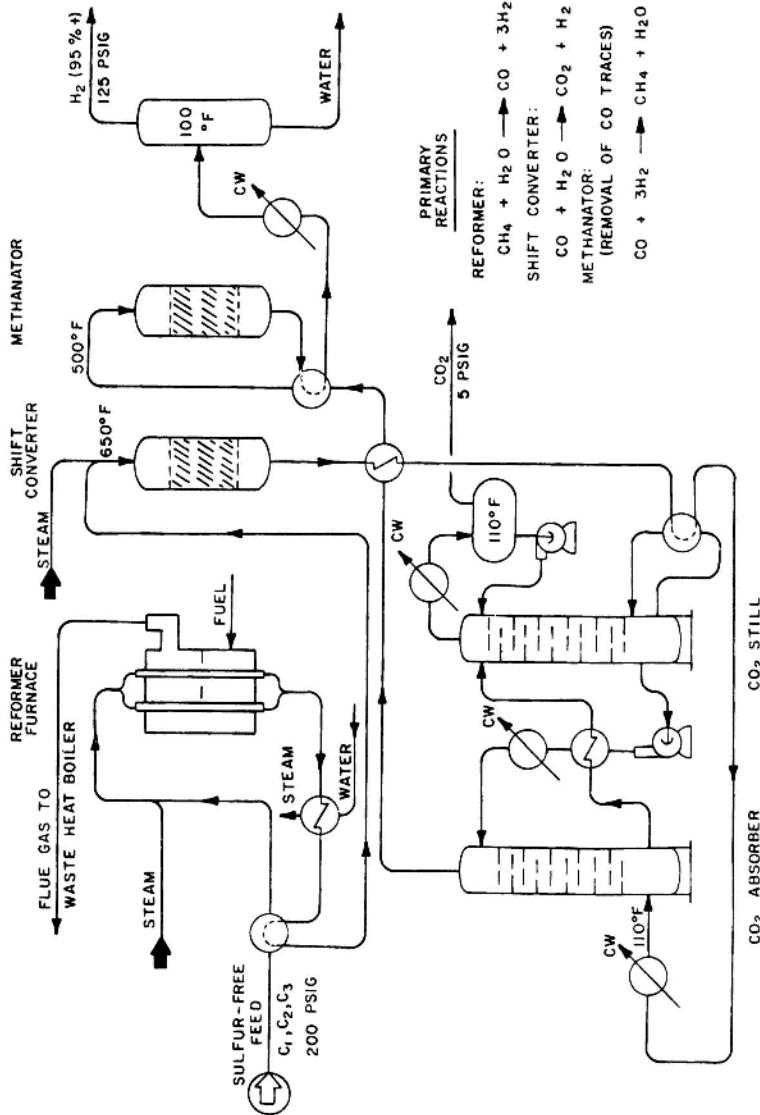


Figure 13.1 Hydrogen production by steam reforming.

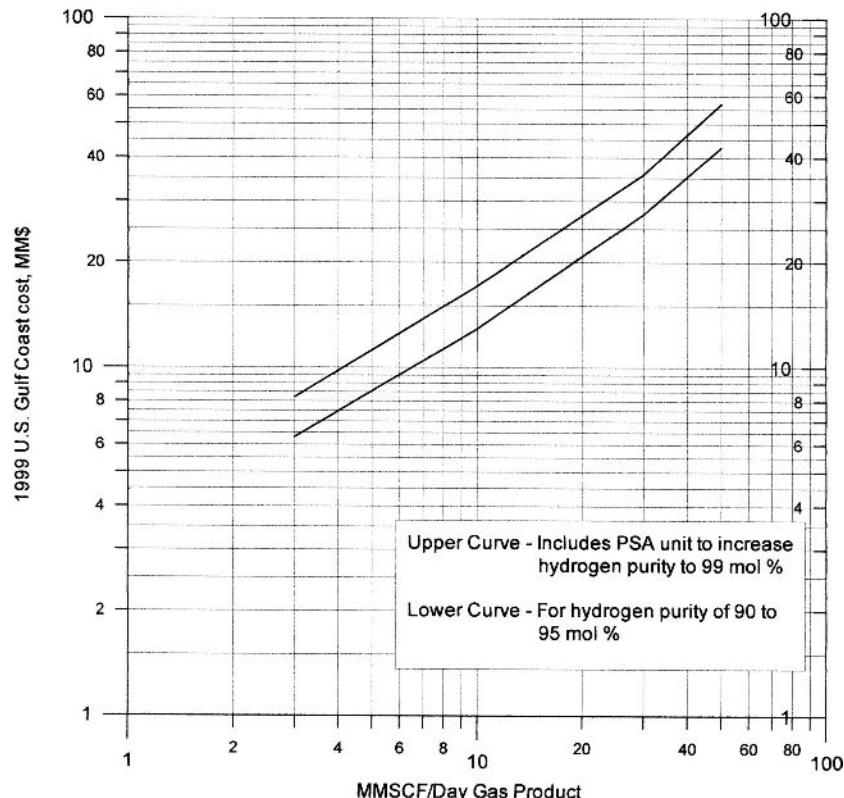
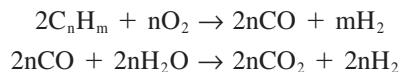


Figure 13.2 Hydrogen production by steam–methane reforming investment cost: 1999 U.S. Gulf Coast. (See Table 13.1.)

shift conversion step. The resulting carbon dioxide is removed by absorption in hot potassium carbonate or other solvents.

Ideally the partial oxidation reactions are as follows:



A good summary of partial oxidation processes has been published [12]. In some refineries a significant amount of hydrogen is present in gas streams vented from hydrocracking or hydrotreating operations. Recovery of this hydrogen should be considered whenever it is necessary to supplement the catalytic

Table 13.1 Hydrogen Production Unit Cost Data

<i>Costs included</i>	
1.	Feed gas desulfurization
2.	Reformer, shift converter, methanator, waste heat boiler, amine (MEA) unit
3.	Hydrogen delivery to battery limits at 250 psig, 100°F, 90 to 95% pure
4.	Initial catalyst charges
<i>Costs not included</i>	
1.	Boiler feed water treating
2.	Cooling water
3.	Dehydration of hydrogen product
4.	Power supply
<i>Utility data</i>	
Power, kWh/lb H ₂	0.15
kWh/kg H ₂	0.33
Cooling water, ^a gal crclt./lb H ₂	65.0
M ³ /kg H ₂	0.54
Fuel, ^b MBTU/lb H ₂	45.0
MJ/kg H ₂	105.0
Treated boiler feed water, ^c gal/lb H ₂	1.0
M ³ /kg H ₂	.01
Catalysts and chemicals, c/lb H ₂	0.50
c/kg H ₂	1.10
Feed gas, ^d mol/mol H ₂	0.26

^a 30°F (17°C) rise.^b LHV basis, heater efficiency included.^c For waste heat boiler.^d Fuel not included.

Note: See Fig. 13.2.

reformer hydrogen to produce an overall refinery hydrogen balance. Three industrial processes are used for recovery of a concentrated hydrogen stream from a dilute gas where the other major components are methane and other hydrocarbon vapors. The three processes are:

1. Cryogenic phase separation
2. Adsorption
3. Diffusion

In the cryogenic phase separation method the gas is cooled to about -200° to -250°F (-129 to -157°C) at pressures ranging from 200 to 500 psig (1380 to 3450 kPa). The resulting vapor phase is typically 90 mol% hydrogen and the liquid phase contains most of the methane and other hydrocarbons. The liquid

phase is expanded to about 50 psig and used to cool the feed gas. This revaporizes the liquid phase. The cold vapor phase is also used to cool the feed gas. Carbon dioxide, hydrogen sulfide, and water vapor must be removed from the feed gas prior to chilling. Conditions required to achieve various hydrogen purities are described in the literature [9].

In the adsorption process the hydrocarbons are adsorbed from the gas on a solid adsorbent (usually a molecular sieve) and the hydrogen leaves the adsorber at the desired purity. Several adsorbent vessels are used, and the feed gas flow is periodically switched from one vessel to another so that the adsorbent can be regenerated. The adsorbed methane and other impurities are released from the adsorbent by simple pressure reduction and purging [4]. Hence, this process is called pressure swing adsorption.

The diffusion process separates hydrogen from methane and other gases by allowing the hydrogen to permeate through a membrane composed of small synthetic hollow fibers [17]. The driving force for this process is the difference between the hydrogen partial pressures on each side of the membrane. Thus a substantial pressure drop must be taken on the hydrogen product to achieve high recoveries.

The most economical method for hydrogen recovery from refinery gas streams depends on the volume of the gas to be processed, the desired hydrogen recovery and purity, and the type of components to be separated. For relatively small streams (less than 2 to 3 MMSCFD) the diffusion process should be considered. For bulk removal of hydrocarbons from relatively large streams (greater than 20 MMSCFD) the cryogenic process should be considered. The adsorption process usually has advantages when the hydrogen must be recovered at purities over 95 mol%.

13.2 GAS PROCESSING UNIT

The main functions of refinery gas processing units are [17]:

1. Recovery of valuable C₃, C₄, C₅, and C₆ components from the various gas streams generated by processing units such as crude distillation units, cokers, cat crackers, reformers, and hydrocrackers
2. Production of a desulfurized dry gas consisting mostly of methane and ethane which is suitable for use as a fuel gas or as feedstock for hydrogen production

In the typical gas processing unit shown in Figure 13.3, low-pressure [0 to 20 psig (0 to 138 kPa)] gases are collected and compressed to approximately 200 psig (1380 kPa) and fed to an absorber-deethanizer. This column usually

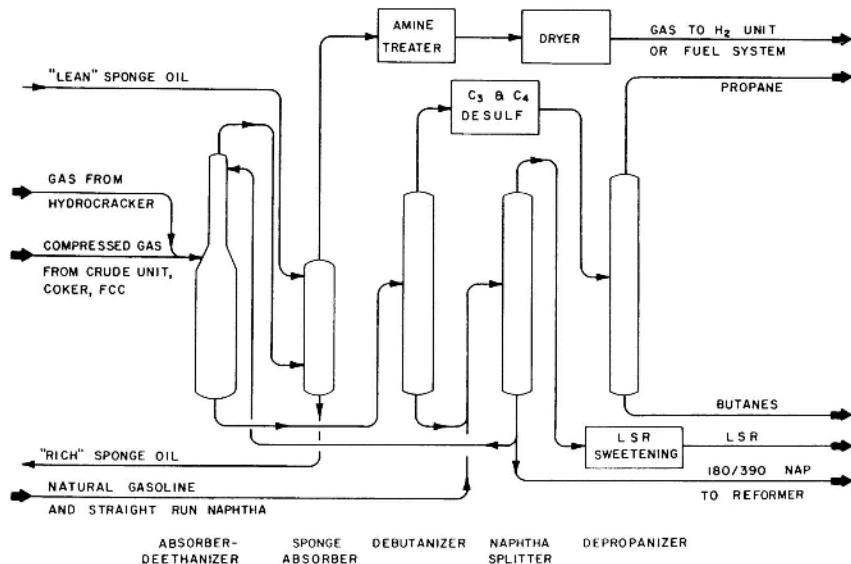


Figure 13.3 Typical gas processing unit.

contains 20 to 24 trays in the absorption section (top) and 16 to 20 trays in the stripping section (bottom). Lean absorption oil is fed to the top tray in sufficient quantity to absorb 85 to 90% of the C₃s and almost all of the C₄s and heavier components from the feed gas and from vapor rising from the stripping section. The lean absorption oil is usually a dehexanized naphtha with an end point (ASTM) of 350 to 380°F (177 to 193°C).

Due to the vapor-liquid equilibrium conditions on the top tray a significant amount of the lighter hydrocarbons (such as C₇) are vaporized from the lean oil and leave the top of the column with the residue gas. This material is recovered in the sponge absorber. The sponge absorber usually contains 8 to 12 trays. A heavy molecular weight, relatively nonvolatile material, such as kerosine or No. 2 fuel oil, is used as sponge oil. This sponge oil is derived as a side cut from the coker fractionator or cat cracker fractionator. The rich sponge oil is returned as a side feed to the column from which it was derived for stripping of the recovered lean oil light ends.

Sufficient reboil heat is added to the bottom of the stripping section of the absorber-deethanizer to eliminate any absorbed ethane and methane from the bottom liquid product. This deethanized rich oil then flows to a debutanizer column where essentially all the recovered propane, propylene, butanes, and butyl-

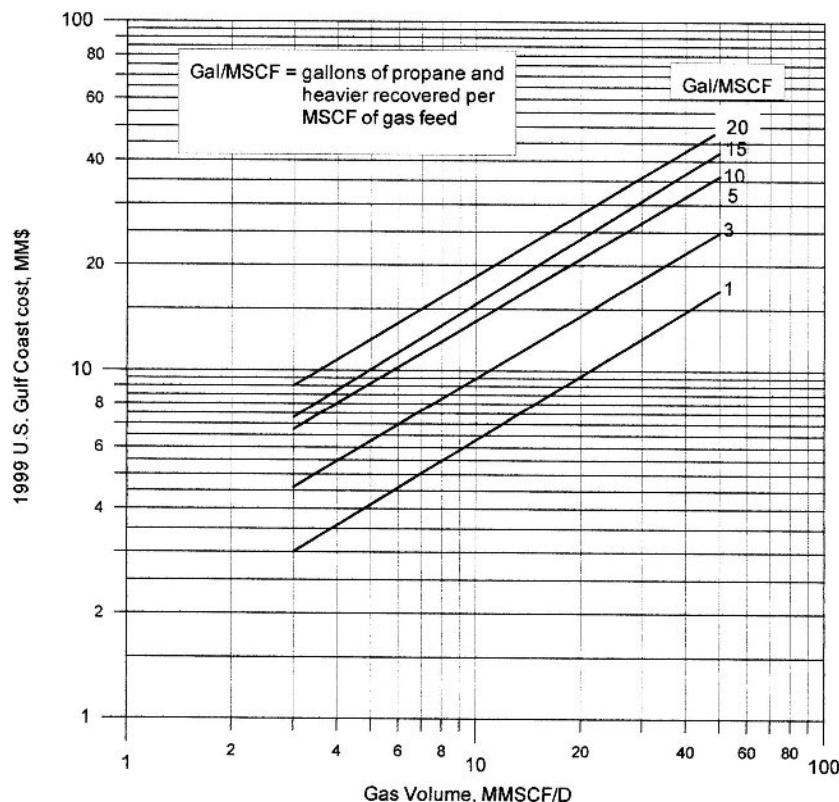


Figure 13.4 Refinery gas processing unit investment cost: 1999 U.S. Gulf Coast. (See Table 13.2.)

enes are fractionated and taken off as overhead product. This type of debutanizer usually operates in the range of 125 to 150 psig (862 to 1035 kPa) and contains 26 to 30 trays. The bottom product from the debutanizer contains pentanes and heavier hydrocarbons recovered from the gas feed to the absorber-deethanizer plus the lean oil. This material is fed to a naphtha splitter. Natural gasoline and/or straight-run naphtha are sometimes fed to this same column. The naphtha splitter produces a C₅, C₆ light straight-run cut overhead and suitable lean absorption oil from the bottom. Bottoms product in excess of the lean oil requirement can be fed to a hydrotreater and reformer. The light straight-run product is desulfurized (or sweetened) and used directly as gasoline blend stock or else isomerized and then used as gasoline blend stock.

The overhead C₃, C₄ product from the debutanizer is condensed, desulfurized, and fed to a depropanizer for separation into propane and butane. The desulfurization is usually accomplished by molecular sieve treating which simultaneously dehydrates the stream.

Overhead gas from the sponge oil absorber is treated by contact with an aqueous solution of diethanolamine (DEA) or other solvents for removal of carbon dioxide and hydrogen sulfide. Extracted hydrogen sulfide is converted to elemental sulfur in a separate unit.

See Table 13.2 and Figure 13.4 for gas processing unit cost data.

13.3 ACID GAS REMOVAL

Gases from various operations in a refinery processing sour crudes contain hydrogen sulfide and occasionally carbonyl sulfide. Some hydrogen sulfide in refinery gases is formed as a result of conversion of sulfur compounds in processes such as hydrotreating, cracking, and coking. Until the period of about 1965 to 1970, it was common practice simply to burn this hydrogen sulfide along with other light gases as refinery fuel, since its removal from the gases and conversion to elemental sulfur was not economical. Recent air pollution regulations, however, require that most of the hydrogen sulfide be removed from refinery fuel gas and converted to elemental sulfur.

In addition to hydrogen sulfide many crudes contain some dissolved carbon dioxide which through distillation finds its way into the refinery fuel gas. These components—hydrogen sulfide and carbon dioxide—are generally termed acid gases. They are removed simultaneously from the fuel gas by a number of different processes, [8] some of which are:

Chemical solvent processes

1. Monoethanolamine (MEA)
2. Diethanolamine (DEA)
3. Methyl-diethanolamine (MDEA)
4. Diglycolamine (DGA)
5. Hot potassium carbonate

Physical solvent processes

1. Selexol
2. Propylene carbonate
3. Sulfinol
4. Rectisol

Table 13.2 Refinery Gas Processing Unit Cost Data*Costs included*

1. Compressors to raise gas pressure from 5 psig to approximately 200 psig
2. Absorber deethanizer utilizing naphtha as absorption oil
3. Sponge oil absorber
4. Debutanizer
5. Naphtha splitter^a
6. C₃/C₄ molecular sieve desulfurizer
7. Depropanizer
8. All related heat exchangers, pumps, scrubbers, accumulators, etc.
9. Initial charge of molecular sieves

Costs not included

1. Gas sweetening^b
2. Butane splitter
3. Hot oil or steam supply for reboilers
4. Liquid product storage
5. Cooling water supply
6. Sponge oil distillation facilities (usually accomplished in cat cracker fractionator, coker fractionator, or crude tower)
7. LSR sweetening^c

Utility data

Process fuel, ^d MBTU/gal total liquid products	14.0
MJ/M ³	3,900.0
Compressor, ^e BHP/MMscfd gas	150.0
kWh/M ³ /day	0.1
Other power, ^f kWh/gal total liquid products	.06
kWh/M ³	16.0
Cooling water, ^g gal/gal total liquid products	100.0

^a When "outside" natural gasoline or straight-run naphtha is fed to naphtha splitter, increase investment obtained from Fig. 13.4 by \$100 for each BPD of such material. This material is not to be included when determining the gal/Mscf parameter for Fig. 13.4.

^b See Fig. 13.6 and Table 13.3.

^c Add \$40 for each BPD of LSR naphtha to be sweetened by caustic washing or "doctor treating."

^d Process fuel requirement can frequently be obtained from heat exchange with hot oil from other refinery units. If sufficient detail is not available to ascertain that heat input can be obtained by exchange as stated above; assume that fired heater must be provided.

^e Gas compressor will generally be motor driven when gas volume is less than 5 MMscfd. In this case it is necessary to add the compressor horsepower to the power requirement shown. For gas volumes in excess of 5 MMscfd, the compressors may be driven by electric motors, gas turbines, reciprocating gas engines or steam turbines. Appropriate adjustments should be made to the utility requirements to provide for operation of gas compressors.

^f Power shown is for operation of process pumps only. All cooling is done with cooling water. No power included for aerial coolers.

^g 30°F (17°C) rise.

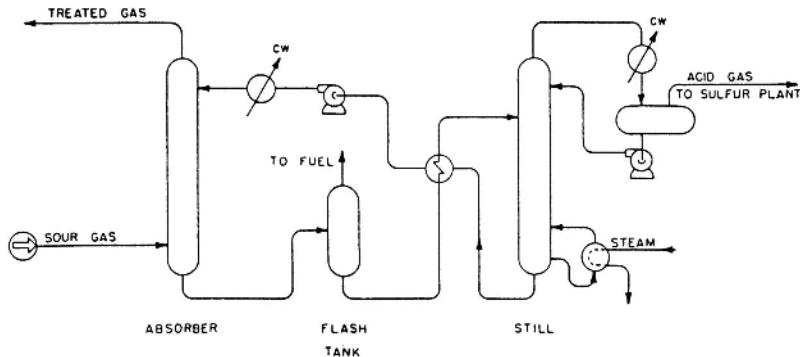


Figure 13.5 Amine treating unit.

Dry adsorbents processes

1. Molecular sieve
2. Activated charcoal
3. Iron sponge
4. Zinc oxide

An excellent bibliography on this subject is given in the GPSA data book [10]. The selection of available processes for a given application involves many considerations. In general, the diethanolamine process has been the most widely used for refinery gas treating. This process uses an aqueous solution of diethanolamine with concentrations of the DEA in the range of 15 to 30 wt%. Methyl-diethanolamine can be used to replace diethanolamine to reduce the absorption of carbon dioxide and thereby produce an acid gas with a higher content of hydrogen sulfide. This provides some marginal improvement in Claus unit capacity or sulfur recovery efficiency. The solution is pumped to the top of an absorber containing about 20 to 24 trays or an equivalent amount of packing such as Pall rings. Hydrogen sulfide and carbon dioxide are removed from the gas by absorption into the solution. Rich solution from the absorber flows into a flash tank which is operated at a lower pressure than the absorber and permits any dissolved or entrained methane and ethane to be vented from the system. The rich solution is then pre-heated and flows to a regenerator or still where the acid gases are stripped from the solution by steam generated in a reboiler. The still also contains about 20 to 24 trays or an equivalent amount of packing. The acid gases are taken from the top of the still through a condenser where most of the steam is condensed. This condensate is separated from the acid gases and returned to the top of the still as reflux. The acid gases are then sent to sulfur recovery unit where the hydrogen sulfide is converted to elemental sulfur. The lean solution is cooled and returned to the top of the absorber (Fig. 13.5)

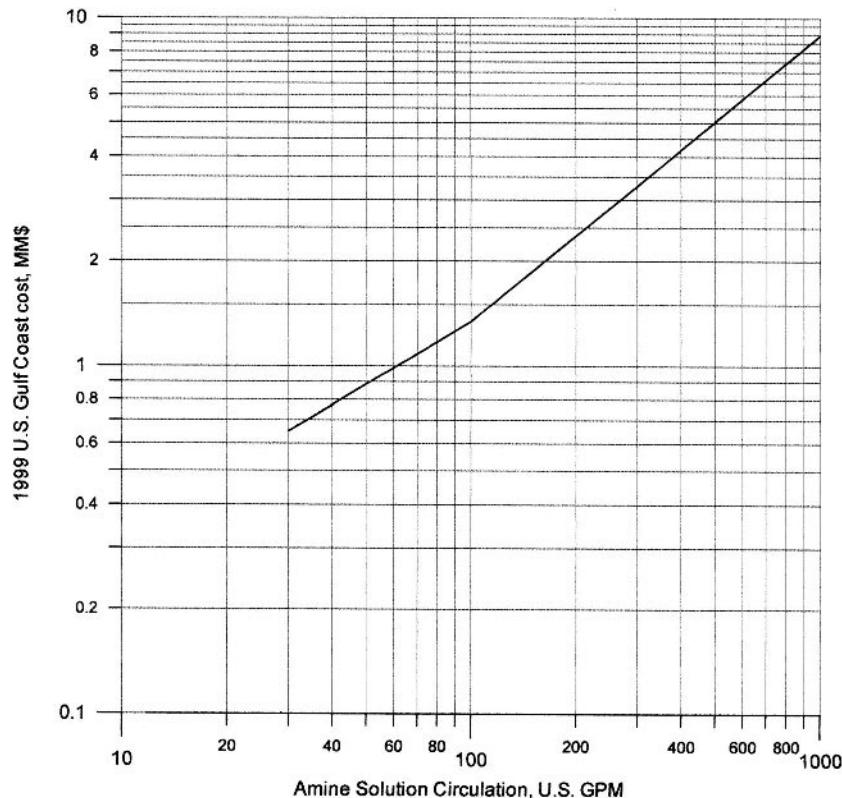


Figure 13.6 Amine-gas treating unit investment cost: 1999 U.S. Gulf Coast. (See Fig. 13.5.)

Operating conditions are usually such that the treated gas will contain less than 0.25 grain of sulfur per 100 scf (4 ppm H₂S) and less than 1.5 vol% carbon dioxide. This is controlled by the amount of solution circulated and the amount of steam generated in the reboiler. The solution rate is set at a value which is in the range of 0.15 to 0.40 gal/scf of acid gases absorbed. The heat input to the reboiler is typically about 600 to 1200 Btu/gal of circulating solution. It is generally considered advisable to have high solution rates to minimize corrosion. However, high solution rates result in increased investment and utility costs, and therefore a compromise is made in the design and operating conditions. Figure 13.6 and Table 13.3 give capital cost and operating cost information.

Table 13.3 Amine Gas Treating Unit Cost Data

<i>Costs included</i>	
1.	Conventional, single flow, MEA or DEA treating system.
2.	Electric-motor driven pumps.
3.	Steam-heated reboiler.
4.	Water-cooled reflux condenser and solution cooler.
<i>Costs not included</i>	
1.	Acid gas disposal.
2.	Cooling water supply.
3.	Steam (or hot oil) supply for regenerator reboiler.
<i>Utility data</i>	
Power, ^a kWh/gal solution circulated	0.01
kWh/M ³	2.64
Fuel, ^b BTU/gal solution circulated	1,000.00
MJ/M ³	280.00
Cooling water, ^c gal/gal solution circulated	4.40
Amine make-up, ^d lb/MMscf inlet gas	2.50
g/M ³	.04

^a Assumes amine pumps driven by electric motors and cooling done with water.

^b Reboiler heat usually supplied as 60 psig steam.

^c 30°F (17°C) rise.

^d In actual practice, amine solution circulation varies in the range of 0.15 to 0.40 gallon per scf of acid gas (H₂S plus CO₂) removed. For preliminary estimates, a value of 0.30 gallon of solution circulation per scf of acid gas can be assumed.

Note: See Fig. 13.5.

13.4 SULFUR RECOVERY PROCESSES

Until 1970, the major reason to recover sulfur from refinery gases was an economic one. The hydrogen sulfide was commonly used with other gases as a refinery fuel and the sulfur dioxide concentrations in the flue gases were within acceptable limits. In those refineries with sulfur recovery units the typical recovery was in the range of 90 to 93% of that contained in the hydrogen sulfide stream. Implementation of federal and state regulations now require recovery of about 99% or more of the sulfur in refinery gas. This requires a two-stage process with a modified Claus unit for the first stage followed by a second stage such as the SCOT process [2,3].

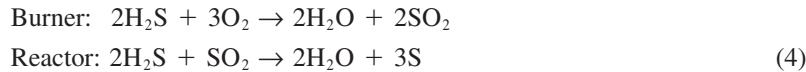
Modified Claus Process

The most practical method for converting hydrogen sulfide to elemental sulfur is the modified Claus process. The original process was reported by Chance and

Claus in 1885 [1,13]. Today, various modifications of the process are used depending upon the hydrogen sulfide concentrations in the gas. The modified Claus process best suited for acid gas containing 50% or more hydrogen sulfide is the partial combustion ("once-through") process. Figure 13.7 is a simplified flow diagram of this process, and Figures 13.8 and 9, and Table 13.4 give unit cost data.

Present refinery practice generally provides for removal of hydrogen sulfide from refinery gas streams by solvent absorption as discussed in the previous section. The acid gas stream recovered from these treating processes contains some carbon dioxide and minor amounts of hydrocarbons, but in most cases the hydrogen sulfide content is over 50%. Therefore, the once-through Claus process is used in most sour crude refineries to convert the hydrogen sulfide to elemental sulfur.

In the partial combustion (once-through) process, the hydrogen sulfide-rich gas stream is burned with one-third the stoichiometric quantity of air and the hot gases are passed over an alumina catalyst to react sulfur dioxide with unburned hydrogen sulfide to produce free sulfur. The reactions are:



The burner is located in a reaction chamber which may be either a separate vessel or a part of the waste heat boiler. The purpose of the reaction chamber is to allow sufficient time for the combustion reaction to be completed before the gas temperature is reduced in the waste heat boiler.

Ammonia frequently is present in the Claus unit feed streams and must be completely destroyed in the reaction furnace to avoid plugging of equipment with ammonium salts. Specially designed burners and combustion zones have been developed for this purpose [14].

The waste heat boiler removes most of the exothermic reaction heat from gases by steam generation. Many types of waste heat boilers are in use. Usually they are arranged so that the gas flows through several tube passes in series with chamber, or "channels," where a portion of the gases may be withdrawn at elevated temperatures to use for reheating the main gas flow stream prior to the catalytic converters. Some elemental sulfur is often condensed and removed from the gas in the waste heat boiler. In some plants a separate condenser is used after the waste heat boiler. The gas temperature entering the first catalytic converter is controlled at about 425 to 475°F (218 to 246°C) which is necessary to maintain the catalyst bed above sulfur dewpoint in order to avoid saturating the catalyst with sulfur and thereby deactivating the catalyst. The reaction between hydrogen sulfide and sulfur dioxide in the converter is also exothermic. Gases from the converter are cooled in the following condenser for removal of most of the elemental sulfur as liquid.

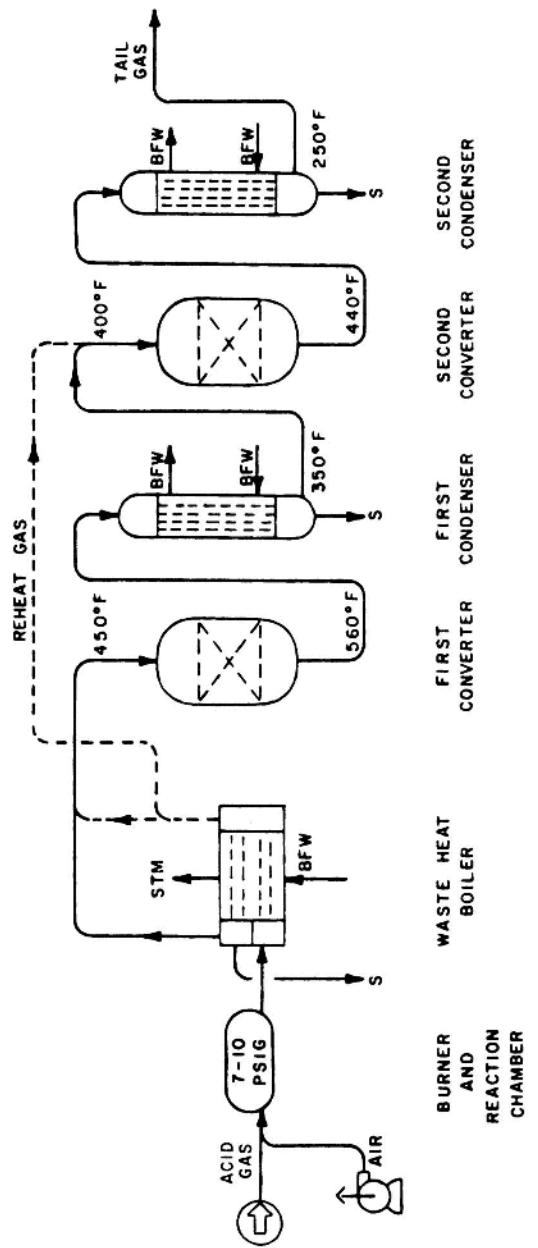


Figure 13.7 Once-through Claus sulfur process.

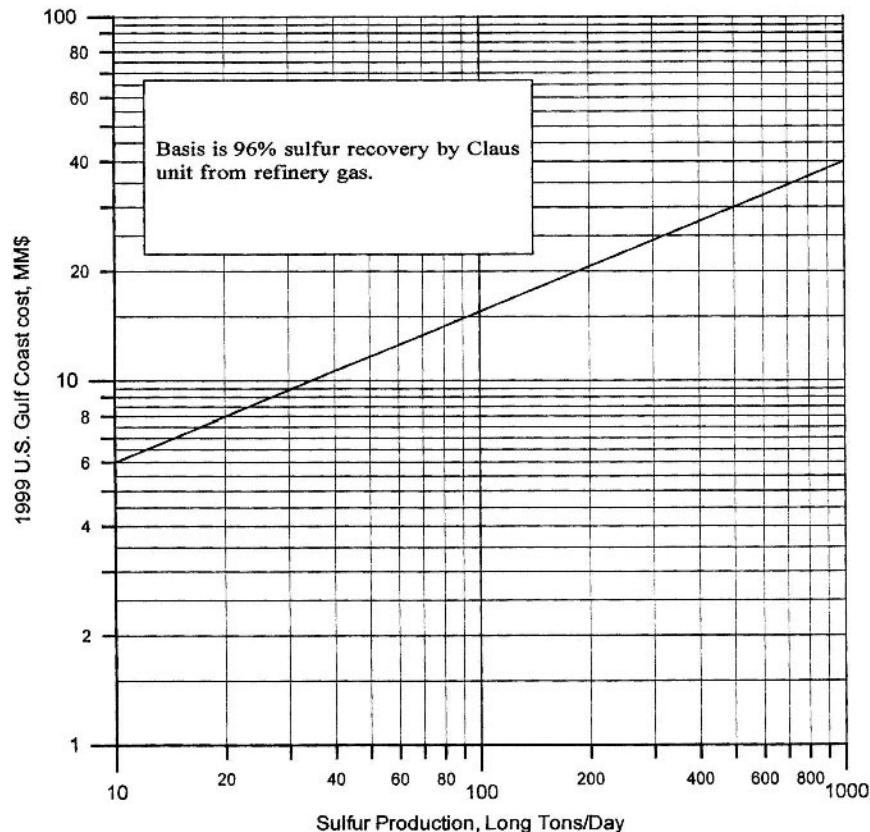


Figure 13.8 Claus sulfur plant investment cost: 1999 U.S. Gulf Coast. (See Table 13.4.)

The condenser outlet temperatures must be maintained above about 275°F (135°C) to avoid solidifying the sulfur. Two converters and condensers in series are indicated in Figure 13.7, but most plants have three converters.

Modifications of the once-through process include various reheat methods for the converter feed temperature control such as heat exchange with converter outlet gases, in-line burners, and fired reheaters. Overall recovery is usually not over 96% and is limited by thermodynamic considerations as described in the literature [1].

Table 13.4 Claus Sulfur Recovery Unit Cost Data

<i>Costs included</i>	
1.	Once-through modified Claus unit designed for 94 to 96% recovery
2.	Three converters (reactors) with initial charge of catalyst
3.	Incinerator and 150 ft tall stack
4.	Sulfur receiving tank and loading pump
5.	Waste heat boiler
<i>Costs not included</i>	
1.	Boiler feed water treating
2.	Boiler blowdown disposal
3.	Solid sulfur storage or reclaiming
4.	Sulfur loading facilities (except for loading pump)
5.	Supply of power and water
6.	Tail-gas clean-up process unit
<i>Utility data</i>	
Power, kWh/long ton of sulfur	100
kWh/MT	98
Boiler feed water, gal/long ton of sulfur	820
M ³ /MT	3
Waste heat steam production at 250 psia (1740 kPa)	
lb/long ton sulfur	6500
kg/MT	2900
Fuel	None
Cooling water	None

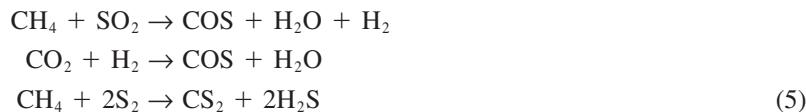
Note: See Fig. 13.8.

When refineries process crude oils with sulfur contents higher than design, it is necessary to recover more sulfur in the Claus unit. An economical method for increasing the capacity of Claus units is the substitution of oxygen for a portion of the combustion air needed in the reaction furnace. This modification can increase the capacity for sulfur production by 50% or more at a relatively small capital cost [15].

Carbon-Sulfur Compounds

Carbonyl sulfide (COS) and carbon disulfide (CS₂) have presented problems in many Claus plant operations due to the fact that they cannot be converted completely to elemental sulfur and carbon dioxide. These compounds may be formed

in the combustion step by reaction of hydrocarbons and carbon dioxide as shown below:



Many more complex reactions are possible. These compounds, if unconverted, represent a loss of recoverable sulfur and an increase in sulfur emission to the atmosphere. Special alumina catalyst is significantly more effective in converting both COS and CS₂ to elemental sulfur than the conventional bromide catalyst [17].

The conversion of COS and CS₂ in the Claus unit may not be sufficient to meet allowable emission limits in some locations. Modifications to the tail-gas unit have been designed to reduce these components to less than 20 ppmv in the outlet. Catalyst containing titanium is used in the tail-gas unit, which is a SCOT process as described in the following paragraph [16].

SCOT Process

As discussed above, Claus unit tail-gas contains small amounts of carbonyl sulfide and carbon disulfide in addition to hydrogen sulfide and sulfur dioxide. In Shell's SCOT process, the Claus tail-gas is combined with a relatively small quantity of hydrogen or a mixture of carbon monoxide plus hydrogen and heated to about 480 to 570°F (250 to 300°C). This hot gas then flows through a fixed catalyst bed where the various sulfur compounds are converted to hydrogen sulfide by reaction with hydrogen. The reactor effluent is cooled to ambient temperature and the hydrogen sulfide is selectively absorbed from the gas with an aqueous amine solvent. The hydrogen sulfide is regenerated from the solvent in a conventional amine still and recycled to the Claus unit feed. The hydrogen sulfide content of the gas exiting the amine absorber is typically in the range of 50 to 400 ppm mol basis [5]. This gas is incinerated to convert the hydrogen sulfide to sulfur dioxide before venting.

Recoveries in excess of 99% can be obtained by addition of tail-gas processing units such as the SCOT process. The addition of a SCOT unit increases the cost of the sulfur recovery facilities by a factor of about 2.0.

13.5 ECOLOGICAL CONSIDERATIONS IN PETROLEUM REFINING

Since the end of World War II, petroleum refineries have made special efforts to minimize discharge of wastes into the surrounding environment. This voluntary

control of emissions was done on the basis of safety, fuel economy, and the economic advantages of good maintenance. Government regulations now require refineries to add facilities for stringent control of emissions or losses of substances deemed to be undesirable or potentially hazardous. Related extra capital costs vary widely but for a new refinery the costs are frequently considered to be in the range of 15 to 20% of the total investment. The total additional cost for installation, operation, and maintenance of these facilities is estimated to be about 10 to 20 cents (U.S., 1993) per gallon of refined products.

The potentially harmful substances which must be carefully controlled include discharge of liquid hydrocarbons into streams, rivers, lakes, and oceans and relief of hydrocarbon vapors into the atmosphere. Waste water must be essentially free of toxic or carcinogenic chemicals. Benzene content of water must be reduced to less than 10 ppm by weight. Stack gases from boilers, process furnaces, FCC regenerators, and internal combustion engines must meet strict limits relative to potentially harmful compounds and particulates. Hydrocarbons, oxides of sulfur (SO_X) and oxides of nitrogen (NO_X) are examples of stack gas components which are limited to very low amounts. Noise levels must also be controlled. Some of the more common control methods are discussed in the following sections.

13.6 WASTE WATER TREATMENT

Typical sources of waste water in refineries are:

1. Runoff surface drainage from leaks, open drains, and spills carried away by rain
2. Crude and product storage tank water drains
3. Desalter water
4. Water drains from atmospheric still reflux drums
5. Water drains from barometric sumps or accumulators on vacuum tower ejectors
6. Water from hydraulic decoking of coke drums
7. Condensed steam from coke-drum purging operations
8. Product fractionator reflux drums on units such as catalytic crackers, hydrotreaters, alkylation units, light ends recovery, and others
9. Cooling tower and boiler water blowdown

Surface water is collected in open trenches and sewer systems and water from process vessels is collected in pipe drain systems. Practically all vessels, tanks, pumps, and low spots in piping are connected to a closed drain system.

Any water which may be contaminated with oil is skimmed in large concrete sumps called API separators. The skimmed oil is pumped to slop tanks and then reprocessed. Some water from the API separators is used in the desalters and the balance is purified by coagulation of impurities in flotation tanks. In this step a mixture of ferric hydroxide and aluminum hydroxide is used to cause the impurities to form a froth or slurry which floats to the top of the water. The froth is withdrawn and thickened or settled. The resulting sludge is then incinerated.

Water from the flotation tanks is oxygenated under pressure and then fed to digestion tanks which may also receive sanitary sewage from the refinery. A controlled flock of bacteria is maintained in the digestion tanks to consume any remaining oils or phenolic compounds. A certain amount of the bacteria is continuously withdrawn from the digestion tanks and incinerated. Water from the digestion tanks may be given a final "polish" in sand filters and reused in the refinery or aerated to increase the oxygen content and subsequently discharged to natural drainage.

Oil-free water blowdown from cooling towers and boilers is neutralized and either evaporated in solar ponds, injected into disposal wells, or diluted with other treated waste water to lower the dissolved solids content and then aerated and discharged to natural drainage.

Acid sludge from sources such as alkylation units is collected in a separate system and neutralized before going to the API separators.

Sour water drained from vessels such as the atmospheric still reflux drums is stripped in a bubble tower with either gas or steam to eliminate dissolved hydrogen sulfide and other organic sulfur compounds before feeding this water to the API separators. The stripped vapors are processed for sulfur recovery as described in Sections 13.3 and 13.4. As a precaution against spills all storage tanks are normally surrounded by earthen dikes of sufficient size to retain the entire volume of oil which the tank can hold.

13.7 CONTROL OF ATMOSPHERIC POLLUTION

The major sources of potential atmospheric pollution include combustion gases exhausted from boilers, process furnaces, the FCC regenerator, and hydrocarbon vapors vented from process equipment and storage tanks. The sulfur dioxide content of combustion gases is controlled to local regulations by limiting the sulfur content of the fuel. Tail-gases from Claus sulfur recovery units are further processed in a tail-gas cleaning unit (TGCU) converting low concentrations of hydrogen sulfide and sulfur dioxide into elemental sulfur and thus achieving over 98% recovery of the inlet sulfur. The final tail-gas is then incinerated and vented

through tall stacks, often 200 feet or more in height, and at sufficient velocity so that resulting ground level sulfur dioxide concentrations are well within safe values.

Hydrocarbon vapors from process equipment and storage tanks are collected in closed piping systems and used for refinery fuel or, in the event of high venting rates during a process upset, the vapors are burned in a flare or burn pit, with special provisions to prevent visible smoke and to ensure complete combustion.

Fluid catalytic crackers are provided with two- to three-stage cyclones to minimize loss of catalyst dust to the atmosphere. In some cases, electrostatic precipitators are employed along with waste heat boilers to eliminate essentially all visible dust from catalytic cracker regenerator flue gases.

Crushing and screening of coke from delayed coking units is generally done in the wet condition to prevent dust losses to the air. The final coke product is often stored in buildings to prevent wind from carrying fine particles into the atmosphere.

13.8 NOISE LEVEL CONTROL

Noise in refineries originates from rotating machinery such as cooler fans, turbines, compressors, engines, and motors. High velocity flow of fluids through valves, nozzles, and piping also contributes to the general noise level. To control these noises, equipment causing the noise is enclosed or insulated. Proper intake and exhaust silencers are provided on blowers, combustion engines, and turbines. In newer refineries the land area used is sufficient so that, combined with the above noise control measures, essentially no noise is heard outside the refinery boundaries.

13.9 CASE-STUDY PROBLEM: SATURATED GAS RECOVERY, AMINE, AND SULFUR RECOVERY UNITS

In order to select the size of the auxiliary units, it is necessary to summarize the outputs of all the major process units to find the quantities of the light components, sulfur, and hydrogen available. The hydrogen requirements of the various hydrotreaters and the hydrocracker must be summarized to determine the hydrogen consumed. See Tables 13.5 through 13.10.

The unsaturated gas plant is included in the cost of the FCC unit and therefore the saturated gas plant is the one to be sized for capital and operating costs.

Table 13.5 Light Ends Summary for Saturated Gas Plant

	H ₂ (lb/h)	C ₂ and lighter (lb/h)	C ₃ (lb/h)	iC ₄ (BPCD)	nC ₄ (BPCD)	S in H ₂ S (lb/h)
Crude units		372	2,341	159	629	
Coker		16,988	6,218	89	418	1,873
Hydrocracker		340	1,263	307	151	1,391
Reformer and HT	3,480	2,050	3,690	360	505	574
Mid dist. HT		1,385	2,500	634	315	1,895
FCC HT		1,193	1,476	374	186	5,037
Isomerization			215	47	128	69
Alkylation					331	
Total	3,480	22,328	17,703	1,970	2,663	10,839

Table 13.6 Saturated Gas Processing Unit Material Balance

Feed to unit	BPCD	lb/h	MW	mol/h	MMscfd	gal liq/Mscf gas feed
H ₂ S		9,377	34	276	2.51	
C ₂ and lighter		6,691	23	291	2.65	
C ₃	1,472	11,105	44	252	2.30	4.7
iC ₄	1,559	15,873	58	274	2.49	5.0
nC ₄	2,008	18,674	58	322	2.93	6.5
Total	5,039	62,065			13.05	16.2

Table 13.7 Saturated Gas Processing Unit and Amine Unit Utility Requirements

	Gas processing unit		Amine unit	
	Per unit	Per day	Per unit	Per day
Fuel, MMBtu	0.014	9,787	0.001	939
Comp. bhp	150	6,957		
Power, MkWh	0.00006	13	0.00001	9
Cooling water circ., Mgal	0.01	21,164	0.0044	2,348
Amine, lb			2.5	116

Table 13.8 Claus and SCOT Units Material Balance

	scfm	lb/h	S, lb/h	LT/d
<i>Feed</i>				
H ₂ S	2,158	11,615	10,933	
N ₂		19,742		
O ₂		5,944		
Total		37,757		
<i>Products</i>				
N ₂		19,742		
H ₂ O		6,687		
Sulfur	10,933	10,933	117.1	
Total		37,757		

Table 13.9 Claus and SCOT Units Utility Requirements

	Claus unit		SCOT unit	
	Per unit	Per day	Per unit	Per day
Fuel, MMBtu			0.001	94
Power, MkWh	0.100	12	0.00001	1
Cooling water circ., Mgal			0.0044	235
Boiler water, Mgal	0.82	2.4		
Steam prod., Mlb	6.5	773.5		
Amine, lb			2.5	11.6

Table 13.10 Hydrogen Unit Utility Requirements

	Per lb H ₂	Total per day	Total per min
Power, MkWh	0.00015	31.7	
Cooling water circ., Mgal	0.065	13,720	5.66
Fuel, MMBtu	0.045	9,499	
BFW, Mgal	0.001	211	
Feed gas, Mscf	0.26/Mscf	10,920	
Cat. and chem., \$	0.005	1,108	

Note: Unit capacity: 42,000,000 scf/d H₂ = 221,636 lb/d H₂.

The amine gas treating unit removes the acid gases (hydrogen sulfide and carbon dioxide) from the gaseous streams in the saturated and unsaturated gas plants. No information is available concerning the concentration of carbon dioxide and it will not be considered for this problem. Typically, the carbon dioxide content of the gas to the unsaturated gas plant is about 1% by volume but here the operation of this unit is included in the FCC operating utilities. The gases from the saturated gas plant are treated in this unit.

SCOT unit utilities depend on the amount of CO₂ in the Claus tail-gas and the purity of hydrogen being fed to the reactor. The type of amine solution used also varies the amount of utilities. The utilities for the SCOT unit can be estimated using the quantities given for amine units in Table 13.3.

A hydrogen balance around the hydrogen consuming and producing units (hydrotreaters, hydrocracker, isomerization, and catalytic reformer) shows a hydrogen consumption of 55,691 Mscf/d, hydrogen production from the reformer of 20,493 Mscf/d, with a net hydrogen deficiency of 35,197 Mscf/d. Environmental restrictions which limit aromatic hydrogen content of gasolines may require reformer severity reduction in the future with a corresponding reduction in hydrogen production from this source. Therefore, a hydrogen unit will be built with a capacity of 42,000 Mscf/d of hydrogen, an approximately 20% safety factor. A steam reforming unit producing 95% pure hydrogen and using natural gas as feed will be constructed for the additional hydrogen needed.

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14

Lubricating Oil Blending Stocks

The large number of natural lubricating and specialty oils sold today are produced by blending a small number of lubricating oil base stocks and additives. The lube oil base stocks are prepared from selected crude oils by distillation and special processing to meet the desired qualifications. The additives are chemicals used to give the base stocks desirable characteristics which they lack or to enhance and improve existing properties. The properties considered important are:

1. Viscosity
2. Viscosity change with temperature (viscosity index)
3. Pour point
4. Oxidation resistance
5. Flash point
6. Boiling temperature
7. Acidity (neutralization number)

Viscosity. The viscosity of a fluid is a measure of its internal resistance to flow. The higher the viscosity, the thicker the oil and the thicker the film of the oil that clings to a surface. Depending upon the service for which it is used, the oil needs to be very thin and free-flowing or thick with a high resistance to flow. From a given crude oil, the higher the boiling point range of a fraction the greater the viscosity of the fraction. Therefore the viscosity of a blending stock can be selected by the distillation boiling range of the cut.

Viscosity index. The rate of change of viscosity with temperature is expressed by the viscosity index (VI) of the oil. The higher the VI, the smaller its change in viscosity for a given change in temperature. The VIs of natural oils range from negative values for oils from naphthenic crudes to about 100 for paraffinic crudes. Specially processed oils and chemical additives can have VIs of 130 and higher. Additives, such as polyisobutylenes and polymethacrylic acid esters, are frequently mixed with lube blending stocks to improve the viscosity-temperature properties of the finished oils. Motor oils must be thin enough at

low temperatures to permit easy starting and viscous enough at engine operating temperatures [180 to 250°F (80 to 120°C)] to reduce friction and wear by providing a continuous liquid film between metal surfaces.

Pour Point. The lowest temperature at which an oil will flow under standardized test conditions is reported in 5°F or 3°C increments as the pour point of the oil. For motor oils, a low pour point is very important to obtain ease of starting and proper start-up lubrication on cold days.

There are two types of pour points, a viscosity pour point and a wax pour point. The viscosity pour point is approached gradually as the temperature is lowered and the viscosity of the oil increases until it will not flow under the standardized test conditions. The wax pour point occurs abruptly as the paraffin wax crystals precipitate from solution and the oil solidifies. Additives that affect wax crystal properties can be used to lower the pour point of a paraffin base oil.

A related test is the cloud point, which reports the temperature at which wax or other solid materials begin to separate from solution. For paraffinic oils, this is the starting temperature of crystallization of paraffin waxes.

Oxidation resistance. The high temperatures encountered in internal combustion engine operation promote the rapid oxidation of motor oils. This is especially true for the oil coming in contact with the piston heads where temperatures can range from 500 to 750°F (260 to 400°C). Oxidation causes the formation of coke and varnishlike asphaltic materials from paraffin-base oils and sludge from naphthenic-base oils [3]. Antioxidant additives, such as phenolic compounds and zinc dithiophosphates, are added to the oil blends to suppress oxidation and its effects.

Flash point. The flash point of an oil has little significance with respect to engine performance and serves mainly to give an indication of hydrocarbon emissions or of the source of the oils in the blend; for example, whether it is a blend of high and low viscosity oils to give an intermediate viscosity or is comprised of a blend of center cut oils. Low flash points indicate greater hydrocarbon emissions during use.

Boiling temperature. The higher the boiling temperature range of a fraction, the higher the molecular weights of the components and, for a given crude oil, the greater the viscosity. The boiling ranges and viscosities of the fractions are the major factors in selecting the cut points for the lube oil blending stocks on the vacuum distillation unit.

Acidity. The corrosion of bearing metals is largely due to acid attack on the oxides of the bearing metals [1]. These organic acids are formed by the oxidation of lube oil hydrocarbons under engine operating conditions and by acids produced as by-products of the combustion process which are introduced into the crankcase by piston blow-by. Motor oils contain buffering materials to neutralize these corrosive acids. Usually the dispersant and detergent additives are formulated to include alkaline materials which serve to neutralize the acid con-

taminants. Lube oil blending stocks from paraffinic crude oils have excellent thermal and oxidation stability and exhibit lower acidities than do oils from naphthenic crude oils. The neutralization number is used as the measure of the organic acidity of an oil; the higher the number, the greater the acidity.

14.1 LUBE OIL PROCESSING

The first step in the processing of lubricating oils is the separation on the crude oil distillation units of the individual fractions according to viscosity and boiling range specifications. The heavier lube oil raw stocks are included in the vacuum fractionating tower bottoms with the asphaltenes, resins, and other undesirable materials.

The raw lube oil fractions from most crude oils contain components which have undesirable characteristics for finished lubricating oils. These must be removed or reconstituted by processes such as liquid-liquid extraction, crystallization, selective hydrocracking, and/or hydrogenation. The undesirable characteristics include high pour points, large viscosity changes with temperature (low VI), poor oxygen stability, poor color, high cloud points, high organic acidity, and high carbon- and sludge-forming tendencies.

The processes used to change these characteristics are:

1. *Solvent deasphalting* to reduce carbon- and sludge-forming tendencies
2. *Solvent extraction* and *hydrocracking* to improve viscosity index
3. *Solvent dewaxing* and *selective hydrocracking* to lower cloud and pour points
4. *Hydrotreating* and *clay treating* to improve color and oxygen stability
5. *Hydrotreating* and *clay treating* to lower organic acidity

Although the main effects of the processes are as described above, there are also secondary effects. For example, although the main result of solvent dewaxing is the lowering of the cloud and pour points of the oil, solvent dewaxing also slightly reduces the VI of the oil.

For economic reasons, as well as process ones, the process sequence is usually in the order of deasphalting, solvent extraction, dewaxing, and finishing. However, dewaxing and finishing processes are frequently reversed [9]. In general, the processes increase in cost and complexity in this same order.

14.2 PROPANE DEASPHALTING

The lighter distillate feedstocks for producing lubricating oil base stocks can be sent directly to the solvent extraction units, but the atmospheric and vacuum

still bottoms require deasphalting to remove the asphaltenes and resins before undergoing solvent extraction. In some cases the highest boiling distillate stream may also contain sufficient asphaltenes and resins to justify deasphalting.

Propane usually is used as the solvent in deasphalting but it may also be used with ethane or butane in order to obtain the desired solvent properties. Propane has unusual solvent properties in that from 100 to 140°F (40 to 60°C) paraffins are very soluble in propane, but the solubility decreases with an increase in temperature until at the critical temperature of propane [206°F (96.8°C)] all hydrocarbons become insoluble. In the range of 100 to 206°F (40 to 96.8°C) the high molecular weight asphaltenes and resins are largely insoluble in propane. Separation by distillation is generally by molecular weight of the components and solvent extraction is by type of molecule. Propane deasphalting falls in between these categories because separation is a function of both molecular weight and type of molecular structure.

The feedstock is contacted with 4 to 8 volumes of liquid propane at the desired operating temperature. The extract phase contains from 15 to 20% by weight of oil with the remainder solvent. The heavier the feed stock, the higher the ratio of propane to oil required.

The raffinate phase contains from 30 to 50% propane by volume and is not a true solution but an emulsion of precipitated asphaltic material in propane [10].

As in most other refinery processes, the basic extraction section of the process is relatively simple, consisting of a cylindrical tower with angle iron baffles arranged in staggered horizontal rows [5] or containing perforated baffles [10] using counter-current flow of oil and solvent. Some units use the rotating disc contactor (RDC) for this purpose.

A typical propane deasphalting unit (Fig. 14.1) injects propane into the bottom of the treater tower, and the vacuum tower bottoms feed enters near the top of the tower. As the propane rises through the tower, it dissolves the oil from the residuum and carries it out of the top of the tower. Between the residuum feed point and the top of the tower, heating coils increase the temperature of the propane–oil extract phase thus reducing the solubility of the oil in the propane. This causes some of the oil to be expelled from the extract phase creating a reflux stream. The reflux flows down the tower and increases the sharpness of separation between the oil portion of the residuum and the asphaltene and resin portion. The asphaltene and resin phase leaving the bottom of the tower is the raffinate and the propane–oil mixture leaving the top is the extract.

The solvent recovery system of the propane deasphalting process, as in all solvent extraction processes, is much more complicated and costly to operate than the treating section. Two-stage flash systems or supercritical techniques are used to recover the propane from the raffinate and extract phases. In the flash system, the first stages are operated at pressures high enough to condense the propane vapors with cooling water as the heat exchange medium. In the high-

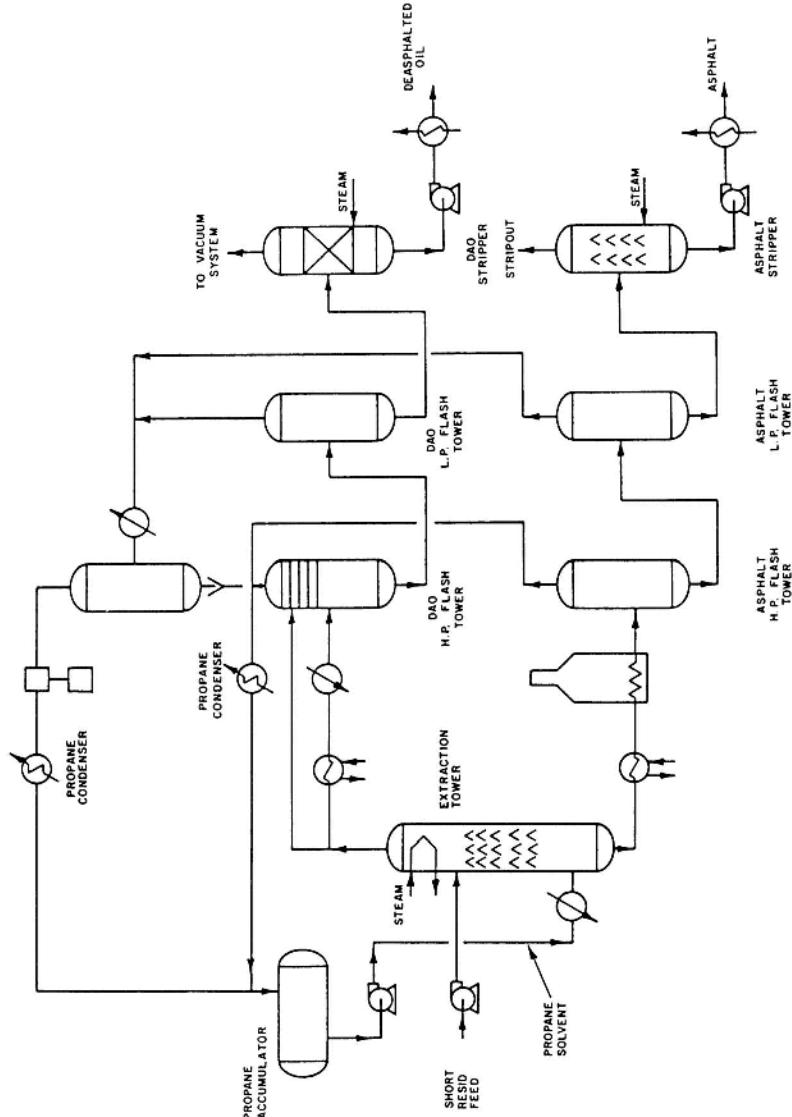


Figure 14.1 Typical propane deasphalter.

pressure raffinate flash tower, foaming and asphalt entrainment can be a major problem. To minimize this, the flash tower is operated at about 550°F (290°C) to keep the asphalt viscosity at a reasonably low level.

The second stages strip the remaining propane from the raffinate and extract at near atmospheric pressure. This propane is compressed and condensed before being returned to the propane accumulator drum.

The propane deasphalting tower is operated at a pressure sufficiently high to maintain the solvent in the liquid phase. This is usually about 500 psig (3448 kPa).

The asphalt recovered from the raffinate can be blended with other asphalts into heavy fuels or used as a feed to the coking unit.

The heavy oil product from vacuum residuum is called bright stock. It is a high-viscosity blending stock that, after further processing, is used in the formulation of heavy-duty lubricants for truck, automobile, and aircraft services.

14.3 VISCOSITY INDEX IMPROVEMENT AND SOLVENT EXTRACTION

There are three solvents used for the extraction of aromatics from lube oil feed stocks and the solvent recovery portions of the systems are different for each. The solvents are furfural, phenol, and N-methyl-2-pyrrolidone (NMP). The purpose of solvent extraction is to improve the viscosity index (VI), oxidation resistance, and color of the lube oil base stock and to reduce the carbon- and sludge-forming tendencies of the lubricants by separating the aromatic portion from the naphthenic and paraffinic portion of the feed stock.

Furfural Extraction

The process flow through the furfural extraction unit is similar to that of the propane deasphalting unit except for the solvent recovery section, which is more complex. The oil feedstock is introduced into a continuous counter-current extractor at a temperature which is a function of the viscosity of the feed; the greater the viscosity, the higher the temperature used. The extraction unit is usually a raschig ring-packed tower or a rotating disc contactor with a temperature gradient from top to bottom of 60 to 90°F (30 to 50°C). The temperature at the top of the tower is a function of the miscibility temperature of the furfural and oil. It is usually in the range 220 to 300°F (105 to 150°C).

The oil phase is the continuous phase, and the furfural-dispersed phase passes downward through the oil. Extract is recycled at a ratio of 0.5:1 to improve the extraction efficiency.

Furfural-to-oil ratios range from 2:1 for light stocks to 4.5:1 for heavy stocks. Solvent losses are normally less than 0.02 wt% of raffinate and extract flow rates. Furfural is easily oxidized and inert gas blankets are maintained on the system to reduce oxidation and polymerization. Sometimes deaeration towers are used to remove dissolved oxygen from the feed. Furfural is subject to thermal decomposition and skin temperatures of heat exchange equipment used to transfer heat to furfural-containing streams must be carefully controlled to prevent polymerization of the furfural and fouling of the heat exchange surfaces.

The furfural is removed from the raffinate and extract streams by flashing and steam-stripping. Furfural forms an azeotrope with water and this results in a unique furfural recovery system. Furfural is purified in the furfural tower by distilling overhead the water-furfural azeotrope vapor which upon condensing separates into water-rich and furfural-rich layers. The furfural-rich layer is recycled to the furfural tower as reflux and the furfural in the water-rich layer is separated from the water by steam-stripping. The overhead vapors, consisting of the azeotrope, are condensed and returned to the furfural-water separator. The bottoms product from the furfural tower is the pure furfural stream, which is sent to the furfural solvent drum.

The most important operating variables for the furfural extraction unit are the furfural-to-oil ratio (F/O ratio), extraction temperature, and extract recycle ratio. The F/O ratio has the greatest effect on the quality and yield of the raffinate, while the temperature is selected as a function of the viscosity of the oil and the miscibility temperature. The extract recycle ratio determines to some extent the rejection point for the oil and the sharpness of separation between the aromatics and naphthenes and paraffins.

Phenol Extraction

The process flow for the phenol extraction unit is somewhat similar to that of the furfural extraction unit but differs markedly in the solvent recovery section because phenol is easier to recover than is furfural.

The distillate or deasphalting oil feed is introduced near the bottom of the extraction tower and phenol enters near the top. The oil-rich phase rises through the tower and the phenol-rich phase descends the tower. Trays or packing are used to provide intimate contact between the two phases. Some of the newer phenol extraction units use either rotating disc contactors (RDC) or centrifugal extractors to contact the two phases. Both the RDC and the centrifugal extractors offer the advantage that much smaller volumes are needed for the separations. As all lube oil refineries operate on a blocked operation basis (that is, charging one feedstock at a time), the lower inventories make it possible to change from one feedstock to another with a minimum loss of time and small loss of off-specification product.

The extraction tower and RDC are operated with a temperature gradient which improves separation by creating an internal reflux. The phenol is introduced into the tower at a higher temperature than the oil. The temperature of the phenol-rich phase decreases as it proceeds down the column and the solubility of the oil in this phase decreases. The oil coming out of the phenol-rich phase reverses direction and rises to the top as reflux. The tower top temperature is kept below the miscible temperature of the mixture, and the tower bottom temperature is usually maintained about 20°F (10°C) lower than the top.

Phenol will dissolve some of the paraffins and naphthenes as well as the aromatics. Water acts as an antisolvent to increase the selectivity of the phenol, and typically from 3 to 8 vol% water is added to the phenol. A decrease in reaction temperature has a similar effect. Raffinate yield is increased by increasing water content and/or decreasing temperature.

The important extraction tower operating variables are:

- Phenol-to-oil ratio (treat rate)
- Extraction temperature
- Percent water in phenol

Treat rates vary from 1:1 to 2.5:1 depending upon the quality and viscosity of the feed and the quality of the product desired. Increasing the treat rate for a given stock improves the VI of the product and decreases the yield. Phenol is recovered from the extract and raffinate streams by distillation and gas or steam stripping. Phenol losses average from 0.02 to 0.04% of circulation rate.

NMP Extraction

The NMP extraction process uses N-methyl-pyrrolidone as the solvent to remove the condensed ring aromatics and polar components from the lubricating oil distillates and bright stocks. This process was developed as a replacement for phenol extraction because of the safety, health, and environmental problems associated with the use of phenol. Several differences between the characteristics of NMP and phenol make it necessary to modify the phenol plant design. These differences include a 40°F (22°C) higher boiling point for NMP, a 115°F (64°C) lower melting point, complete miscibility of NMP with water, no azeotrope formation of NMP with water, and a 69% lower viscosity than phenol at 122°F (50°C). A simplified process flow diagram in which the solvent is recovered by flashing and stripping with steam at pressures above atmospheric is shown in Figure 14.2 [3].

A portion of the distillate or deasphalting oil feed is used as the lean oil in an absorption tower to remove the NMP from the exiting stripping steam. The rich oil from the absorption tower is combined with the remainder of the feed, which is heated to the desired temperature before being introduced near the bottom of the treater tower. The hot solvent enters near the top of the tower. Specially

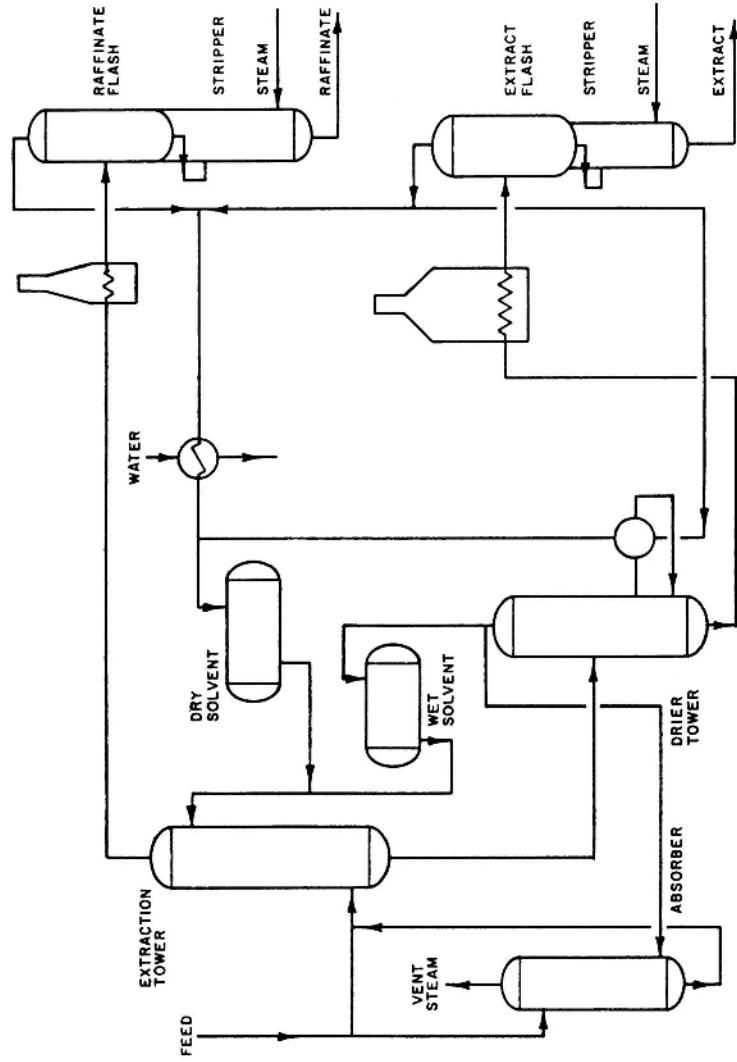


Figure 14.2 NMP extraction unit using steam-stripping for solvent recovery.

Table 14.1 Viscosity Index of Hydrocarbons

Type of hydrocarbon	Viscosity index
n-Paraffins	175
i-Paraffins	155
Mononaphthene	142
Dinaphthenes+	70
Aromatics	50

Source: Ref. 11.

designed cascade weir trays are used to mix and re-mix the NMP-rich and oil-rich phases as they pass through the tower.

The solvent is stripped from the raffinate and extract by distillation and steam-stripping. Recovery of NMP is better than that for phenol, and NMP losses are only 25 to 50% those of phenol.

The lower viscosity of NMP gives greater through-put for a given size tower. This results in lower construction costs for a grass-root plant and up to a 25% increase in through-put for converted phenol plants.

Solvent-to-oil ratios for a given feedstock and quality product are the same for NMP and phenol extraction, but raffinate oil yields average 3 to 5% higher for the NMP extraction.

14.4 VISCOSITY INDEX IMPROVEMENT AND HYDROCRACKING

Components of lubricating oil fractions which have high viscosity indices are the mononaphthalenes and isoparaffins (see Table 14.1) [7,11]. Hydrocracking of vacuum gas oils increases the paraffin concentration and the viscosity index of a lube oil feedstock [8] and produces increasing quantities of the mononaphthalenes and isoparaffins as hydrocracking severity increases. Hydrogenation of polycyclic aromatic compounds to polynaphthenic ring compounds, breaking of polynaphthenic rings, and isomerization of n-paraffins are promoted by high conversion, low space velocity, and low reaction temperature [11].

14.5 DEWAXING

All lube stocks, except those from a relatively few highly naphthenic crude oils, must be dewaxed or they will not flow properly at ambient temperatures. Dewax-

ing is one of the most important and most difficult processes in lubricating oil manufacturing. There are two types of processes in use today. One uses refrigeration to crystallize the wax and solvent to dilute the oil portion sufficiently to permit rapid filtration to separate the wax from the oil. The other uses a selective hydrocracking process to crack the wax molecules to light hydrocarbons.

Solvent Dewaxing

There are two principal solvents used in the United States in solvent dewaxing processes: propane and ketones. Dichloroethane-methylene is also used in some other countries. The ketone processes use either a mixture of methyl ethyl ketone (MEK) with methyl isobutyl ketone (MIBK) or MEK with toluene. The solvents act as a diluent for the high molecular weight oil fractions to reduce the viscosity of the mixture and provide sufficient liquid volume to permit pumping and filtering. The process operations for both solvent processes are similar but differ in the equipment used in the chilling and solvent recovery portions of the process. About 85% of the dewaxing installations use ketones as the solvent and the other 15% use propane. The comparative advantages and disadvantages of the processes are [10]:

Propane

1. Readily available, less expensive, and easier to recover.
2. Direct chilling can be accomplished by vaporization of the solvent, thus reducing the capital and maintenance costs of scraped-surface chillers.
3. High filtration rates can be obtained because of its low viscosity at very low temperatures.
4. Rejects asphaltenes and resins in the feed.
5. Large differences between filtration temperatures and pour point of finished oils [25 to 45°F (15 to 25°C)].
6. Requires use of a dewaxing aid.

Ketones

1. Small difference between filtration temperature and pour point of dewaxed oil [9 to 18°F (5 to 10°C)].
 - a. Lower pour point capability
 - b. Greater recovery of heat by heat exchange
 - c. Lower refrigeration requirements
2. Fast chilling rate. Shock chilling can be used to improve process operations
3. Good filtration rates but lower than for propane.

Ketone Dewaxing

The most widely used processes use mixtures of MEK–toluene and MEK–MIBK for the solvent. MEK–benzene was used originally, but health hazards associated with the handling of benzene as well as its cost resulted in the use of MEK–toluene in its place. MEK–MIBK mixtures have fewer health problems than the earlier used compositions. A simplified process flow diagram is shown in Figure 14.3.

Solvent is added to the solvent-extracted oil feed, and the mixture is chilled in a series of scraper-surface exchangers and chillers. Additional solvent is added to the feed to maintain sufficient liquid for easy handling as the temperature is decreased and the wax crystallizes from solution. Cold filtrate from the rotary filters is used as the heat exchange medium in the exchangers and a refrigerant, usually propane, in the chillers. The cold slurry is fed to the rotary filters for removal of the crystalline wax. The filter cake is washed with cold solvent, and an inert gas blanket, at a slight positive pressure, is maintained on the filters and also used to “blow back” the wax cake from the filter cloth and release it before it reaches the filter drum scraper knife.

The solvent is recovered from the filtrate and the wax by heating and two-stage flashing followed by steam-stripping.

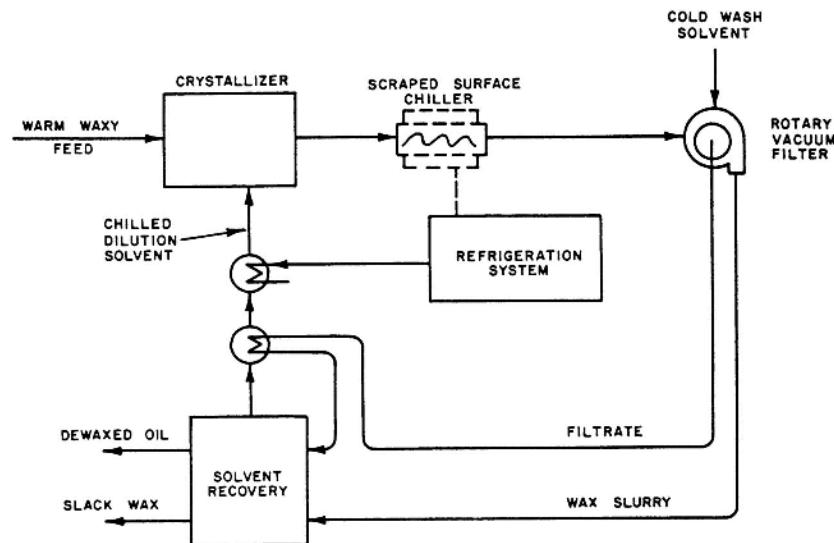


Figure 14.3 Exxon DILCHILL dewaxing unit. (From Ref. 3.)

The water introduced into the system by the steam-stripping is removed continuously by a series of phase separations and distillations. The overheads from the steam-strippers are combined and condensed. The condensate separates into two phases in the decanter drum with the aqueous phase containing about 3.5 mol% ketones and the ketone-rich phase about 3 mol% water. The ketone phase is fed into the top of the solvent dehydration tower as reflux and the water-rich phase is fed into the ketone stripper. The ketone is stripped from the water-rich phase with steam, and water is discharged from the bottom of the tower into the sewer.

The products from the dewaxing unit are a dewaxed oil and a slack wax. The dewaxed oil next must go through a finishing step to improve its color and color stability. The slack wax is used either for catalytic cracker feed or undergoes a de-oiling operation before being sold as industrial wax.

Dilchill Dewaxing

The Dilchill Dewaxing Process was developed by Exxon. It is a modification of the ketone dewaxing process which uses shock chilling of the waxy oil feed by direct injection with very cold solvent in a highly agitated mixer. The wax crystals formed are larger and more dense than the crystals formed in scraped-surface chillers. Higher filtration rates and better oil removal are achieved, resulting in lower capital and operating costs as well as higher dewaxed oil yields. The scraped-surface coolers are eliminated, but the chillers are still necessary.

Propane Dewaxing

Propane dewaxing differs from ketone dewaxing in that the propane is used both as a diluent and a refrigerant for direct chilling. As a diluent, it dilutes the oil phase so it is fluid and acts as the carrying medium after the wax crystallizes. As a refrigerant, it chills the oil by being evaporated batchwise from the propane-waxy oil solution. The cooling rate usually averages about 3°F (1.5°C) per minute, but ranges from almost 7°F (4°C) per minute at the beginning of the chilling cycle to about 2°F (1°C) at the end. In propane dewaxing, the chilling rate is limited to avoid shock chilling because it results in poor wax crystal formation and growth. The amount of dilution required is a function of the viscosity of the oil and ranges from a 1.5:1 ratio of propane to fresh feed for light stocks to 3:1 for heavy stocks [5].

Waxy oil feed is mixed with propane, cooled to about 80°F (27°C), and charged into the warm solution drum under sufficient pressure to prevent vaporization of the propane. From the solution drum, it is charged into one of the two batch chillers where it is cooled at a controlled rate by evaporation of the propane. It usually takes about 30 minutes to chill the mixture to the desired temperature.

The slurry is then discharged into the filter feed drum. The cycle is arranged so that while one chiller is being used to chill a batch, the other chiller is first discharged into the filter feed drum then refilled from the warm solution drum.

The wax is separated from the oil on rotary filters. The wax cake is washed with cold propane while on the filter to remove and recover as much oil as practical. Cold propane vapors are used to release the filter cake.

Most of the propane in the dewaxed oil and wax stream is recovered by heating each of the streams to about 320°F (160°C) and flashing at a pressure sufficiently high that the propane can be condensed with refinery cooling water. The remaining propane is recovered by low-pressure flashing and a final steam-stripping of each of the streams. The propane from the low-pressure flash is compressed, condensed, and returned to the propane storage drum.

A dewaxing aid such as Paraflow™ (a naphthalene-chlorinated wax condensation product) and/or Acryloid™ (a methacrylate polymer) is frequently added to the waxy oil feed at a level of 0.05 to 0.2 liquid volume percent on feed to modify the wax crystal structure. This results in higher filtration rates and denser wax cakes from which it is easier to wash the oil.

Selective Hydrocracking

There are two types of selective hydrocracking processes for dewaxing oil, one uses a single catalyst for pour point reduction only and the other uses two catalysts to reduce the pour point and improve the oxygen stability of the product [4,6].

For the pour point reduction operation, both processes use synthetic shape-selective zeolite catalysts which selectively crack the n-paraffins and slightly branched paraffins. Zeolites with openings about 6 Å in diameter provide rapid cracking rates for n-paraffins with the rate decreasing rapidly as the amount of branching increases.

The Mobil Lube Dewaxing Process uses a fixed-bed reactor packed with two catalysts, and the process flow is similar to that of hydrotreating unit. Severity of operation is controlled by the furnace outlet temperature (reactor temperature). Essentially no methane or ethane is formed in the reaction. A similar British Petroleum (BP) process produces propane, butane, and pentane in the ratio 2:4:3 by weight. Reaction conditions for the Mobil and BP processes appear to be similar with the following considered typical ranges:

Reactor temp., °F (°C)	560–700 (290–370)
Reactor pres., psig (kPa)	300–2,000 (2,070–13,800)
H ₂ partial pres., psig (kPa)	250–1,500 (1,725–10,340)
Gas rate, scf/bbl (Nm ³ /t)	500–5,000 (100–1,000)
H ₂ consumption, scf/bbl (Nm ³ /t)	20–40 (100–200)

Yields of dewaxed oil of similar pour point from the same feed stocks vary from 0 to 15% greater than from solvent dewaxing (SDW) with the increase reflecting the difficulty of separating the oil from the wax in the SDW processes.

The feed to the selective hydrocracking unit is solvent-extracted oil from the aromatic extraction units. The advantages claimed over conventional solvent dewaxing units include:

1. Production of very low pour and cloud point oils from paraffinic stocks.
2. Lower capital investment.
3. Improved lube oils base stock yields.
4. A separate hydrofinishing operation is not necessary.

14.6 HYDROFINISHING

Hydrotreating of dewaxed lube oil stocks is needed to remove chemically active compounds that affect the color and color stability of lube oils. Most hydrotreating operations use cobalt–molybdate catalysts and are operated at a severity set by the color improvement needed. Organic nitrogen compounds seriously affect the color and color stability of oils, and their removal is a major requirement of the operation [10].

The process flow is the same as that for a typical hydrotreating unit. Representative operating conditions are:

Reactor temp., °F(°C)	400–650 (200–340)
Reactor pres., psig (kPa)	500–800 (3,450–5,525)
LHSV, v/h/v	0.5–2.0
H ₂ as rate, scf/bbl (Nm ³ /t)	500 (100)

Usually finished oil yields are approximately 98% of dewaxed oil feed.

14.7 FINISHING BY CLAY CONTACTING

Many older lube oil processing plants use contacting of the dewaxed oil with activated clays at elevated temperatures to improve the stability of the finished oils in engine service. Polar compounds (aromatic and sulfur and nitrogen containing molecules) are adsorbed on the clay and removed by filtration. Spent clay disposal and operating restrictions have generally caused the clay treating to be replaced by hydrofinishing.

14.8 ENVIRONMENTAL IMPACTS

Stricter environmental requirements and mileage standards for new cars have created a growing demand for high-quality multigrade motor oils which have lower volatility and oil consumption characteristics and reduced thickening of the oil by oxidation during service which increases fuel consumption. Solvent-refined oils have difficulty in meeting the new standards and are increasingly being replaced with hydrocracked and poly-alpha-olefin based oils, especially in the lower viscosity grades such as 5W-30 and 10W-30 multigrades [12].

The low-viscosity multigrade oils are typically blended from low-viscosity mineral-based oils which have volatilities and tendency to high oil-consumption and rapid thickening by oxidation during service. Hydrocracking of base stocks, followed by solvent extraction to remove partially hydrocracked aromatic compounds [11], offers a more cost-effective route than production of poly-alpha-olefins [13].

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15

Petrochemical Feedstocks

The preparation of hydrocarbon feed stocks for petrochemical manufacture can be a significant operation in today's petroleum refineries. There are three major classes of these feedstocks according to use and method of preparation. These are aromatics, unsaturates (olefins and diolefins), and saturates (paraffins and cycloparaffins). Aromatics are produced using the same catalytic reforming units used to upgrade the octanes of heavy straight-run naphtha gasoline blending stocks. For petrochemical use the aromatic fraction is concentrated by solvent extraction techniques. Some of the unsaturates are produced by the fluid catalytic cracking unit, but most have to be produced from refinery feedstocks by steam-cracking or low molecular weight polymerization of low molecular weight components.

To provide better continuity from regular refinery operations, the petrochemical feedstock preparation will be covered in the order (1) aromatics, (2) unsaturates, and (3) saturates.

15.1 AROMATICS PRODUCTION

For aromatics production for petrochemical use, the catalytic reformer can be operated at higher severity levels than for motor gasoline production. Highly naphthenic feedstocks also aid in high aromatics yields because the dehydration of naphthenes is the most efficient reaction taking place and provides the highest yield of aromatics. Table 15.1 illustrates the increase in aromatics yields as the reformer operating severity is increased [the clear research octane number (RON) is the measure of operating severity].

The C₆–C₈ aromatics (benzene, toluene, xylene, and ethylbenzene) are the large volume aromatics used by the petrochemical industry with benzene having the greatest demand. The product from the catalytic reformer contains all of these aromatics and it is separated into its pure components by a combination of solvent extraction, distillation, and crystallization. In addition, because of the much

Table 15.1 Aromatics Yield
as a Function of Severity

Product RON	Percent aromatics
90	54
95	60
100	67
103	74

greater demand for benzene, the excess of the toluene and xylenes over market needs can be converted to benzene by hydrodealkylation.

Solvent Extraction of Aromatics

Present separation methods for recovery of aromatics from hydrocarbon streams use liquid–liquid solvent extraction to separate the aromatic fraction from the other hydrocarbons. Most of the processes used by U.S. refineries use either polyglycols or sulfolane as the extracting solvent. The polyglycol processes are the Udex process developed by Dow Chemical Company and licensed by UOP and the Tetra process licensed by the Linde Division of Union Carbide. The solvents used are tetraethylene glycol for the Tetra process and usually diethylene glycol for the Udex process, although dipropylene glycol and triethylene glycol can also be used. The Sulfolane process was originally developed by the Royal Dutch/Shell group and is licensed worldwide by UOP. It uses sulfolane (tetrahydrothiophene 1-1 dioxide) as the solvent and a simplified process flow diagram is shown in Figure 15.1a.

The important requirements for a solvent are [8]:

1. High selectivity for aromatics versus nonaromatics
2. High capacity (solubility of aromatics)
3. Capability to form two phases at reasonable temperatures
4. Capability of rapid phase separation
5. Good thermal stability
6. Noncorrosivity and nonreactivity

The Udex process, using polyglycols, was the first of the solvent extraction processes to find widespread usage. Many of these units are still in operation in U.S. refineries but, since 1963, most new units have been constructed using the Sulfolane or Tetra processes (Fig. 15.1b). At a given selectivity, the solubility

of aromatics in sulfolane is about double that in triethylene glycol. The higher solubility permits lower solvent circulation rates and lower operating costs.

Both the polyglycol and sulfolane solvent processes use a combination of liquid–liquid extraction and extractive stripping to separate the aromatics from the other hydrocarbons [1,2,8] because of the characteristics of polar solvents. As the concentration of aromatics in the solvent increases, the solubility of the nonaromatic hydrocarbons in the extract phase also increases. This results in a decrease in the selectivity of the solvent and a carryover of some of the nonaromatic hydrocarbons with the extract phase to an extractive stripper. In the extractive stripper an extractive distillation occurs and the nonaromatic hydrocarbons are stripped from the aromatic–solvent mixture and returned as reflux to the extraction column. The solvent is then recovered from the nonaromatic hydrocarbon-free extract stream leaving an extract which contains less than 1000 ppm (<0.1%) aliphatics. (See Fig. 15.2.)

Aromatics recoveries are typically equal to or better than 99.9, 99.0, and 97.0% for benzene, toluene, and xylenes, respectively.

Because of the high affinity of the polar solvents for water and the low solubilities in the nonaromatic hydrocarbon raffinate phase, the solvent is recovered from the raffinate phase by washing with water. The water is returned to either the extractive stripper (Tetra) or extract recovery column (Sulfolane) for recovery of the solvent.

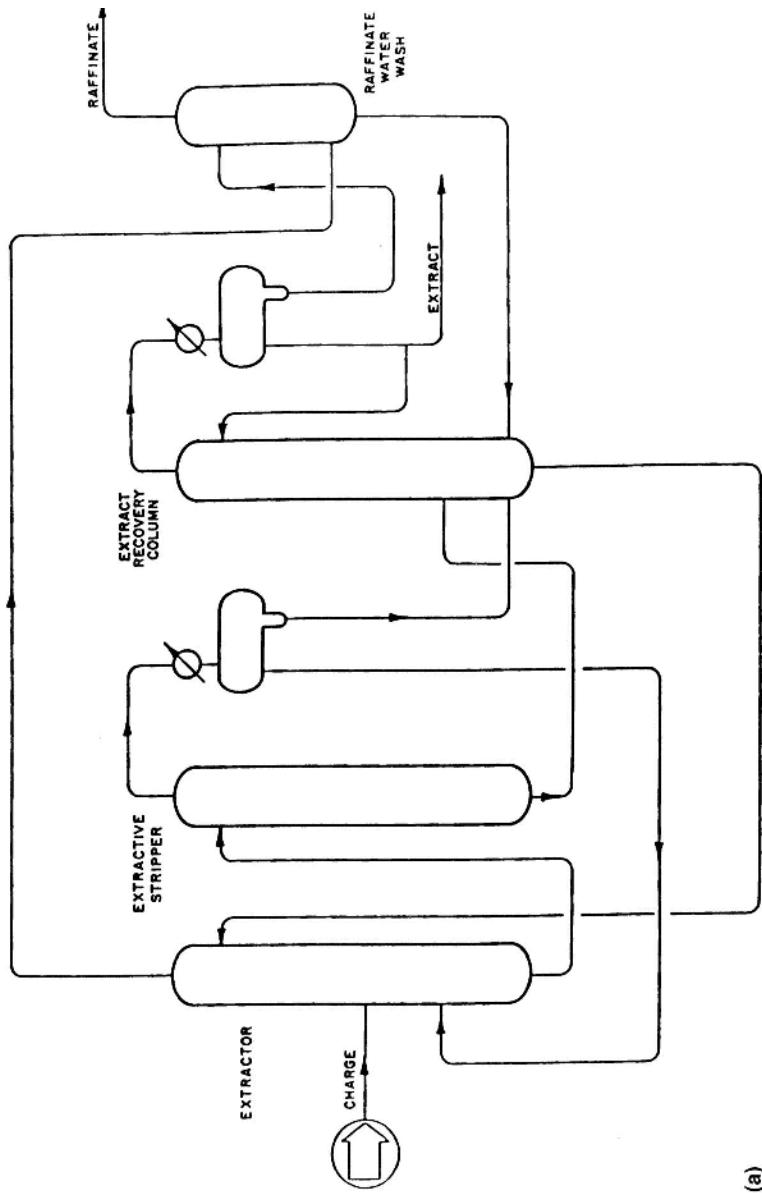
The water content of the solvents is carefully controlled and used to increase the selectivity of the solvents. The water content of the polyglycols is kept in the range of 2 to 10 wt% and that of sulfolane is maintained at about 1.5 wt%.

The solvent quality is maintained in the Sulfolane process by withdrawing a slip stream from the main solvent recirculation stream and processing it in a solvent reclaiming tower to remove any high-boiling contaminants that accumulated. The Tetra process solvent quality is maintained by using a combination of filtration and adsorption to remove accumulated impurities.

Sulfolane and the polyglycols have thermal stability problems, and the skin temperatures of heat exchange equipment must be limited. For sulfolane, skin temperatures must be kept below 450°F (232°C).

Aromatics Separation

Benzene and toluene can be recovered from the extract product stream of the extraction unit by distillation. The boiling points of the C₈ aromatics are so close together (Table 15.2) that separation by distillation becomes more difficult and a combination of distillation and crystallization or adsorption is used. The ethylbenzene is first separated from the mixed xylenes in a three-unit fractionation tower with 120 trays per unit for a total of 360 trays. Each unit is about 200 feet in height, and the units are connected so they operate as a single fractionation



(a)

Figure 15.1a Sulfolane aromatics extraction unit.

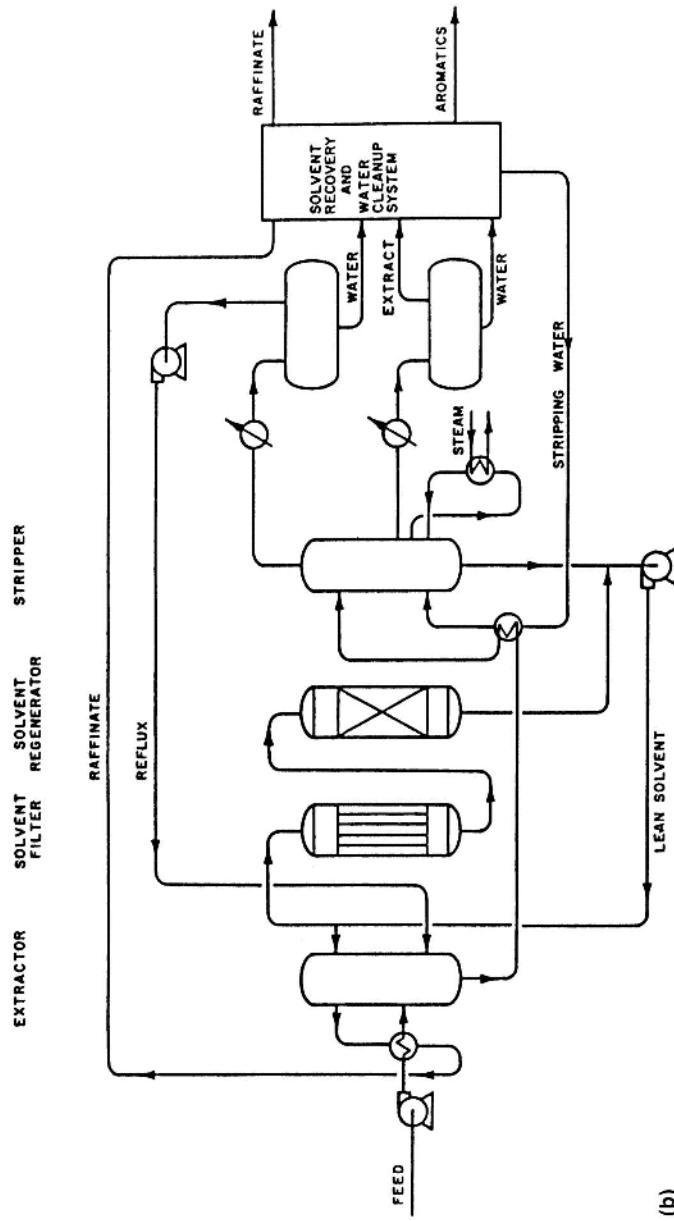


Figure 15.1b Tetra aromatics extraction unit.

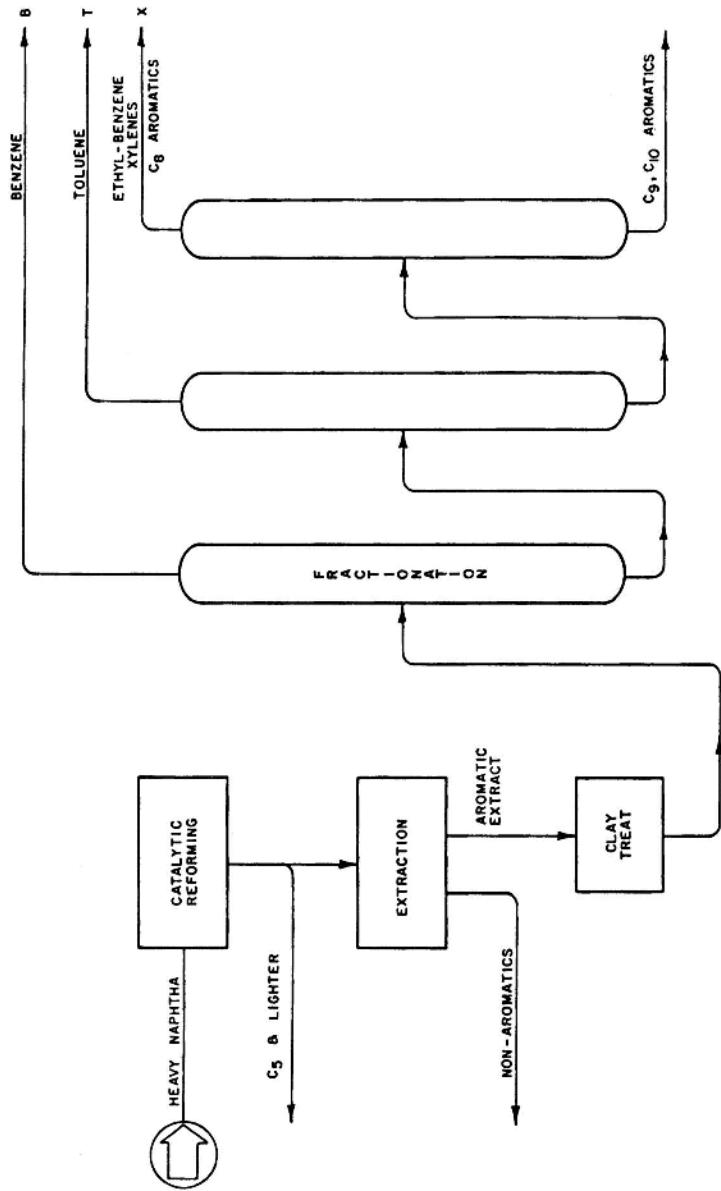


Figure 15.2 Sequence of aromatics recovery operations.

Table 15.2 Boiling and Melting Points of Aromatics

	Boiling points		Melting points	
	°F	°C	°F	°C
Benzene	176.2	80.1	42.0	5.5
Toluene	231.2	110.6	-139.0	-95.0
Ethylbenzene	277.1	136.2	-139.0	-95.0
p-Xylene	281.0	138.4	55.9	13.3
m-Xylene	282.4	139.1	-54.2	-47.9
o-Xylene	291.9	144.4	-13.3	-25.2

tower of 360 trays. High reflux ratios are needed to provide the desired separation efficiency because the difference between the boiling points of ethylbenzene and p-xylene is only about 3.9°F (2°C). This is a very energy-intensive operation and, with today's energy costs, it is usually less costly to make ethylbenzene by alkylating benzene with ethylene.

A typical processing sequence for the separation of C₈ aromatics is shown in Figure 15.3. After removal of the ethylbenzene by super-fractionation, the o-xylene along with the higher boiling C₉⁺ aromatics is separated from the p- and m-xyles by fractionation. The boiling point of o-xylene is more than 9.6°F (5°C) greater than that of its closest boiling isomer, m-xylene, and it can be separated economically in a 160-plate distillation column. The overhead stream from this column is a mixture of m- and p-xyles and the bottoms stream contains o-xylene and the C₉⁺ aromatics. The bottoms stream is processed further in a 50-tray rerun column to separate 99+% purity o-xylene from the C₉⁺ aromatics.

The mixed m- and p-xylene overhead stream from the fractionator is sent to either the Parex unit or the crystallization unit to separate the m- and p-xyles. The UOP Parex process uses adsorption of p-xylene on a molecular sieve adsorbent to separate the m- and p-xyles. The adsorbent is selected such that p-xylene molecules will be adsorbed and the m-xylene molecules will pass through the adsorbent bed. Recoveries of 96% per pass of pure p-xylene can be achieved [4] as compared with 60–65% recovery of p-xyles by the freeze-crystallization process.

The p-xylene usually is stripped from the adsorbent with p-diethylbenzene or a mixture of diethylbenzene isomers. The UOP process uses a simulated moving-adsorbant-bed design.

If fractional crystallization is used for separation, the mixed m- and p-xylene overhead stream from the fractionator is fed to the crystallization unit to

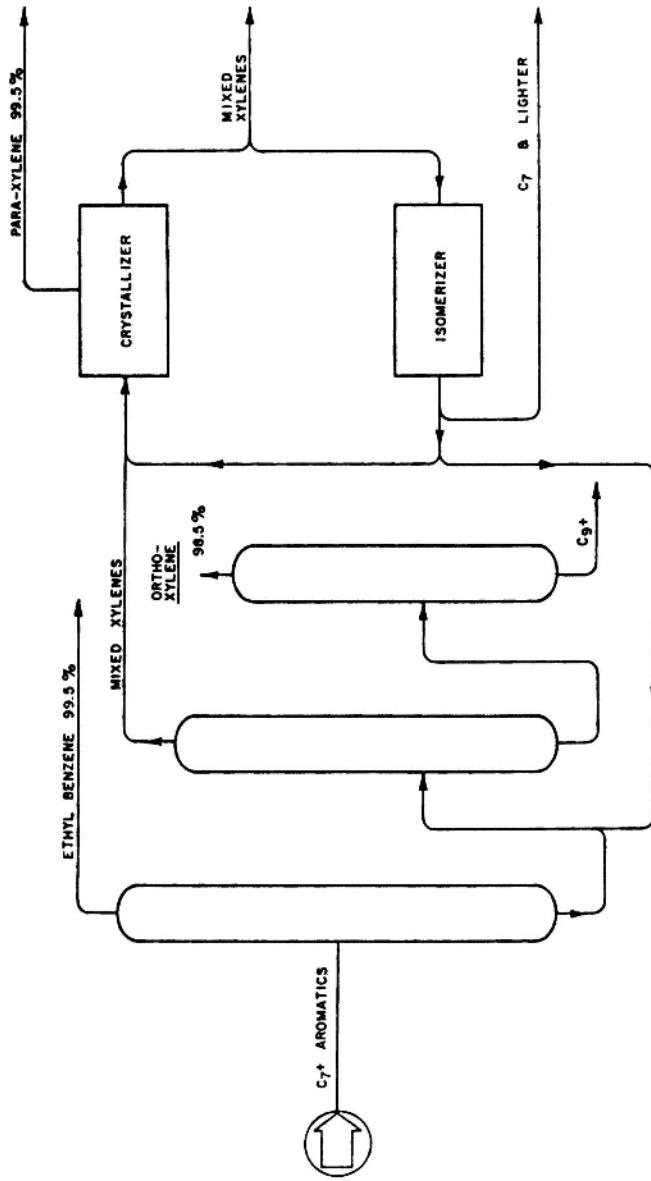


Figure 15.3 Processing sequence to produce C₈ aromatics.

separate the m- and p-xlenes. The solidification point of p-xylene is 55.9°F (13.3°C), while that of m-xylene is -54.2°F (-47.9°C). A simplified flow diagram of the solvent extraction process is shown in Figure 15.4 [8].

The xylenes feed is dried, chilled to about -40°F (-40°C) and charged to staged crystallizers. Ethylene is used as the refrigerant in indirect chilled surface-scraped heat exchangers, and the mixture is chilled to -60°F (-50°C) in the first crystallizer stage and to -90°F (-68°C) in the second stage. The second-stage crystallizer effluent is charged to a combination solid and screen bowl centrifuge to separate the p-xylene crystals from the mother liquor. The operation of this centrifuge is critical to the cost effectiveness of this process because it controls the subsequent purification costs and the overall refrigeration requirements of this separation [8].

The p-xylene crystals from the centrifuge are purified in a series of partial remelting, recrystallization, and centrifugation stages. The temperatures are increased for each remelting and recrystallization stage and the filtrate from each stage is recycled to the preceding stage. This counter-current operation gives a high-purity p-xylene product from the last stage. The m-xylene-rich filtrate stream is used as feedstock for a xylene isomerization unit or sent to gasoline blending.

The m-xylene-rich stream from the crystallizer and the o-xylene stream from the rerun column can be converted to p-xylene by a xylene isomerization process if demand for p-xylene warrants it. The process flow diagram for this process is similar to the isomerization process in Chapter 10. The catalyst used is a zeolite–non-noble metal catalyst developed by Mobil.

The aromatic-rich feedstock is mixed with hydrogen, heated to 700–800°F (375–425°C), and charged to a fixed-bed reactor containing a non-noble metal catalyst at a pressure of about 150 psig (1034 kPa). The mixture is isomerized to a near-equilibrium mixture of o-, m-, and p-xlenes [6,8]. After cooling, the xylenes are separated from the hydrogen-rich gas in a flash separator and from other hydrocarbons in distillation columns. The xylene-rich stream is returned to the p-xylene crystallization unit or the Parex unit as feed.

Other isomerization processes are used to maximize p-xylene production by both isomerizing o- and m-xlenes and by converting ethylbenzene into xylenes [8]. A two-stage process is generally used for conversion of aromatic hydrocarbons with two or more carbons in the side chains, with the first stage for partial hydrogenation and the second for dehydrogenation. A single-stage process can also be used. The catalysts are either silica-alumina containing a small amount of platinum or molecular sieve silica-alumina catalysts containing about 1% platinum. The equilibrium concentration of p-xylene obtained in the effluent is about 24%.

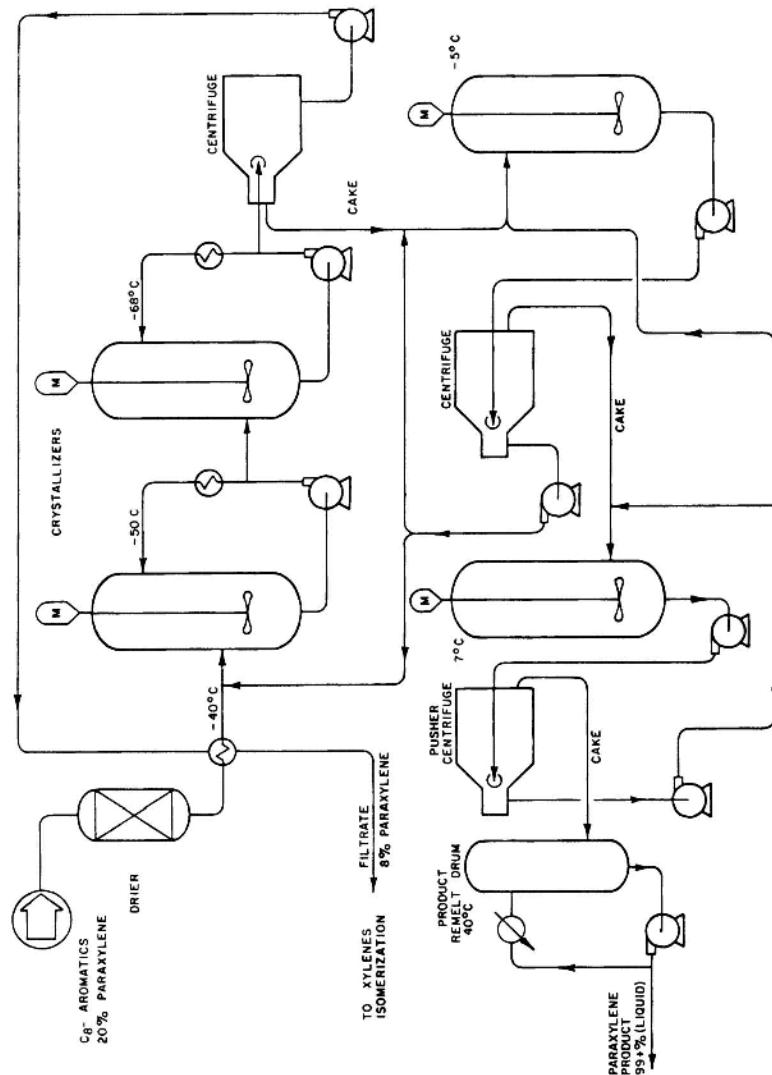


Figure 15.4 p-xylene by crystallization.

Benzene

The primary source of benzene is from the refinery catalytic reforming unit, but substantial amounts of benzene are also produced by the hydrodealkylation of toluene. The process flow for a hydrodealkylation unit (HDA) is also similar to that of an isomerization unit. The feed can be toluene or a mixture of toluene and xylenes. It is heated to 1175°F (630°C) at 600 psig (4140 kPa) and charged to an open noncatalytic reactor ($L/D > 20$) where thermal dealkylation of toluene and xylenes takes place during the residence time of 25–30 seconds. The hydrogenation step in the dealkylation reaction is highly exothermic [22,000 Btu/lb-mole (12,220 cal/g-mole) of H_2 consumed], and temperature is controlled by injection of quench hydrogen at several points along the reactor. The hydrodealkylation reaction results in the conversion of about 90% of the aromatics in the feed and selectively favors about 95% of the conversion to benzene. A small amount of polymer is also formed, primarily diphenyl. A small amount of hydrogen sulfide or carbon disulfide is added to the feed to prevent catastrophic corrosion of the furnace tubes, and a small amount of the polymer is recycled to minimize polymer formation [8].

15.2 UNSATURATE PRODUCTION

Although a substantial amount of C_3 and C_4 olefins are produced by the fluid catalytic cracking unit in the refinery and some C_2 and C_3 olefins by the cat cracker and coker, the steam-cracking of gas oils and naphthas is the most important process for producing a wide range of unsaturated hydrocarbons for petrochemical use. Ethylene is also produced by thermal cracking ethane and propane.

Steam-cracking is the thermal cracking and reforming of hydrocarbons with steam at low pressure, high temperature, and very short residence times (generally <1 second).

The hydrocarbon is mixed with steam in the steam/hydrocarbon weight ratio of 0.2 to 0.8 and fed into a steam-cracking furnace. Residence times in the cracking zone range from 0.3 to 0.8 seconds with a coil outlet temperature between 1400 and 1500°F (760–840°C), a coil outlet pressure in the range 10 to 20 psig (69–138 kPa). The coil outlet stream is quickly quenched to about 600°F (320°C) to stop the cracking and polymerization reactions. Recent designs of steam-crackers utilize heat transfer in a steam generator or transfer-line heat exchanger with a low-pressure drop to lower the coil outlet temperature quickly with a maximum amount of heat recovery. The quenched furnace outlet stream is sent to a primary fractionator where it is separated into a gas stream and liquid product streams according to boiling point range. The gases are separated into individual components as desired by compression and high-pressure fraction-

ation. Streams involved in low-temperature rectification must be desiccant dried to remove water and prevent ice and hydrate formation.

Paraffins obtained from the dewaxing of lubricating oil base stocks are frequently steam-cracked to produce a wide range of linear olefins, usually with from 11 to 16 carbon atoms per molecule. Mild steam-cracking conditions are employed because the object is to minimize the formation of high molecular weight olefins. As with catalytic cracking, the reactions favor the breaking of the paraffinic chain near its center with the formation of one paraffinic molecule and one olefinic molecule. Typical operating conditions are given in Table 15.3 [7].

The purity of the feedstock has a major effect on the product quality. The petrolatum (high molecular weight microcrystalline waxes) obtained from the dewaxing of lubricating oil base stocks contains from 85 to 90% straight- and branched-chain paraffins with the remainder naphthenes and aromatics. Aromatics are especially undesirable, and the wax stream must be deoiled before being used as a steam-cracker feed stock. By choosing a feedstock with an initial boiling point greater than the end point of the desired product, it not only increases the yield of the desired olefins but also makes it possible to separate the product olefins from the feed paraffins by distillation. A typical product stream contains above 80% mono-olefins with only a small percentage less than 11 carbons or more than 16 carbons.

Linear mono-olefins are also produced by several catalytic processes. The overall process consists of a vapor-phase catalytic dehydrogenation unit followed by an extraction unit to extract the linear olefins from the paraffin hydrocarbons by adsorption on a bed of solid adsorbent material. The olefins are desorbed with a hydrocarbon boiling at a lower temperature than the olefin product to make it easy to separate the olefin product from the desorbant. The desorbant hydrocarbon is recycled internally in the extraction section. The olefin product contains about 96 wt% linear olefins of which about 98% are mono-olefins. Approximately 93 wt% of the linear paraffins in the feed are converted to linear olefins [3,8].

Table 15.3 Steam-Cracking Conditions

	Naphtha	Wax
Coil outlet temp., °F (°C)	1100–1650 (730–900)	1100–1200 (595–650)
Pres., psig (kPa)	45 (310)	15–30 (103–207)
Steam/HC, wt%	0.3–0.9	0.12–0.15
C ₃ conversion, wt%	60–80	8–10

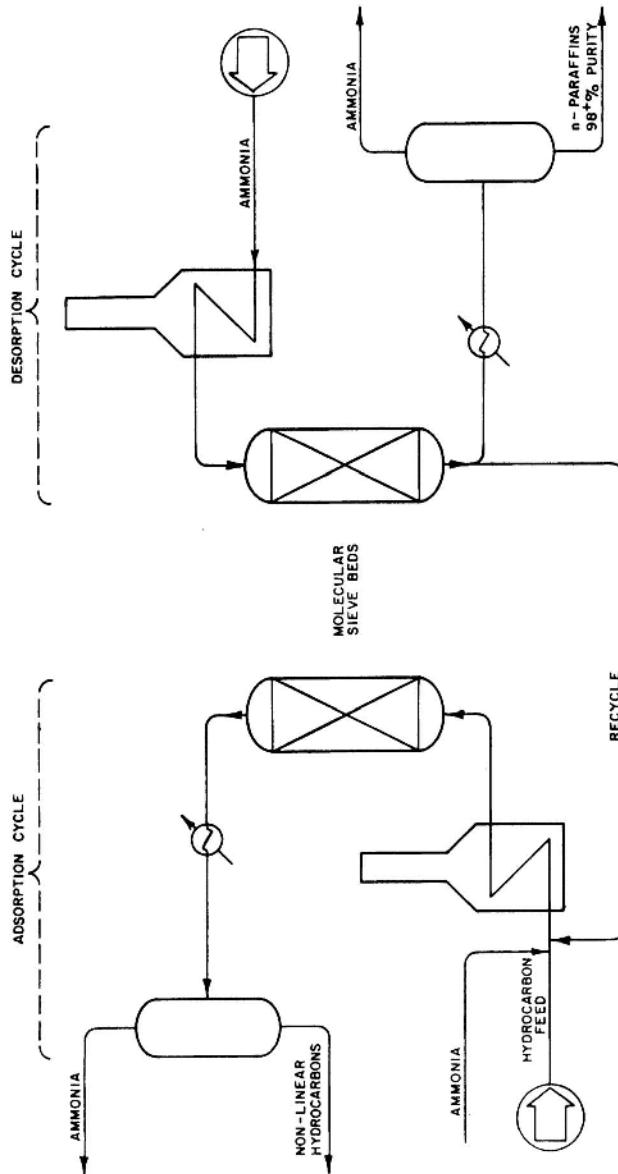


Figure 15.5 n-paraffin recovery by adsorption.

15.3 SATURATED PARAFFINS

Normal Paraffins

Normal paraffins are recovered from petroleum fractions by vapor-phase adsorption on molecular sieves having an average pore diameter of 5 Å. A simplified process flow diagram for the Exxon Ensorb process is shown in Figure 15.5. The adsorption takes place in the vapor phase at pressures of 5 to 10 psig (35–69 kPa) and temperatures from 575 to 650°F (300–350°C). Ammonia is used to desorb the normal paraffins. A semi-batch operation using two beds of 5-Å molecular sieves permits continuous operation with one bed being desorbed while the other bed is on-stream. The sieves gradually lose capacity because of contamination with polymerization products and are regenerated by controlled burn-off of the high molecular weight hydrocarbons. Run times of about 12 months between regenerations are common.

The greatest demand for n-paraffins are for use in the manufacture of biodegradable detergents using straight-chain paraffins with from 11 to 14 carbons per molecule.

Cycloparaffins

Cycloparaffins are usually prepared by the hydrogenation of the corresponding aromatic compound. For example, cyclohexane is prepared by the hydrogenation of benzene. There are a number of processes licensed for this purpose [8].

The hydrogenation of benzene is carried out over platinum or Raney nickel supported on alumina or silica-alumina. The hydrogenation reaction is highly exothermic with the release of about 1150 Btu/lb (640 kcal/kg) of benzene converted to cyclohexane. Reactor temperature is controlled by recycling and injecting a portion of the cyclohexane produced into the reactors [8].

Tetralin and decalin are prepared by the hydrogenation of naphthalene using the same hydrogenation catalysts as used for producing cyclohexane. Here, benzothiophene is a common impurity in naphthalene and causes the rapid deactivation of the nickel and platinum catalysts. It is necessary under these conditions to use a cobalt–molybdenum catalyst which has been presulfided to activate it [8].

NOTES

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ADDITIONAL READING

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16

Additives Production from Refinery Feedstocks

16.1 USE OF ALCOHOLS AND ETHERS

In the United States during the 1970s, various high octane additives began to be blended into motor gasoline to maintain octane levels as the use of TEL was reduced. Methanol and ethanol were used because of their availability and previous use in special situations. These alcohols were gradually replaced or supplemented with various ethers. Methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME) evolved as having more desirable blending and combustion characteristics than the alcohols.

One of the main advantages of ethers relative to alcohols is the lower blending vapor pressure of the ethers. These are summarized in Table 16.1. The reason for the high blending vapor pressure of the alcohols is that they form minimum boiling azeotropes with some of the hydrocarbons in the gasoline. Ethers form significantly fewer azeotropes and those that are formed reduce vapor pressure rather than increasing it. Maintaining gasoline vapor pressures below about 8 psi RVP (55 kPa) is considered an important factor in minimizing hydrocarbon vapor losses to the atmosphere. Atmospheric hydrocarbons in the presence of nitrogen oxides and sunlight are believed to form ozone through a sequence of complex chemical reactions.

The potential benefits of adding oxygenated hydrocarbons to gasoline can be summarized as follows:

1. Less carbon monoxide emissions are possible.
2. Unburned hydrocarbon emissions are reduced.
3. Ozone content in the lower atmosphere of highly populated areas may be reduced part of the time during certain weather conditions.
4. Octane requirements for good engine performance can be met without use of TEL.

Table 16.1 Typical Properties of Some Fuel Ethers and Alcohols

	MTBE	ETBE	TAME	MeOH	EtOH
Blending octane, (R + M)/2	109	110	105	118	114
Blending RVP, psig	8	4	3	60+	19
RVP psig	8	4	1.5	4.6	2.4
Atm. boiling point, °F	131	161	187	148	173
Molecular weight	88.15	102.18	102.18	32.04	46.07
wt% O ₂	18.2	15.7	15.7	50.0	33.7
Density, 60/60	0.74	0.77	0.77	0.79	0.79

Note: Blending values for octane and RVP vary to a small extent depending on concentration in gasoline and gasoline composition. Table values are typical from several published sources [6,16,13].

5. Most gasoline produced from FCCUs (catalytic cracking) contains relatively volatile olefins such as isobutylene and isoamylene. These components are some of the more reactive ozone-formers when vaporized. Reacting these olefins with alcohol to produce ethers decreases gasoline volatility and increases octane.

The disadvantages are as follows:

1. The combined capital and operating costs for producing methanol from methane and MTBE or other ethers from existing sources of isobutylene are more than the costs for converting the isobutylene to alkylate. This incremental cost difference is increased very significantly if the isobutylene is obtained by increasing severity of cat cracker operation or by converting butanes to isobutylene.
2. Compared to using butane and butylenes for alkylate production or blending, carbon dioxide emissions to the atmosphere are significantly increased when the fuel required to produce the MTBE from methane and butane is added to the vehicular emissions. This increase in carbon dioxide emission and consumption of hydrocarbons is on the order of 25 to 50% per gallon of fuel product. The actual value depends on whether isobutylene, isobutane, or normal butane is available as feedstock.

Beginning about 1990, regional and federal environmental regulatory establishments in the United States required gasoline to contain specified minimum amounts of chemically combined oxygen. The published objective was to reduce the amount of carbon monoxide released to the atmosphere. A secondary potential benefit was a desired reduction of atmospheric ozone due to assumed lower reactivity of resulting volatile emissions compared to the replaced hydrocarbons.

These requirements have resulted in most refiners blending MTBE and/or TAME in the gasoline. Small refineries usually purchase MTBE from merchant plants. In larger refineries, MTBE and TAME are made by reacting isobutylene and/or isoamylene in the light naphtha from the FCCU with purchased methanol.

Other sources of isobutylene include:

1. By-product from steam-cracking of naphtha or light hydrocarbons for production of ethylene and propylene
2. Catalytic dehydrogenation of isobutane
3. Conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides [2]
4. Light naphtha from refinery coking units

The direct blending of ethanol is used extensively in Brazil and to a lesser extent in the United States and Canada. The ethanol used is produced by fermentation of agricultural products (corn, sugar cane, etc.).

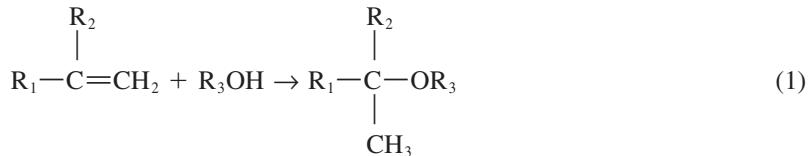
The Environmental Protection Agency (EPA) has approved several different blends of oxygenates in gasoline. Some of these are listed below.

Oxygenate component	Nominal vol% in gasoline	Maximum wt% O ₂ in gasoline
Ethanol	10	3.5
MTBE	15	2.7
Methanol + TBA	4.75 + 4.75	3.5

The upper limits of oxygen content were based on the theory that NOX emissions would increase if these limits are exceeded. The data regarding this concern are not conclusive and, therefore, the limits may not be necessary and may be removed [10].

16.2 ETHER PRODUCTION REACTIONS

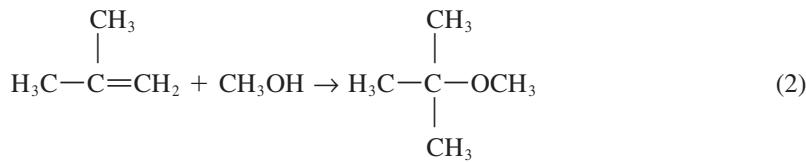
Alcohols and iso-olefins will react to form ethers according to the following equation:



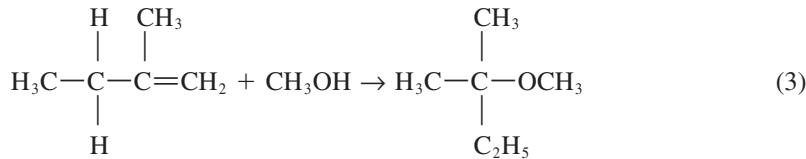
In equation (1) R₁, R₂, and R₃ represent different alkyl groups. These reactions are reversible. Production of ethers is favored by low temperatures and is exothermic. Therefore, cooling of the reactors is required to assume optimum conversion. Reactor temperatures are controlled in the range of 140 to 200°F (60 to 93°C). Pressures are about 200 psig (1380 kPa), just high enough to maintain liquid phase conditions. Acidic resin ion exchange catalysts are used to promote the reactions [1,4].

The general reaction of methanol with an isoolefin is the addition of a methoxy group to the unsaturated tertiary carbon atom. The reactions for producing MTBE and TAME are shown below.

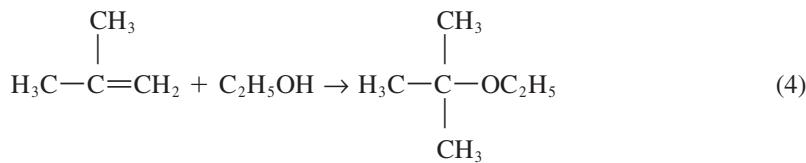
Methyl tertiary butyl ether (MTBE)



Tertiary amyl methyl ether (TAME)



Ethanol reacts in the same way with isobutylene to form ethyl tertiary butyl ether (ETBE)



16.3 ETHER PRODUCTION PROCESSES

At least six variations of commercial processes are described in the literature [4,7,11,14]. All of the processes can be modified to react isobutylene or isoamylene with methanol or ethanol to produce the corresponding ether. All use an acidic ion exchange resin catalyst under controlled temperature and pressure conditions. Temperature control of the exothermic reaction is important to maximize

conversion and minimize undesirable side reactions and catalyst deactivation. The reaction is usually carried out in two stages with a small excess of alcohol to achieve iso-olefin conversions of over 99%.

The basic difference between the various processes is in reactor design and the method of temperature control. The licensed processes include:

1. Fixed-bed adiabatic reactors with downflow liquid phase and a cooled external recirculation loop to control temperature
2. Fixed-bed adiabatic reactors, as above, but with a limited amount of vaporization at the outlet to control the temperature
3. Catalyst in tubes, with external cooling
4. Upflow liquid phase “expanded-bed” with an external cooling loop

In addition to the above variations, some of the process use a structured packing containing catalyst in a distillation tower as a second-stage reactor. One such process carrying the trademark Ethermax is licensed by UOP LLC [6,7]. The process is based on technology developments of Hüls AG of Germany, Koch Engineering Company, and UOP. Figure 16.1 is a simplified flow diagram of the process. The following process description is based on feeding isobutylene and methanol to produce MTBE.

Isobutylene and a small excess stoichiometric amount of methanol join a controlled quantity of recycle from the reactor effluent and are cooled prior to entering the top of the primary reactor.

The combined feeds and recycle are all liquids. The resin catalyst in the primary reactor is a fixed bed of small beads. The reactants flow down through the catalyst bed and exit the bottom of the reactor. Effluent from the primary reactor contains MTBE, methanol, and unreacted C₄ olefins and usually some C₄ paraffins which were in the feed.

A significant amount of the effluent is cooled and recycled to control the reactor temperature. The net effluent feeds a fractionator with a section containing catalyst. This is Koch's proprietary reaction with distillation (RWD) technology; therefore, the fractionator is called the RWD column. The catalyst section, located above the feed entry, is simply structured packing with conventional MTBE resin catalyst between the corrugated mesh plates. MTBE is withdrawn as the bottom product and unreacted methanol vapor and isobutylene vapor flow up into the catalyst reaction to be converted to MTBE.

The advantages of a RWD column include essentially complete iso-olefin conversions. A very detailed discussion of this technology was published by De-Garmo and coworkers [3]. The excess methanol and unreacted hydrocarbons are withdrawn from the RWD column reflux accumulator and fed to a methanol recovery tower. In this tower, the excess methanol is extracted by contact with water. The resultant methanol–water mixture is distilled to recover the methanol, which is then recycled to the primary reaction.

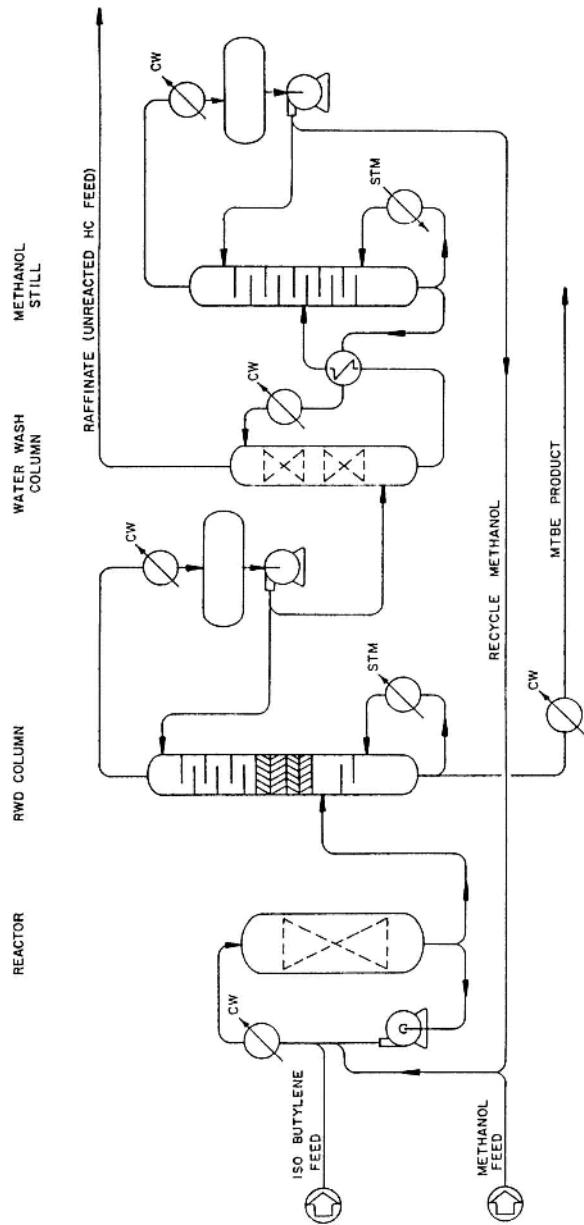
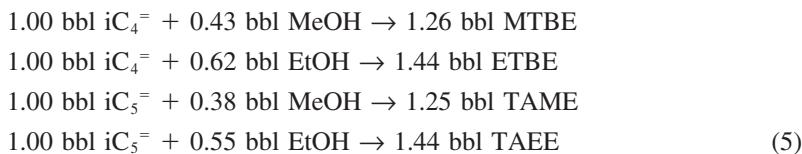


Figure 16.1 UOP LLC ethermax process.

16.4 YIELDS

The overall conversion of isobutylene to MTBE is over 99%, and the methanol consumption is essentially stoichiometric. The volume yields are given below [12]:

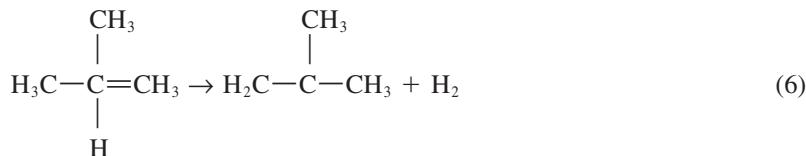


16.5 COSTS FOR ETHER PRODUCTION

Capital costs can be approximated from Figure 16.2 and Table 16.2. The capital and operating costs have been found to correlate best with total hydrocarbon feed (excluding alcohol) as opposed to iso-olefin feed or ether production. Therefore, the iso-olefin content of the feedstock must be known to estimate the cost for producing a given amount of ether. For example, the C₄ cut of FCC gasoline typically contains 15 to 18 vol% isobutylene. The C₅ to 430°F (220°C) FCC gasoline typically contains about 8 to 12 vol% isoamylene.

16.6 PRODUCTION OF ISOBUTYLENE

In a refinery having both cat cracking and coking operations, the total available isobutylene and isoamylene is only enough to produce oxygenates (MTBE, ETBE, TAME) equivalent to an oxygen content of 0.3 to 0.6 wt% of the gasoline pool. In order to meet a 2.0 wt% oxygen requirement, additional isobutylene is produced by dehydrogenation of isobutane according to the following reaction:



The resulting isobutylene is separated from the hydrogen and then combined with either methanol or ethanol to produce MTBE or ETBE as previously described.

The reaction is endothermic (about 53,000 BTU/pound mol at 1000°F). Relatively high temperatures and low pressures are required to obtain reasonable conversion. Figure 16.3 illustrates the conversions theoretically possible assum-

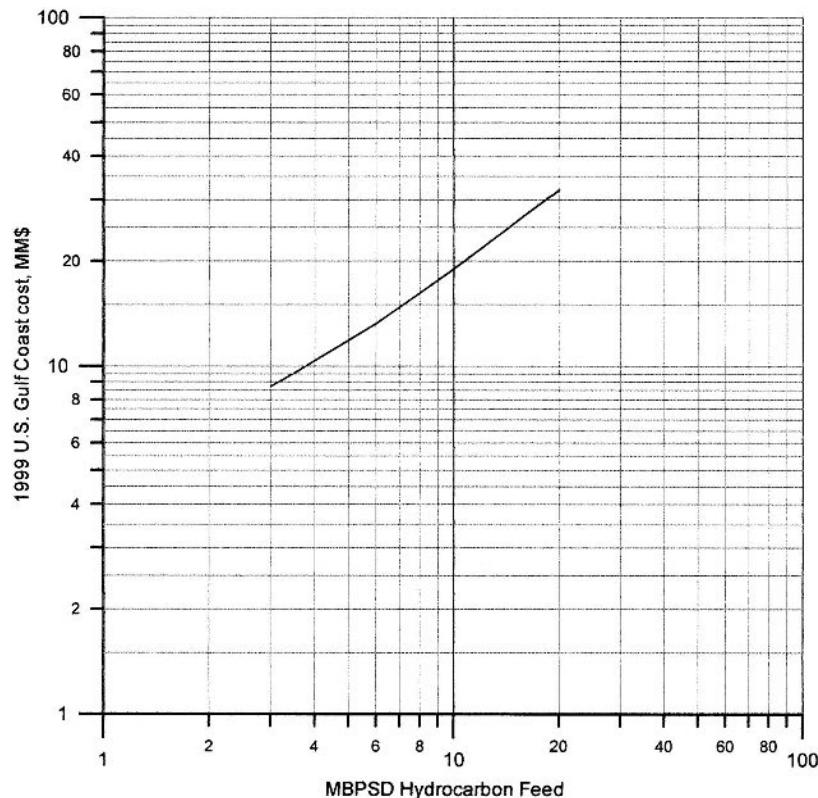


Figure 16.2 Ether production facility cost. (see Table 16.2.)

ing no minor side reactions occur. The pressures shown are the sum of the equilibrium partial pressures of the isobutane plus isobutylene plus hydrogen. This is the reactor outlet total pressure only if there are no other molecular species present. With current catalysts, it is important to limit the temperatures to about 1100 to 1200°F (593 to 649°C) to minimize formation of undesirable species which add to the cost of downstream separation facilities. These unwanted products can amount to about 5 to 10 wt% of the feed. They may include primarily methane, ethane, ethene, propane, propene, propadiene, some butane (from the feed), and butene 1 and 2.

A potential alternative to dehydrogenation of isoparaffins for iso-olefin production is the isomerization of normal olefins. At present, commercial processes for this alternative are in the development stages.

Table 16.2 Ether Production Unit Cost Data

<i>Costs included</i>	
1.	Two-stage reaction system with MTBE column and methanol recovery system similar to Fig. 16.1
2.	Initial catalyst fill and paid-up royalty
<i>Costs not included</i>	
1.	Cooling water, power, and steam supply
2.	Feed prefractionation
3.	Feed or product storage
4.	Raffinate treating for saturation of olefins or trace oxygenates removal
<i>Utility data (per barrel of hydrocarbon feed excluding alcohol)</i>	
Power, kWh/bbl feed	1.0
kWh/MT feed	10.0
Steam, lb/bbl feed, 150 psig	350
kg/MT feed, 1035 kPa	1590
Cooling water, gal/bbl feed (30°F rise)	500
kg/MT feed (17°C rise)	1900
Catalyst replacement, \$/bbl feed	.50
\$/MT feed	5.00
Fuel	None

Note: See Fig. 16.2.

16.7 COMMERCIAL DEHYDROGENATION PROCESSES

Although thermal, noncatalytic process configurations can be used to produce isobutylene from isobutane, catalytic processes have been favored because of their greater selectivity. Three catalytic processes are used in major installations in North America. These are Houdry's CATOFIN, Philips Petroleum's STAR and UOP LLC's OLEFLEX. A fourth catalytic process licensed by Snamprogetti Yarsintez was developed in Russia.

These processes have single-pass conversions in the range of about 50 to 60% with selectivities of about 88 to 90%. This means that about 88 to 90 mol% of the converted isobutane becomes isobutylene. Each one of these processes utilizes very different technology for providing the endothermic heat of reaction and for regenerating the catalyst by burning off the small amount of coke which accumulates on the catalyst. Coke yields are generally less than 0.5 wt% of the feed. A very good table comparing these processes has been made by Maples [9]. The main features of each process are described in the following sections.

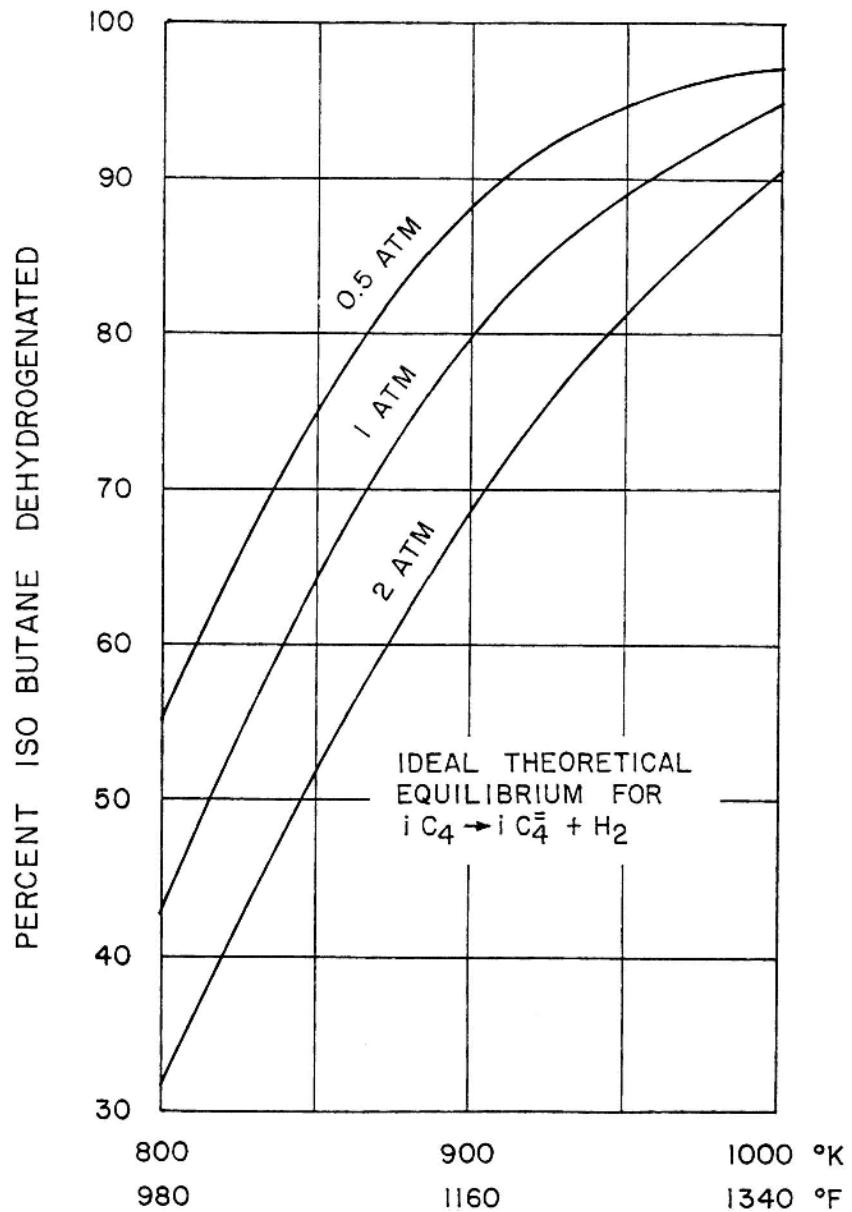


Figure 16.3 Isobutane dehydrogenation.

16.8 HOUDRY'S CATOFIN

This process, originally developed by Houdry, is now owned by United Catalysts Inc. and licensed by ABB Lummus Crest. The process utilizes three or more horizontal reactors with fixed beds of catalyst. The pelleted catalyst is chromic oxide on alumina. The reactors operate in parallel on offset time cycles in the following sequence:

1. On-stream dehydrogenation of isobutane
2. Steam purge
3. Reheat catalyst with preheated air and simultaneous combustion of coke formed during Step 1
4. Evacuation of residual air
5. Return to on-stream operation

The switching times on individual reactors are offset so that the overall process is continuous. The overall cycle time depends on the size of the reactors and the required feed rate. The total cycle may be repeated on each reactor about two or three times per hour. The sequencing and switching of valves is fully automated with appropriate safety interlocks.

16.9 PHILLIPS PETROLEUM'S STAR

This process utilizes a pelleted catalyst containing a noble metal on an alumina base. The catalyst is contained as a fixed bed in tubes which are externally fired to provide the heat of reaction. This allows the reaction to be conducted at essentially isothermal conditions, thereby reducing undesirable thermal cracking reactions. Steam is fed through the catalyst with the hydrocarbon. This lowers the partial pressure of the reactants, consequently allowing higher conversions at a given temperature, about as indicated on Figure 16.2. Steam addition also reduces coke formation and helps to hold the reaction temperature more uniformly. Use of steam as a partial pressure diluent instead of other gases, such as nitrogen, reduces the cost of the downstream separation and recovery facilities because the steam can be condensed from the reactor effluent. The catalyst does deactivate due to coke deposition and therefore periodic regeneration is required.

Multiple passes of tubes are provided in the reactor/furnace so that only a small portion of the reactor is in the regeneration step at any one time, thereby allowing the process to be operated continuously. The regeneration is done approximately as follows:

1. Stop hydrocarbon feed while continuing steam flow long enough to purge the reactants.
2. Add air to the steam flow.

3. Stop air and continue steam flow to purge air.
4. Restart hydrocarbon feed.

The process equipment may be economically sized so that a given number of catalyst tubes ("bank") can be regenerated in about one hour, and regeneration of each such bank occurs only two or three times in a 24-hour period.

16.10 UOP LLC's OLEFLEX

This process, developed and licensed by UOP LLC, is an extension of two successful UOP LLC technologies:

1. UOP LLC trademarked Pacol process for producing mono-olefins from kerosine range paraffins
2. UOP LLC trademarked CCR Platforming process

The catalyst contains platinum on a unique spherical alumina support. The reaction section has three reactors in series with preheat before the first reactor and reheat before the second and third reactors to provide the heat of reaction. The reactants plus hydrogen recycle gas flow radially through the very slowly downward-moving beds of catalyst. Sufficient hydrogen partial pressure is maintained so that coke formation on the catalyst is less than 0.02 wt% of the hydrocarbon feed. This reduces catalyst regeneration requirements to the order of once in a period of about three to ten days. Consequently, catalyst regeneration can be completely discontinued for several days, if necessary for maintenance, without interrupting olefin production. However, normal operation involves the continuous transfer of catalyst from reactor 1 to reactor 2 to reactor 3 to continuous regeneration and then return to reactor 1.

16.11 SNAMPROGETTI/YARSINTEZ PROCESS

This process was developed in the former Soviet Union and is essentially similar to a fluid-bed cat cracker. The catalyst is a promoted chromium oxide powder. Isobutane feed vapor and superheated steam fluidize the catalyst in the reactor where the dehydrogenation occurs. Spent catalyst is withdrawn continuously from the reactor and transferred to the regenerator. Coke is burned off the catalyst in the regenerator, and additional fuel is used to increase the catalyst temperature before returning it to the reactor.

16.12 COSTS TO PRODUCE ISOBUTYLENE FROM ISOBUTANE

Capital costs can vary by 100% for any given installation because of the substantial differences between the various process technologies. As an example, facili-

Table 16.3 Nomenclature for Some Common Ethers

Acronym	Common name	IUPAC name
MTBE	Methyl tertiary butyl ether	2 methyl 2 methoxy propane
ETBE	Ethyl tertiary butyl ether	2 ethyl 2 methoxy propane
TAME	Tertiary amyl methyl ether	2 methyl 2 methoxy butane
TAEE	Tertiary amyl ethyl ether	2 ethyl 2 methoxy butane

ties for converting 12,000 BPD of isobutane into about 9700 BPD of isobutylene may cost somewhere in the range of \$75 million to \$150 million (basis U.S. Gulf Cost, 1992). This yield implies a conversion of 90% at 90% selectivity. The cost would include dehydrogenation, separation and recycle of unconverted isobutane, initial catalyst, and paid-up royalties. The costs would not include utility supplies, feed or product storage, nor butane isomerization.

Utility requirements also vary substantially. Typical 1992 U.S. Gulf Coast costs for labor, utilities, catalysts, and chemicals are in the range of \$3 to \$6 per barrel of isobutylene produced. These costs do not include the cost of the isobutane feed.

16.9 INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTS NOMENCLATURE

The use of common nomenclature for hydrocarbons and other organic compounds is the general practice in the refining industry and has been followed in this chapter. Table 16.3 shows a comparison of the common designation and IUPAC nomenclature for some of the ethers which can be blended in gasoline.

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17

Cost Estimation

Although detailed discussions of various capital cost estimating methods are not part of the intended scope of this work, some comments are pertinent. All capital cost estimates of industrial process plants can be classified as one of four types:

1. Rule-of-thumb estimates
2. Cost-curve estimates
3. Major equipment factor estimates
4. Definitive estimates

The capital cost data presented in this work are of the second type—cost-curve estimates.

17.1 RULE-OF-THUMB ESTIMATES

The rule-of-thumb estimates are, in most cases, only an approximation of the order of magnitude of cost. These estimates are simply a fixed cost per unit of feed or product. Some examples are:

- Complete coal-fired electric power plant: \$2,500/kW
- Complete synthetic ammonia plant: \$200,000/TPD
- Complete petroleum refinery: \$25,000/BPD

These rule-of-thumb factors are useful for quick ballpark costs. Many assumptions are implicit in these values and the average deviation from actual practice can often be more than 50%.

17.2 COST-CURVE ESTIMATES

The cost-curve method of estimating corrects for the major deficiency illustrated above by reflecting the significant effect of size or capacity on cost. These curves

indicate that costs of similar process units or plants are related to capacity by an equation of the following form:

$$\frac{\text{Plant A cost}}{\text{Plant B cost}} = \frac{(\text{Plant A capacity})}{(\text{Plant B capacity})^x} \quad (1)$$

This relationship was reported by Lang [4], who suggested an average value of 0.6 for the exponent (X). Other authors have further described this function [12,13]. Cost curves of this type have been presented for petroleum refinery costs in the past [2,6].

The curves presented herein have been adjusted to eliminate certain costs such as utilities, storage, offsite facilities, and location cost differentials. Separate data are given for estimating the costs of these items. The facilities included have been defined in an attempt to improve accuracy.

It is important to note that most of the cost plots have an exponent which differs somewhat from the 0.6 value. Some of the plots actually show a curvature in the log-log slope which indicates that the cost exponent for these process units varies with capacity. Variations in the log-log slope (cost exponent) range from about 0.5 for small capacity units up to almost 1.0 for very large units. This curvature, which is not indicated in the previously published cost-curves, is due to paralleling equipment in large units and to disproportionately higher costs of very large equipment such as vessels, valves, pumps, etc. The curvature in the log-log slope of cost plots has been described by Chase [1].

The cost-curve method of estimating, if carefully used and properly adjusted for local construction conditions, can predict actual costs within 25%. Except in unusual circumstances, errors will probably not exceed 50%.

17.3 MAJOR EQUIPMENT FACTOR ESTIMATES

Major equipment factor estimates are made by applying multipliers to the costs of all major equipment required for the plant or process facility. Different factors are applicable to different types of equipment, such as pumps, heat exchangers, pressure vessels, etc. [3]. Equipment size also has an effect on the factors.

It is obvious that prices of major equipment must first be developed to use this method. This requires that heat and material balances be completed in order to develop the size and basic specifications for the major equipment.

This method of estimating, if carefully followed, can predict actual costs within 10 to 20%.

A shortcut modification of this method uses a single factor for all equipment. A commonly used factor for petroleum refining facilities is 4.5. The accuracy of this shortcut is of course less than when using individual factors.

17.4 DEFINITIVE ESTIMATES

Definitive cost estimates are the most time-consuming and difficult to prepare but are also the most accurate. These estimates require preparation of plot plans, detailed flow sheets and preliminary construction drawings. Scale models are sometimes used. All material and equipment are listed and priced. The number of man-hours for each construction activity is estimated. Indirect field costs, such as crane rentals, costs of tools, supervision, etc., are also estimated.

This type of estimate usually results in an accuracy of $\pm 5\%$.

17.5 SUMMARY FORM FOR COST ESTIMATES

The items to be considered when estimating investment from cost-curves are:

- Process units
- Storage facilities
- Steam systems
- Cooling water systems
- Subtotal A
- Offsites
- Subtotal B
- Special costs
- Subtotal C
- Location factor
- Subtotal D
- Contingency
- Total

17.6 STORAGE FACILITIES

Storage facilities represent a significant item of investment costs in most refineries. Storage capacity for crude oil and products varies widely at different refineries. In order to properly determine storage requirements the following must be considered: the number and type of products, method of marketing, source of crude oil, and location and size of refinery.

Installed costs for “tank-farms” vary from \$60 to \$80 per barrel of storage capacity. This includes tanks, piping, transfer pumps, dikes, fire protection equipment, and tank-car or truck loading facilities. The value is applicable to low vapor pressure products such as gasoline and heavier liquids. Installed costs for butane

storage ranges from \$90 to \$120 per barrel, depending on size. Costs for propane storage range from \$100 to \$130 per barrel.

17.7 LAND AND STORAGE REQUIREMENTS

Each refinery has its own land and storage requirements, depending on location with respect to markets and crude supply, methods of transportation of the crude and products, and number and size of processing units. Availability of storage tanks for short-term leasing is also a factor as the maximum amount of storage required is usually based on shutdown of processing units for turnaround at 18- to 24-month intervals rather than on day-to-day processing requirements. If sufficient rental tankage is available to cover turnaround periods, the total storage and land requirements can be materially reduced, as the land area required for storage tanks is a major portion of refinery land requirements.

Three types of tankage are required: crude, intermediate, and product. For a typical refinery which receives the majority of its crude by pipeline and distributes its products in the same manner, about 13 days of crude storage and 25 days of product storage should be provided. The 25 days of product storage is based on a three-week shutdown of a major process unit. This generally occurs only every 18 months or two years, but sufficient storage is necessary to provide products to customers over this extended period. A rule-of-thumb figure for total tankage, including intermediate storage, is approximately 50 barrels of storage per BPD crude oil processed.

The trend to producing many types of gasolines and oxygenated components can increase blending and product storage requirements by about 50%.

W. L. Nelson indicates that in 1973 the average refinery had 69 days of total storage capacity [7]. In 1999 the range was about 25 to 90 days of total storage.

The land requirements are frequently dictated by considerations other than process or storage because of the desire to provide increased security, to be isolated from neighboring buildings, etc. If operational matters are the prime consideration, the land necessary for operational and storage facilities is about four acres per 1000 BPCD crude capacity.

Nelson has summarized land used for 32 refineries from 1948 to 1971 [8]. The land in use when the refineries were built ranged as a function of refinery complexity from 0.8 acres to 5.7 acres per 1000 BPD crude capacity. Land actually purchased, though, was much more than this, and varied from 8 to 30 acres per 1000 BPD. This additional land provided a buffer zone between the refinery and adjacent property and allowed for expanding the capacity and complexity of the refinery. In a summary article on land and storage costs [9], Nelson suggests that five acres of land per 1000 BPCD crude capacity be used for planning purposes.

Land provided for growth and expansion to other processes, such as petrochemicals, should not be included in the investment costs against which the return on investment is calculated. Land purchased for future use should be charged against the operation for which it is intended or against overall company operations.

17.8 STEAM SYSTEMS

An investment cost of \$150.00 per lb/hr of total steam generation capacity is used for preliminary estimates. This represents the total installed costs for gas- or oil-fired, forced draft boilers, operating at 250 to 300 psig and all appurtenant items such as water treating, deaerating, feed pumps, yard piping for steam, and condensate.

Total fuel requirements for steam generation can be assumed to be 1200 Btu (LHV) per pound of steam.

A contingency of 25% should be applied to preliminary estimates of steam requirements.

Water makeup to the boilers is usually 5 to 10% of the steam produced.

17.9 COOLING WATER SYSTEMS

An investment cost of \$150.00 per gpm of total water circulation is recommended for preliminary estimates. This represents the total installed costs for a conventional induced-draft cooling tower, water pumps, water treating equipment, and water piping. Special costs for water supply and blowdown disposal are not included.

The daily power requirements (kWh/day) for cooling water pumps and fans is estimated by multiplying the circulation rate in gpm by 0.6. This power requirement is usually a significant item in total plant power load and should not be ignored.

The cooling tower makeup water is about 5% of the circulation. This is also a significant item and should not be overlooked.

An “omission factor,” or contingency of 15%, should be applied to the cooling water circulation requirements.

17.10 OTHER UTILITY SYSTEMS

Other utility systems required in a refinery are electric power distribution, instrument air, drinking water, fire water, sewers, waste collection, and others. Since

these are difficult to estimate without detailed drawings, the cost is normally included in the offsite facilities.

Offsites

Offsites are the facilities required in a refinery which are not included in the costs of major facilities. A typical list of offsites is shown below:

- Electric power distribution
- Fuel oil and fuel gas facilities
- Water supply, treatment, and disposal
- Plant air systems
- Fire protection systems
- Flare, drain and waste containment systems
- Plant communication systems
- Roads and walks
- Railroads
- Fence
- Buildings
- Vehicles
- Product and additives blending facilities
- Product loading facilities

Obviously, the offsite requirements vary widely between different refineries.

The values shown below can be considered as typical for grassroots refineries when estimated as outlined in this text.

Crude oil feed (BPSD)	Offsite costs (percent of total major facilities costs ^a)
Less than 30,000	50
30,000–100,000	30
More than 100,000	20

^a Major facilities as defined herein include process units, storage facilities, cooling water systems, and steam systems.

Offsite costs for the addition of individual process units in an existing refinery can be assumed to be about 20 to 25% of the process unit costs.

Special Costs

Special costs include the following: land, spare parts, inspection, project management, chemicals, miscellaneous supplies, and office and laboratory furniture. For preliminary estimates these costs can be estimated as 4% of the cost of the process units, storage, steam systems, cooling water systems, and offsites. Engineering costs and contractor fees are included in the various individual cost items.

Contingencies

Most professional cost estimators recommend that a contingency of at least 15% be applied to the final total cost determined by cost-curve estimates of the type presented herein.

The term contingencies covers many loopholes in cost estimates of process plants. The major loopholes include cost data inaccuracies when applied to specific cases and lack of complete definition of facilities required.

Escalation

All cost data presented in this book are based on U.S. Gulf Coast construction averages for the year 1999. This statement applies to the process unit cost curves, as well as values given for items such as cooling water systems, steam plant systems, storage facilities, and catalyst costs. Therefore, in any attempt to use the data for current estimates some form of escalation or inflation factor must be applied. Many cost index numbers are available from the federal government and from other published sources. Of these, the Chemical Engineering Plant Cost Index and the Nelson-Farrar Refinery (Inflation) Index are the most readily available and probably the most commonly used by estimators and engineers in the U.S. refining industry.

The use of these indices is subject to errors inherent in any generalized estimating procedure, but some such factor must obviously be incorporated in projecting costs from a previous time basis to a current period. It should be noted that the contingencies discussed in the previous section are not intended to cover escalation.

Escalation or inflation of refinery investment costs is influenced by items which tend to increase costs as well as by items which tend to decrease costs. Items which increase costs include obvious major factors, such as:

1. Increased cost of steel, concrete, and other basic materials on a per ton basis
2. Increased cost of construction labor and engineering on a per hour basis
3. Increased costs for excessive safety standards and exaggerated pollution control regulations

4. Increase in the number of reports and amount of superfluous data necessary to obtain local, state, and federal construction permits

Items which tend to decrease costs are basically all related to technological improvements. These include:

1. Process improvements developed by the engineers in research, design, and operation
2. More efficient use of engineering and construction manpower

Examples of such process improvements include improvement of fractionator tray capacities, improved catalysts which allow smaller reactors, and improved instrumentation allowing for consistently higher plant feed rates.

Plant Location

Plant location has a significant influence on plant costs. The main factors contributing to these variations are climate and its effect on design requirements and construction conditions; local rules, regulations, codes, taxes, etc; and availability and productivity of construction labor.

Relative hydrocarbon process plant costs on a 1999 basis at various locations are given below:

Location	Relative cost
U.S. Gulf Coast	1.0
Los Angeles	1.4
Portland, Seattle	1.2
Chicago	1.3
St. Louis	1.5
Detroit	1.3
New York	1.7
Philadelphia	1.5
Alaska, North Slope	3.0
Alaska, Anchorage	2.0

17.11 APPLICATION OF COST ESTIMATION TECHNIQUES

Although economic evaluation will not be discussed until the next chapter, an example problem illustrating the methods to estimate capital and operating costs

and return on investment is included here to aid in clarifying the principles discussed in this chapter. The illustrative problem is relatively simple but the same techniques and procedures can be applied to the most complex refinery economic evaluation.

Statement of Problem

For the following example of a simplified refinery, calculate:

1. The products available for sale.
2. Investment.
3. Operating costs.
4. Simple rate of return on investment.
5. True rate of return on investment.

Also prepare a basic block flow diagram (Fig. 17.1). The following data are available:

1. Crude charge rate: 30,000 BPSD.
2. Crude oil sulfur content: 1.0 wt%.
3. Full-range naphtha in crude: 4,000 BPSD
240°F MBP
56° API gravity
11.8 K_w.
4. Light gas oil in crude: 4,000 BPSD.
5. Heavy gas oil in crude: 4,000 BPSD.
6. Vacuum gas oil in crude: 6,000 BPSD.
7. Vacuum residual in crude: 12,000 BPSD.
8. On-stream factor: 93.15%.
9. Cost of makeup water: \$0.20/1000 gal.
10. Cost of power: \$0.04 kWh.
11. LHV of heavy gas oil: 5.5 MMBtu/bbl.
12. Replacement cost for desulfurizer catalyst is \$1/lb.
13. Replacement cost for reformer catalyst is \$5/lb.
14. Insurance annual cost is 0.5% of plant investment.
15. Local taxes annual cost is 1.0% of plant investment.
16. Maintenance annual cost is 5.5% of plant investment.
17. Misc supplies annual cost is 0.15% of plant investment.
18. Average annual salary plus payroll burden for plant staff and operators is \$70,000.
19. Value of crude oil and products at refinery is:

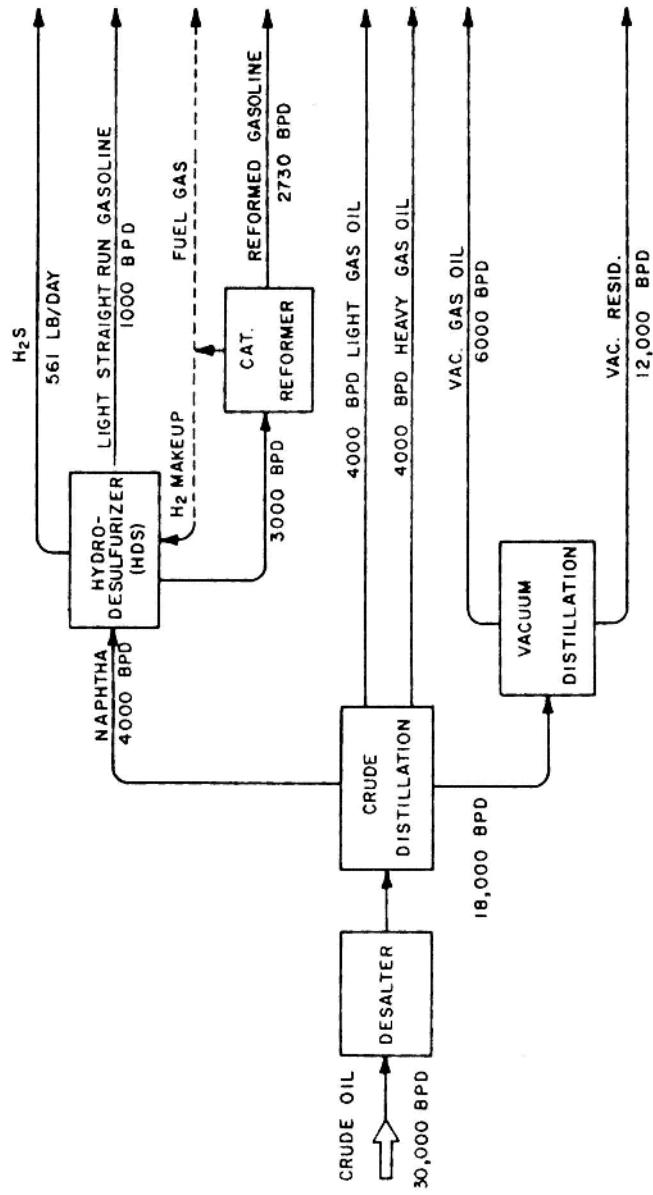


Figure 17.1 Block flow diagram for sample problem.

	\$/bbl
Crude	21.50
Gasoline	32.00
Light gas oil	30.00
Heavy gas oil	28.00
Vacuum gas oil	24.00
Vacuum residual	21.00

20. Depreciation allowance: 15 year, straight-line.
21. Corporate income tax: 50% of taxable income.
22. Location: St. Louis, Missouri.
23. Construction period: 1999.
24. Escalation rate (applicable to construction costs only) is 3% per year.

Process Requirements

The crude oil is to be desalted and fractionated to produce full-range naphtha, light gas oil, heavy gas oil, and "atmospheric bottoms." The latter cut is fed to a vacuum unit for fractionation into vacuum gas oil and vacuum residuals. The full-range naphtha is to be hydrodesulfurized. After desulfurization, the light straight-run (LSR) portion (i.e., the material boiling below 180°F) of the full-range naphtha is separated for blending into the gasoline product. The balance of the naphtha is fed to a catalytic reformer which is operated to produce a reformate having a research octane number (clear) of 93. This reformate plus the LSR are mixed to make the final gasoline product. Propane and lighter hydrocarbons, including the hydrogen, which are produced in the catalytic reformer are consumed as fuel. The necessary hydrogen makeup for the hydrodesulfurizer is, of course, taken from these gases before they are burned as fuel. The balance of the fuel requirement is derived from light gas oil. The hydrogen sulfide produced in the hydrodesulfurizer is a relatively small amount and is burned in an incinerator. No other product treating is required. It can be assumed that sufficient tankage for approximately 12 days storage of all products is required. The total storage requirement will thus be approximately 360,000 barrels.

The preceding information, in addition to that contained in this book, is sufficient for solution of the problem.

Catalytic Reformer

Calculate properties of feed to reformer. Given total naphtha stream properties as follows:

Mid-boiling point: 240°F
 API gravity: 56°API
 K_w : 11.8

The material boiling below 180°F (LSR) is not fed to the reformer. After desulfurizing the total naphtha, the LSR is fractionated out. The problem is to estimate the volume and weight of the LSR assuming a distillation curve is not available. This LSR is then deducted from the total naphtha to find the net reformer feed. This is done as shown in the following steps:

1. Assume that butane and lighter hydrocarbons in the naphtha are negligible. Thus, the lightest material would be isopentane (iC_5) with a boiling point of 82°F. Hence, the mid-boiling point of the LSR would be approximately $(82 + 180)(0.5) = 131°F$.
2. Assume that the LSR has the same K_w as the total naphtha (i.e., 11.8).
3. From general charts [see Ref. 5, chapter 2] relating K_w , mean average boiling point, and gravity, find the gravity of the LSR. This is 76.5° API.
4. The gravity of the naphtha fraction boiling above 180°F is next determined by a similar procedure. The mid-boiling point for the total naphtha is given above as 240°F, and the initial boiling point was estimated in Step 1 as 82°F. Therefore, the naphtha end point can be estimated as shown:

$$240 + (240 - 82) = 398°F$$

Now the approximate mid-boiling point of the reformer feed is estimated as

$$(180 + 398)(0.5) = 289°F$$

Using a K_w of 11.8, the reformer feed gravity is found (as in Step 3) to be 52.5 API.

5. With the above estimates of gravity of both the LSR and reformer feed, it is now possible to estimate the relative amounts of each cut which will exist in the total naphtha stream. This is done by weight and volume balances as shown below. Use simplified nomenclature:

V_{LSR} = gallons LSR
 V_{RF} = gallons reformer feed
 V_N = gallons total naphtha
 W_{LSR} = pounds LSR
 W_{RF} = pounds reformer feed
 W_N = pounds total naphtha
 lb/gal LSR = 5.93(67.5°API)
 lb/gal RF = 6.41(52.5°API)
 lb/gal V_N = 6.29(56°API)

Volume balance (hourly basis):

$$\begin{aligned} V_N &= (4000)(42/24) = 7000 \text{ gal/hr} \\ V_{LSR} + V_{RF} &= 7000 \text{ gal/hr} \end{aligned}$$

Weight balance (hourly basis):

$$\begin{aligned} V_N(6.29) &= (7000)(6.29) = 44,030 \text{ lb/hr} \\ V_{LSR}(5.93) + V_{RF}(6.41) &= 44,030 \text{ lb/hr} \end{aligned}$$

Simultaneous solution of the two equations for V_{LSR} and V_{RF} gives:

$$\begin{aligned} V_{LSR} &= 1750 \text{ gal/hr} = 1000 \text{ BPD} \\ V_{RF} &= 5250 \text{ gal/hr} = 3000 \text{ BPD} \end{aligned}$$

6. The above information should then be tabulated as shown below to ascertain that all items balance.

Stream	°API	lb/gal	gal/hr	lb/hr	BPD
LSR	67.5	5.93	1,750	10,378	1,000
Reformer feed	52.5	6.41	5,250	33,652	3,000
Total naphtha			7,000	44,030	4,000

7. Before proceeding, it should be emphasized that the above methods for approximating the naphtha split into LSR and reformer feed are satisfactory for preliminary cost and yield computations, such as this example, but not for final design calculations.

8. The reformer feed properties can now be used with the yield curves in the text. The following yields are based on production of 93 RON reformat. From the yield curves:

vol% C_5^+ : 86.0
 vol% C_4S : 5.0 ($iC_4/nC_4 = 41.5/58.5$)
 wt% C_1 and C_2 : 1.1
 wt% C_3 : 1.92
 wt% H_2 : 1.75

With the above data, complete the following table:

Component	gal/hr	lb/gal	lb/hr	BPD	Mscf/day
H ₂			589		2,682
C ₁ and C ₂			370		145 ^a
C ₃	153	4.23	646		133
iC ₄	109	4.69	511	62	
nC ₄	154	4.86	748	88	
C ₅ ⁺	4,515	6.82	30,788 ^b	2,580	
Total			33,652	2,730	2,960
Feed	5,250	6.29	33,652	3,000	—

^a Assume lb C₁/lb C₂ = 0.5 (i.e., C₁, C₂ = 23.3 mol wt).

^b lb/hr C₅⁺ obtained by difference from total feed less other products.

Naphtha Desulfurizer

Assume crude oil = 1.0% sulfur. Then, from curve for miscellaneous crudes, naphtha contains 0.05% sulfur (240°F MBP). Calculate amount of sulfur produced. Assume K_w for desulfurized feed is 11.8. This combined with 240°F MBP gives a naphtha API gravity of 56° API (see reformer calculations).

$$56^{\circ}\text{API} = 6.29 \text{ lb/gal}$$

$$\text{wt\% S in naphtha} = S_N = (4000)(42)(6.29)(0.0005) = 528 \text{ lb/day}$$

$$\text{Maximum H}_2\text{S formed} = 32(528) = 561 \text{ lb/day}$$

$$\begin{aligned} \text{Theoretical H}_2 \text{ required} &= 561 - 528 \\ &= 33 \text{ lb/day} \\ &= 16.5 \text{ mol/day} \\ &= 6.26 \text{ Mscf/day} \end{aligned}$$

Makeup H₂ required (see Ref. 8) is about 100 to 150 scf/bbl, or

$$(4000)(0.15) = 600 \text{ Mscf/day}$$

Hydrogen from catalytic reformer is 2682 Mscf/day, which is more than adequate.

Table 17.1 gives a summary of investment and utilities costs.

Calculation of Direct Annual Operating Costs

After completing the investment and yield calculations the annual operating costs of the refinery can be determined. Operating costs can be considered to include three major categories:

Table 17.1 Summary of Investment and Utilities Costs

	BPSD	\$ ($\times 10^3$) 1999 Gulf Coast	Cooling water (gpm)	lb/hr stm.	kW	Fuel (MMBtu/hr)
Desalter	30,000	2,200	63		20	
Crude unit	30,000	42,000	3,125	12,500	1,125	63
Vacuum unit	18,000	18,000	1,875	7,500	225	23
Naphtha desulfurizer	4,000	7,700	833	1,000	333	17
Reformer	3,000	13,500	833	3,750	375	38
Initial catalyst (desulfurizer)		Included				
Initial catalyst (reformer)		600				
Subtotal		84,000	6,729	24,750	2,078	141
Cooling water sys- tem, 7,740 gpm ^a		1,160			194	
Steam system, 30,900 lb/hr ^b		4,635				37
Storage ^c	12 days ^d	89,795	6,729	24,750	2,272	178
Subtotal		18,000				
Offsites ^c	(30%)	107,795				
Subtotal		32,339				
Location factor	1.5	140,134				
Spec cost factor	1.04 ^e					
Contingency	1.15 ^e					
Escalation	(1.03) ²					
Total		256,453				

^a Add 15% excess capacity to calculated cooling water circulation.^b Add 25% excess capacity to calculated steam supply.^c Individual values for utilities in the storage and offsite categories are accounted for by notes a and b.^d 360,000 barrels at average cost of \$50.00/bbl.^e These factors are compounded.^f This is the projected cost at the location in St. Louis in 2001. No paid-up royalties are included.

1. Costs which vary as a function of plant throughput and on-stream time. These include water makeup to the boilers and cooling tower, electric power, fuel, running royalties, and catalyst consumption.
2. Costs which are a function of the plant investment. These include insurance, local taxes, maintenance (both material and labor), and miscellaneous supplies.

3. Costs which are determined by the size and complexity of the refinery. These include operating, clerical, technical, and supervisory personnel.

The following sections illustrates development of the above costs.

On-Stream Time

Refineries generally have an on-stream (full capacity) factor of about 92 to 96%. For this example, a factor of 93.15% (340 days per year) is used.

Water Makeup

1. To cooling tower ($30^{\circ}\text{F}\Delta t$):

1% evaporation for $10^{\circ}\text{F}\Delta t$

1/2% windage loss

1% blowdown to control solids concentration

$$\text{Cooling tower, makeup} = (3)(1\%) + 1/2\% + 1\% = 4 \frac{1}{2}\%$$

$$\text{makeup} = 0.045 \times 7740 \text{ gpm} = 348 \text{ gpm}$$

2. To boiler:

Average boiler blowdown to control solids concentration can be assumed to be 5%.

$$\text{Boiler makeup} = (0.05)(30,900) = 1545 \text{ lb/hr} = 3.1 \text{ gpm.}$$

$$\text{Total makeup water} = 351 \text{ gpm.}$$

Average cost to provide makeup water is approximately \$0.20/1000 gallons.

$$\text{Therefore, annual water makeup cost is } (351)(1440)(340)(0.20)(10^{-3}) = \$34,370.$$

Power

Industrial power costs range from \$0.025/kWh (in locations where there is hydroelectric power) to \$0.06/kWh. For this example, use \$0.04/kWh.

$$\begin{aligned} \text{Power cost} &= (2212)(24)(340)(0.04) \\ &= \$722,000 \text{ per year} \end{aligned}$$

Fuel

In this example, no separate charge will be made for fuel, since it is assumed that the refinery will use some of the heavy gas oil products for fuel. The amount

of gas oil consumed must be calculated, so that this quantity can be deducted from the products available for sale.

From the summary tabulation of utilities, we require 178 MMBtu/hr for full-load operation. This fuel is supplied by combustion of reformer off-gas supplemented with heavy gas oil. Some of the reformer off-gas is consumed in the hydrodesulfurizer, and this quantity (hydrogen portion only) must be deducted from available fuel. A fuel balance is made as shown below to determine the amount of heavy gas oil consumed as fuel.

Step 1: From reformer calculations the available fuel gas is:

Component	Total (lb/hr)	HDS ^a usage (lb/hr)	Available for fuel (lb/hr)
H ₂	589	132	457
C ₁	123		123
C ₂	246		246
C ₃	646		646
Total	1,604	132	1,472

^a From desulfurizer calculations, hydrogen makeup was 600 Mscfd.

In petroleum work, "standard conditions" are 60°F and 14.696 psia. At these conditions, 1 pound mole = 379.5 scf. Thus, hydrogen consumed in HDS unit is:

$$\frac{600,000}{(24)(379.5)} (2) = 132 \text{ lb/hr}$$

Step 2: Calculated lower heating value (LHV) of available fuel gas is:

Component	Total (lb/hr)	LHV ^a (Btu/lb)	LHV (MMBtu/hr)
H ₂	457	51,600	23.6
C ₁	123	21,500	2.6
C ₂	246	20,420	5.0
C ₃	646	19,930	12.9
Total	1,472		44.1

^a From Refs. 5 and 10 or other convenient source.

Step 3: Heavy gas oil required for fuel. Assume 5.5 MMBtu/bbl LHV, then:

$$\frac{178 - 44.1}{5.5} (24) = 584 \text{ BPSD}$$

Step 4: Heavy gas oil remaining for sale:

$$4000 - 584 = 3416 \text{ BPSD}$$

Royalties

The reformer is a proprietary process and, therefore, royalties must be paid. On a running basis, these range from \$0.08 to \$0.15 per barrel of feed. For this example, use a value of \$0.10:

$$\text{Annual cost} = (0.10)(3000)(340) = \$102,000$$

Catalyst Consumption:

Catalyst consumption costs are as follows:

Desulfurizer: 0.002 lb/bbl; \$1/lb:

$$(\text{Annual cost} = (4000)(340)(0.002)(1) = \$2700)$$

Reformer: 0.004 lb/bbl; \$5 per lb:

$$\text{Annual cost} = (3000)(340)(0.004)(5) = \$20,400$$

$$\text{Total catalyst cost: } \$2700 + \$20,400 = \$23,100/\text{yr.}$$

Insurance

This cost usually is 0.5% of the plant investment per year.

$$(\$256,453,000)(0.005) = \$1,282,000$$

Local Taxes

Usually local taxes account for 1% of the plant investment per year:

$$(\$256,453,000)(0.01) = \$2,565,000/\text{yr}$$

Maintenance

This cost varies between 3 and 8% of plant investment per year. For this example, use an average value of 5.5% (includes material and labor):

$$(\$256,453,000)(0.055) = \$14,100,000/\text{yr}$$

Miscellaneous Supplies

This item includes miscellaneous chemicals used for corrosion control, drinking water, office supplies, etc. An average value is 0.15% of the plant investment per year:

$$(\$256,453,000)(0.0015) = \$385,000/\text{yr}$$

Plant Staff and Operators

The number of staff personnel and operators depends on plant complexity and location. For this example, the following staff could be considered typical of a modern refinery:

	No. per shift	Total payroll
Refinery manager		1
Operations manager		1
Maintenance manager		1
Engineers		3
Operators	4	18
Lab personnel		2
Technicians		2
Clerical personnel		<u>4</u>
Total		32

Assume average annual salary plus payroll burden is \$60,000 per person. Total annual cost for staff and operators is thus:

$$(\$60,000)(32) = 1,920,000/\text{yr}$$

Note that maintenance personnel are not listed above since this cost was included with the maintenance item. Also note that it takes about 4 1/2 men on the payroll for each shift job to cover vacations, holidays, illness, and fishing time.

Table 17.2 gives a summary of direct annual operating costs.

Table 17.2 Summary of Direct Annual Operating Costs

	\$/yr ($\times 10^3$)
Makeup water	34
Power	722
Fuel ^a	—
Royalties	102
Catalyst	23
Insurance	1,282
Local taxes	2,565
Maintenance	14,100
Miscellaneous supplies	385
Plant staff and operators	1,920
Subtotal	21,133
Contingency (5%)	1,057
Total ^b	22,190

^a Fuel quantity is deducted from available heavy gas oil for sale.

^b Additional items such as corporate overhead, research and development, sales expense, etc. are omitted from this example.

Calculation of Income Before Income Tax

Sales are summarized in the following table:

Product	BPD	MBPY	\$/bbl	\$/yr ($\times 10^3$)
Gasoline				
LSR	1,000			
Reformate	2,730			
Total	3,730	1,268	32.00	40,580
Light gas oil	4,000	1,360	30.00	40,800
Heavy gas oil	3,416	1,161	28.00	32,500
Vaccum gas oil	6,000	2,040	24.00	48,960
Vaccum residual	12,000	4,080	21.00	85,680
Total				248,520
Crude cost	30,000	10,200	21.50	219,300
Direct operating costs				22,190
Income before income tax				7,030

Calculation of Return on Investment

Investment = \$256,453,000.

	\$/yr ($\times 10^3$)
Income before tax	7,030
Less depreciation allowance ^a	<u>17,098</u>
Taxable income	None
Income tax at 50%	None
Income after tax	7,030
Plus depreciation allowance	n.a.
Cash flow	7,030
Return on investment (% per year)	2.74
Payout period (years)	36.48

^a 15-year, straight-line.

Note: True rate of return (discounted cash flow) basis: 20-year life, no salvage value (see Appendix D). Interest on capital during construction period and average feedstock and product inventories are not considered in above product. These items would result in an increase in investment and a decrease in the rate of return.

A project that has a simple payout time of 36 years and a useful operating life of only 20 years has a negative rate of return. Therefore the calculation of a true rate of return or discounted cash flow is not necessary.

This demonstrates that, under the stated typical 1999 conditions, a simple 30,000 BPD refinery is not economically justified.

PROBLEMS

1. Calculate the chemical and utility requirements for a crude unit consisting of both atmospheric and vacuum fractionation towers charging 100,000 BPCD of the assigned crude oil and producing typical side, overhead, and bottom streams. Using assigned utility and chemical costs, calculate the cost per barrel of charge and total annual costs for chemicals and utilities.
2. Calculate the DCFROR on a 100,000 BPCD crude unit charging the assigned crude oil and producing typical side, overhead, and bottom

streams. Use product values from *Oil Gas J.* and for those streams not listed base on equivalent heating value of closest comparable listed product. Construction costs should be brought to current value by use of *Nelson Indices*. Include total operating and materials costs. Use 30-year useful life with salvage value equal to cost of removal. Construction began 2 years before unit start-up. Land costs are \$400,000 and the labor requirement is 3 persons per shift.

NOTES

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18

Economic Evaluation

Economic evaluations are generally carried out to determine if a proposed investment meets the profitability criteria of the company or to evaluate alternatives. There are a number of methods of evaluation and a good summary of the advantages and disadvantages of each is given in Perry's *Chemical Engineers' Handbook* [5]. Most companies do not rely upon one method alone but utilize several to obtain a more objective viewpoint.

As this is primarily concerned with cost estimation procedures, there will be no attempt to go into the theory of economics, but equations will be presented which are used for the economic evaluation calculations. There is a certain amount of basic information needed to undertake the calculations for an economic evaluation of a project [2,3,6,7].

18.1 DEFINITIONS

Depreciation

Depreciation arises from two causes: deterioration and obsolescence. These two causes do not necessarily operate at the same rate, and the one having the faster rate determines the economic life of the project. Depreciation is an expense and there are several permissible ways of allocating it. For engineering purposes depreciation is usually calculated by the straight-line method for the economic life of the project. Frequently economic lives of 10 years or less are assumed for projects of less than \$250,000.

Working Capital

The working capital (WC) consists of feed and product inventories, cash for wages and materials, accounts receivable, and spare parts. A reasonable figure is the sum of the above items for a 30-day period.

Annual Cash Flow

The annual cash flow (ACF) is the sum of the earnings after taxes and the depreciation for a one-year period.

Sensitivity Analysis

Uncertainties in the cost of equipment, labor, operation, and raw materials as well as in future prices received for products can have a major effect on the evaluation of investments. It is important in appraising the risks involved to know how the outcome would be affected by errors in estimation, and a sensitivity analysis is made to show the changes in the rate of return due to errors of estimation of investment costs and raw material and product prices. These will be affected by the type of cost analysis performed (rough estimate or detailed analysis), stability of the raw material and product markets, and the economic life of the project. Each company will have its own bases for sensitivity analyses but when investment costs are derived from the installed-cost figures in this book, the following values are reasonable:

	Decrease by	Increase by
Investment cost	15%	20%
Raw materials costs	3	5
Product prices	5	5
Operating volumes	5	2

Product and Raw Material Cost Estimation

It is very important that price estimation and projections for raw materials and products be as realistic as possible. Current posted prices may not be representative of future conditions, or even of the present value to be received from an addition to the quantities available on the market. A more realistic method is to use the average of the published low over the past several months.

18.2 RETURN ON ORIGINAL INVESTMENT

This method is also known as the engineer's method, du Pont method, or the capitalized earning rate. It does not take into account the time value of money,

but, because of this, offers a more realistic comparison of returns during the latter years of the investment. The return on original investment is defined as:

$$\text{ROI} = \frac{\text{Average yearly profit} \times 100}{\text{Original fixed investment} + \text{working capital}} \quad (1)$$

The return on investment should be reported to two significant figures.

18.3 PAYOUT TIME

The payout time is also referred to as the cash recovery period or years to pay out. It is calculated by the following formula and is expressed to the nearest one-tenth year:

$$\text{Payout time} = \frac{\text{Original depreciable fixed investment}}{\text{Annual cash flow}} \quad (2)$$

If the annual cash flow varies, the payout time can be calculated by adding the cash income after income taxes for consecutive years until the sum is equal to the total investment. The results can be reported to a fractional year by indicating at what point during the year the cash flow will completely offset the depreciable investment.

18.4 DISCOUNTED CASH FLOW RATE OF RETURN

This method is called the investors' return on investment, internal rate of return, profitability index, and interest rate of return as well as discounted cash flow. A trial-and-error solution is necessary to calculate the average rate of interest earned on the company's outstanding investment in the project. It can also be considered as the maximum interest rate at which funds could be borrowed for investment in the project with the project breaking even at the end of its expected life.

The discounted cash flow is basically the ratio of the average annual profit during construction and earning life to the sum of the average fixed investment, working capital, and the interest charged on the fixed and working capital that reflects the time value of money. This ratio is expressed as a percentage rather than a fraction. Discounted cash flow is discussed in detail, with an example of its use, in Appendix E.

In order to compare investments having different lives or with variations in return during their operating lives, it is necessary to convert rates of return to a common time basis for comparison. While any time may be taken for this comparison, the plant startup time is usually taken as the most satisfactory. Ex-

penditures prior to startup and income and expenditures after startup are converted to their worth at startup. The discussion to follow is based upon the predicted startup time being the basis of calculation.

Expenditures Prior to Startup

The expenditures prior to startup can be placed in two categories: those that occur uniformly over the period of time before startup and lump-sum payments that occur in-an-instant at some point before the startup time. Construction costs are generally assumed to be disbursed uniformly between the start of construction and the startup time, although equivalent results can be obtained if they are considered to be a lump-sum disbursement taking place halfway between the start of construction and startup. The present worth of construction costs that are assumed to occur uniformly over a period of years, T, prior to startup can be calculated using either continuous interest compounding or discrete (annual) interest compounding.

Continuous interest compounding:

$$P_0 = \left(\frac{CC}{T} \right) \left(\frac{e^{iT} - 1}{i} \right)$$

Discrete (annual) interest compounding:

$$P_0 = \left(\frac{CC}{T} \right) \left(\frac{\ln[1/(1+i)]}{[1/(1+i)]^T - [1/(1+i)]^{(t-1)}} \right)$$

where

P = worth at startup time

CC = total construction cost

T = length of construction period in years before startup

i = annual interest rate.

The cost of the land is a lump-sum disbursement. In the equation given, it is assumed that the land payment coincides with the start of construction. If the disbursement is made at some other time, then the proper value should be substituted for T.

Continuous interest compounding:

$$P_0 = (LC)e^{iT}$$

Discrete (annual) interest compounding:

$$P_0 = (LC)(1 + i)^T$$

where

LC = land cost

T = years before startup time that payment was made

i = annual interest rate.

Expenditures at Startup

Any costs which occur at startup time do not have to be factored, but have a present worth equal to their cost. The major investment at this time is the working capital, but there also may be some costs involved with the startup of the plant that would be invested at this time.

Income After Startup

The business income is normally spread throughout the year, and a realistic interpretation is that 1/365 of the annual earnings is being received at the end of each day. The present-worth factors for this type of incremental income are essentially equal to the continuous-income present-worth factors [1]. Even though the present worth of the income should be computed on a continuous-income basis, it is a matter of individual policy as to whether continuous or discrete compounding of interest is used [1,4]. The income for each year can be converted to the reference point by the appropriate equation.

Continuous-income, continuous-interest:

$$P_0 = (ACF) \left(\frac{e^i - 1}{i} \right) e^{-in}$$

Continuous-income, with interest compounded annually:

$$P_0 = (ACF) \left(\frac{[1/(1+i)^n] - [1/(1+i)]^{(n-1)}}{\ln[1/(1+i)]} \right)$$

where

ACF = annual cash flow for year N

n = years after startup

i = annual interest rate

For the special case where the income occurs uniformly over the life of the project after startup, the calculations can be simplified.

Uniform continuous-income, continuous-interest:

$$P_0 = (ACF) \left(\frac{e^i - 1}{i} \right) \left(\frac{e^{in} - 1}{ie^{in}} \right)$$

Uniform continuous-income, with interest compounded annually:

$$P_0 = (ACF) \frac{[1/(1 + i)]^n - [1/(1 + i)]^{n-1}}{\ln[1/(1 + i)]} \quad (3)$$

There are certain costs which are assumed not to depreciate and which are recoverable at the end of the normal service life of the project. Among these are the cost of land, working capital, and salvage value of equipment. These recoverable values must be corrected to their present worth at the startup time.

Continuous interest:

$$P_0 = (SV + LC + WC)e^{-in} \quad (4)$$

Interest compounded annually:

$$P_0 = (SV + LC + WC) \left(\frac{1}{(1 + i)} \right)^n \quad (5)$$

where

SV = salvage value, \$

LC = land cost, \$

WC = working capital, \$

i = annual interest rate, decimal/yr

n = economic life, yr

For many studies, the salvage value is assumed equal to dismantling costs and is not included in the recoverable value of the project.

It is necessary to use a trial-and-error solution to calculate the discounted cash flow rate of return because the interest rate must be determined that makes the present value at the startup time of all earnings equal to that of all investments. An example of a typical balance for continuous-income and continuous-interest with uniform annual net income is:

$$(LC)(e^{iT}) + (CC)\left(\frac{e^{it} - 1}{i}\right)\left(\frac{1}{T}\right) + WC \\ - (ACF)\left(\frac{e^i - 1}{i}\right)\left(\frac{e^{in} - 1}{ie^{in}}\right) - (SV + LC + WC)\left(\frac{1}{e^{in}}\right) = 0 \quad (6)$$

All of the values are known except i , the effective interest rate. An interest rate is assumed and if the results give a positive value, the trial rate of return is too high and the calculations should be repeated using a lower value for i . If the calculated value is negative, the trial rate is too low and a higher rate of return should be tested. Continue the trial calculations until the rate of return is found which gives a value close to zero.

The return on investment should be reported only to two significant figures.

18.5 CASE-STUDY PROBLEM: ECONOMIC EVALUATION

The estimated 1999 construction costs of the refinery process units and their utility requirements are listed in Table 18.1.

The cooling water and steam systems and water makeup requirements were calculated according to the guidelines set up in Chapter 17.

The estimated refinery construction start is expected to be August, 2000, and the process startup date is anticipated to be in August, 2002. Inflation rates of 3% per year are used to bring the costs to their values in 2002.

The working capital is assumed to be equal to 10% of the construction costs. A review of the refinery manning requirements indicates that approximately 139 people will be required to operate the refinery, exclusive of maintenance personnel. The maintenance personnel are included in the 4.5% annual maintenance costs. An average annual salary of \$60,000, including fringe benefits, is used.

A 20-year life will be assumed for the refinery with a dismantling cost equal to salvage value. Straight-line depreciation will be used.

The federal tax rate is 38%, and the state rate is 7%.

Investment costs and utility requirements are summarized in Table 18.1, operating costs in Table 18.2.

A summary of overall costs and realizations is given in Table 18.3, annual costs and revenues in Table 18.4, and total investment costs in Table 18.5, together with payout time and rates of return on investment.

Table 18.1 Investment Costs and Utilities

	BPCD	Percent on-stream ^a	BPSD	\$ (×10 ³), 1999	Power, (MWh/d)	Cooling water, gpm	Process steam	Fuel (MMBtu/h)	MMBtu/h
Desalter	100,000	96.9	103,200	4,200	10	277	87	25.0	292
Atmospheric crude still	100,000	96.9	103,200	61,500	50	417	2,336	21.0	92
Vacuums pipe still	54,147	96.9	55,879	38,000	11				
Coker	20,366	96.1	21,193	114,000	25	990		24.0	119
Middle distillate HT ^b	32,053	96.8	33,113	55,200	192	11,130		13.4	267
FCC HT ^b	36,144	96.8	37,339	60,000	217	12,550		15.0	301
FCC unit ^b	35,421	95.7	37,012	103,200	213	12,300		(44.3)	
HC unit ^b	10,621	97.1	10,928	94,500	138	3,319		33.2	89
Naphtha HT ^b	18,040	96.8	18,636	21,400	^c	^c		^c	^c
Reformer ^b	18,040	96.8	18,636	55,000	90	7,520		27.1	300
Isomerization ^b	5,828	96.8	6,021	22,300	6	3,237		49	
Alkylation ^b	5,735	97.2	5,900	24,600	15	10,577		1.91	178
Polymerization	3,170	96.1	3,170	2,300		417		3.1	3
H ₂ unit, MMscfd	42	97.1	43.3	41,000	32	5,660	147	396	
Said, gas plant, MMscfd	13	96.9	13.4	21,000	13	14,697		408	

W I Nelson Oil Gas I 69(11) 86(1971)

W.L. Nelson, On Call J-0971-1, 801 L-1171.
Catalyst cost for initial charge and paid-up royalty included in unit construction cost; \$1,459,00 for middle distillate HT, \$1,644,000 for FCC HT, \$3,940,000 for FCC unit, \$3,763,000 for HC, \$812,000 for naphtha HT, \$5,170,000 for reformer, \$1,662,000 for isomerization, and \$229,000.

Included with reformer utilities for alkylation unit royalty.

Table 18.2 Summary of Operating Costs

	\$/yr ($\times 10^3$)
Chemicals and catalysts	6,342
Water makeup	576
Power	19,783
Fuel	53,000
Insurance	9,985
Local taxes	19,970
Maintenance	89,866
Miscellaneous supplies	2,995
Plant staff and operators	<u>8,340</u>
Total ^a :	210,857

^a Additional items, such as corporate overhead, research and development vary among refineries and companies. These items are omitted here.

Table 18.3 Refinery Annual Summary (1999 Prices)

	BPCD	(\$/bbl)	\$/yr ($\times 10^3$)
<i>Raw materials (costs)</i>			
North Slope crude	100,000	16.65	607,725
n-Butane	796	14.70	4,270
Methane, Mscf/day	10,920	2.25 ^a	8,968
MTBE	1,595	37.80	<u>22,006</u>
Total			642,969
<i>Products (realizations)</i>			
Fuel gas, MMBtu/day	25,415	2.25	20,872
LPG	3,115	14.50	46,486
Gasoline	53,182	25.26	490,333
Jet fuel	24,729	26.30	237,386
Distillate fuel (No. 2)	19,996	25.30	184,653
Coke, ton/day	825	20.00 ^b	6,023
Sulfur, LT/day	117	58.00 ^c	<u>2,479</u>
Total			958,232

Table 18.4 Costs and Revenues

	\$/yr ($\times 10^3$)
<i>Gross income</i>	958,232
<i>Production costs</i>	
Raw materials	642,969
Operating costs	210,857
Depreciation	<u>99,852</u>
Total	953,678
<i>Income before tax</i>	4,554
Less federal and state income tax	1,928
Net income	2,626
Cash flow	102,478

Table 18.5 Total Investment

Construction costs	1,997,033,000
Land cost	5,000,000
Working capital	<u>199,703,000</u>
Total	2,201,736,000
Return on original investment	0.12%
Payout time	19.5 years
Discounted cash flow rate of return	0.0%

18.6 CASE-STUDY PROBLEM: ECONOMIC SOLUTION

Storage Costs

Based on 50 bbl of storage per BPCD crude oil processed. Assume 21 days storage provided for n-butane (n-butane: 5,260 BPD \times 21 days = 110,460 bbl). Total storage (5,000,000 bbl) less spheroid storages (110,460 bbl) yields, 4,889,540 bbl general storage.

	Cost, \$ ($\times 10^3$)
General storage at \$70/bbl (4,889,540) (\$70) =	342,268
Spheroid storage at \$105/bbl (110,460) (\$105) =	<u>11,598</u>
Total storage =	353,866

Investment Cost

1999 investment cost = 1,882,395,000 (Table 18.3)

Inflation rate estimated at 3% per year

Completion data scheduled for August, 2002

Estimated completed cost = $(1,882,395,000) (1.03)^3 = \$1,997,033,000$

Water Makeup Cost

1. Cooling tower (makeup = 5%)

Makeup = $(0.05)(104,434 \text{ gpm}) = 5222 \text{ gpm}$

2. To boiler (boiler makeup = 5%; total steam produced = 212,700 lb/hr)

Makeup = $(212,700)(0.05) = 10,635 \text{ lb/hr} = 21 \text{ gpm}$

3. Process water = 240 gpm

Total makeup water, then, is 5,483 gpm.

Annual water makeup cost:

$(5483 \text{ gpm})(1440 \text{ min/day})(365 \text{ days/hr})(\$0.20/\text{kgal}) = \$576,373$

Chemical and Catalysts Costs

	\$/CD
Desalter	
Demulsifier: 500 lb/day × \$1.50/lb	750
Caustic: 200 lb/day × \$0.65/lb	130
Mid. dist. HT: 32,053 BPD × 0.03	962
FCC HT: 36,144 × 0.03	1,084
FCC: 35,421 BPD × 0.15	5,313
Naphtha HT: 18,040 BPD × 0.03	541
Catalytic reformer: 18,040 BPD × 0.10	1,804
Isomerization: 5,828 BPD × 0.05	291
Alkylation	
2,240 lb HF/day × \$0.69/lb	1,546
1,490 lb NaOH/day × \$0.19/lb	283
Hydrocracker: 16,930 BPD × 0.20	3,386
Hydrogen unit	1,108
Amine treater: 116 lb/day × \$1.45/lb	168
SCOT unit: 6 lb/day × \$1.45/lb	<u>9</u>
Total	17,375

$(17,375)(365) = \$6,341,875/\text{yr}$

Power Costs

Power usage = 1,084,000 kWh/day at \$0.05 per kWh
Annual cost = $(1,084,000)(365)(\$0.05) = \$19,783,000$

Fuel

Fuel requirements = 2,689 MMBtu/hr
Fuel gas purchased = $(2,689 \text{ MMBtu/hr})(\$2.25/\text{MMBtu}) = \$6,050/\text{hr}$
Annual cost = $(6,050)(24)(365) = \$53,000,000/\text{yr}$

Insurance Costs

Average of 0.5% of plant investment per year:
 $(\$1,997,033,000)(0.005) = \$9,985,165$

Local Taxes

Average of 1% of plant investment per year:
 $(1,997,033,000)(0.01) = \$19,970,330$

Maintenance Costs

Average of 4.5% of plant investment per year, including material and labor:
 $(1,997,033,000)(0.045) = \$89,866,485$

Miscellaneous Supplies Costs

Average of 0.15% of plant investment per year:
 $(\$1,997,033,000)(0.0015) = \$2,995,549$

From the above analysis it is apparent that the estimated rate of return on the investment does not warrant the risk involved. There will have to be a greater spread between the product prices and the raw materials costs to make the building of a 100,000 BPCD refinery an investment worth making.

PROBLEMS

1. Determine the discounted cash flow rate of return, return on investment, and payout time for a refinery with the following specifications:

Construction cost = \$210,000,000
Working capital = \$21,000,000
Land cost = \$4,200,000
Annual raw materials cost = \$283,000,000
Annual gross income = \$433,000,000
Annual operating costs = \$31,300,000

Assume a three-year construction time, a 20-year useful life with straight-line depreciation, and federal and state income taxes of 48% and 8%, respectively. Dismantling costs will equal salvage value.

2. For the conditions listed in problem 1, what would be the effect of the DCFRR if the construction took (a) four years? (b) two years?
3. What would be the DCFRR, payout time, and return on investment for the refinery listed in problem 1 if (a) the refinery were operated at 95% capacity? (b) operating costs were decreased by 1%?
4. Using the specifications of problem 1, make a sensitivity analysis as described in Section 14.1. What factors will be of greatest concern with respect to accurate forecasting?
5. If the declining balance method of depreciation is used instead of the straight-line method for the refinery in problem 1, what would the rates of return be during the first ten years of operation?

NOTES

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Appendix A

Definitions of Refining Terms

Acid heat A test which is indicative of unsaturated components in petroleum distillates. The test measures the amount of reaction of unsaturated hydrocarbons with sulfuric acid (H_2SO_4).

Acid number An ASTM test which determines the organic acidity of a refinery stream.

AGO Atmospheric gas oil. A diesel fuel and No. 2 heating oil blending stock obtained from the crude oil as a side stream from the atmospheric distillation tower.

Alkylate The product of an alkylation process.

Alkylate bottoms A thick, dark brown oil containing high molecular weight polymerization products of alkylation reactions.

Alkylation A polymerization process uniting olefins and isoparaffins; particularly, the reacting of butylene and isobutane using sulfuric or hydrofluoric acid as a catalyst to produce a high-octane, low-sensitivity blend agent for gasoline.

Aluminum chloride treating A quality improvement process for steam-cracked naphthas using aluminum chloride ($AlCl_3$) as a catalyst. The process improves the color and odor of the naphtha by the polymerization of undesirable olefins into resins. The process is also used when production of resins is desirable.

Aniline point The minimum temperature for complete miscibility of equal volumes of aniline and the test sample. The test is considered an indication of the

paraffinicety of the sample. The aniline point is also used as a classification of the ignition quality of diesel fuels.

API gravity An arbitrary gravity scale defined as:

$$^{\circ}\text{API} = \frac{141.5}{\text{Specific gravity } 60/60^{\circ}\text{F}} - 131.5$$

This scale allows representation of the specific gravity of oils, which on the 60/60°F scale varies only over a range of 0.776 by a scale which ranges from less than 0 (heavy residual oil) to 340 (methane).

ARC Atmospheric reduced crude. The bottoms stream from the atmospheric distillation tower.

Aromatic A type of hydrocarbon compound containing at least one benzene ring.

ASO Acid soluble oil. Obtained from side reactions in the alkylation process.

ASTM distillation A standardized laboratory batch distillation for naphthas and middle distillates carried out at atmospheric pressure without fractionation.

ASTM distillation range Several distillation tests are commonly referred to as "ASTM distillations." These are usually used in product specification. These ASTM distillations give results in terms of percent distilled versus temperature for a simple laboratory distillation with no fractionation. The values do not correspond to those of refinery process distillations where fractionation is significant.

Barrel A volumetric measure of refinery feedstocks and products equal to 42 U.S. gallons.

Barrels per calendar day (BPCD) Average flow rates based on operating 365 days per year.

Barrels per stream day (BPSD) Flow rates based on actual on-stream time of a unit or group of units. This notation equals barrels per calendar day divided by the service factor.

Battery limits (BL) The periphery of the area surrounding any process unit which includes the equipment for that particular process.

B-B Butane–butylene fraction.

BFOE Barrels fuel oil equivalent, based on net heating value (LHV) of 6,050,000 Btu per BFOE.

Bitumen That portion of petroleum, asphalt, and tar products which will dissolve completely in carbon disulfide (CS_2). This property permits a complete separation from foreign products not soluble in carbon disulfide.

Blending One of the final operations in refining, in which two or more different components are mixed together to obtain the desired range of properties in the final product.

Blending octane number When blended into gasoline in relatively small quantities, high octane materials behave as though they had octane numbers higher than shown by laboratory tests on the pure material. The effective octane numbers of the material in the blend is known as the blending octane number.

Blocked operation Operation of a unit, e.g., a pipestill, under periodic change of feed (one charge stock is processed at a time rather than mixing charge stocks) or internal conditions in order to obtain a required range of raw products. Blocked operation is demanded by critical specifications of various finished products. This frequently results in a more efficient operation because each charge stock can be processed at its optimum operation conditions.

Bright stock Heavy lube oils (frequently the vacuum still bottoms) from which asphaltic compounds, aromatics, and waxy paraffins have been removed. Bright stock is one of the feeds to a lube oil blending plant.

Bromine index Measure of amount of bromine reactive material in a sample; ASTM D-2710.

Bromine number A test which indicates the degree of unsaturation in the sample (olefins and diolefins); ASTM D-1159.

Bottoms In general, the higher-boiling residue which is removed from the bottom of a fractionating tower.

C Clear or unleaded.

CABP Cubic average boiling point.

Caffeine number A value related to the amount of carcinogenic compounds (high molecular weight aromatics referred to as tars) in an oil.

Carbon residue Carbon residue is a measure of the coke-forming tendencies of oil. It is determined by destructive distillation in the absence of air of the sample to a coke residue. The coke residue is expressed as weight percent of the original sample. There are two standard ASTM tests, Conradson carbon residue (CCR) and Ramsbottom carbon residue (RCR).

Catalyst A substance that assists a chemical reaction to take place but which is not itself chemically changed as a result.

Catalyst/oil ratio (C/O) The weight of circulating catalyst fed to the reactor of a fluid-bed catalytic cracking unit divided by the weight of hydrocarbons charged during the same interval.

Catalytic cycle stock That portion of a catalytic cracker reactor effluent which is not converted to naphtha and lighter products. This material, generally 340⁺F (170⁺C), may either be completely or partially recycled. In the latter case the remainder will be blended to products or processed further.

Cetane index A number calculated from the average boiling point and gravity of a petroleum fraction in the diesel fuel boiling range, which estimates the cetane number of the fraction. An indication of carbon-to-hydrogen ratio.

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. This quality, specified for middle distillate fuels, is synonymous with the octane number of gasolines.

CFR Combined feed ratio. Ratio of total feed (including recycle) to fresh feed.

CGO Coker gas oil.

Characterization factor An index of feed quality, also useful for correlating data on physical properties. The Watson (UOP) characterization factor is defined as the cube root of the mean average boiling point in degrees Rankine divided by the specific gravity. An indication of carbon-to-hydrogen ratio.

Clarified oil Decanted oil from the FCC unit.

Clay treating An elevated temperature and pressure process usually applied to thermally cracked naphthas to improve stability and color. The stability is increased by the adsorption and polymerization of reactive diolefins in the cracked naphtha. Clay treating is used for treating jet fuel to remove surface-active agents which adversely affect the water separator index specifications.

Clear Without lead. Federal regulations require that fuels containing lead must be dyed.

Cloud point The temperature at which solidifiable compounds present in the sample begin to crystallize or separate from the solution under a method of prescribed chilling. Cloud point is a typical specification of middle distillate fuels; ASTM D-2500.

Conradson carbon A test used to determine the amount of carbon residue left after the evaporation and pyrolysis of an oil under specified conditions. Expressed as weight percent; ASTM D-189.

Correlation index (CI) The U.S. Bureau of Mines factor for evaluating individual fractions from crude oil. The CI scale is based upon straight-chain hydrocarbons having a CI value of 0 and benzene having a value of 100. An indication of the hydrogen-to-carbon ratio.

Cracking The breaking down of higher molecular weight hydrocarbons to lighter components by the application of heat. Cracking in the presence of a suitable catalyst produces an improvement in yield and quality over simple thermal cracking.

Crude assay distillation See fifteen-five distillation.

CSO Clarified slurry oil (decanted oil).

Cut That portion of crude oil boiling within certain temperature limits. Usually the limits are on a crude assay true boiling point basis.

Cut point A temperature limit of a cut, usually on a true boiling point basis although ASTM distillation cut points are not uncommon.

Cycloparaffin A paraffin molecule with a ring structure.

DAO Deasphalting oil. The raffinate product from the propane deasphalting unit.

Decanted oil The bottoms stream from the FCC unit distillation tower after catalyst has been separated from it.

Density The density crude oil and petroleum fractions is usually specified in °API, specific gravity, or kilograms per cubic meter (kg/m^3). The numerical values of specific gravity and kg/m^3 are equal; that is, a fraction with a specific gravity of 0.873 has a density of $0.873 \text{ kg}/\text{m}^3$. The API scale runs opposite to that of specific gravity, with larger values for less dense materials and smaller values for more dense fractions (water = 10° API). By definition, °API is *always* for a liquid at 15.6°C (60°F).

Dewaxing The removal of wax from lubricating oils, either by chilling and filtering, solvent extraction, or selective hydrocracking.

Diesel index (DI) A measure of the ignition quality of a diesel fuel. Diesel index is defined as:

$$\text{DI} = \frac{(\text{°API}) (\text{aniline point})}{100}$$

The higher the diesel index, the more satisfactory the ignition quality of the fuel. By means of correlations unique to each crude and manufacturing process, this quality can be used to predict cetane number (if no standardized test for the latter is available).

DIPE Di-isopropyl ether. An oxygenate used in motor fuels.

Distillate Any stream that has been vaporized and then condensed to a liquid.

Doctor test A method for determining the presence of mercaptan sulfur petroleum products. This test is used for products in which a “sweet” odor is desirable for commercial reasons, especially naphtha; ASTM D-484.

Dry gas All C_1 to C_3 material, whether associated with a crude or produced as a by-product of refinery processing. Convention often includes hydrogen in dry gas yields.

End point Upper temperature limit of a distillation.

Endothermic reaction A reaction in which heat must be added to maintain reactants and products at a constant temperature.

ETBE Ethyl tertiary butyl ether. An oxygenate gasoline blending compound to improve octane and reduce carbon monoxide emissions. Produced by reacting ethanol with isobutylene.

Exothermic reaction A reaction in which heat is evolved. Alkylation, polymerization, and hydrogenation reactions are exothermic.

FBP The final boiling point of a cut, usually on an ASTM distillation basis.

FOE Barrels of fuel oil equivalent [6.05×10^6 Btu (LHV)].

FVT The final vapor temperature of a cut. Boiling ranges expressed in this manner are usually on a crude assay true boiling point basis.

Fifteen-five (15/5) distillation A laboratory batch distillation performed in a fifteen-theoretical-plate fractionating column with a five-to-one reflux ratio. A good fractionation results in accurate boiling temperatures. For this reason, this distillation is referred to as the true boiling point (TBP) distillation. This distillation corresponds very closely to the type of fractionation obtained in a refinery.

Fixed carbon The organic portion of the residual coke obtained on the evaporation to dryness of hydrocarbon products in the absence of air.

Flash point The temperature to which a product must be heated under prescribed conditions to release sufficient vapor to form a mixture with air that can be readily ignited. Flash point is used generally as an indication of the fire and explosion potential of a product; ASTM D-56, D-92, D-93, D-134, D-1310.

Flux The addition of a small percentage of a material to a product in order to meet some specification of the final blend.

Foots oil Oil and low melting materials removed from slack wax to produce a finished wax.

Free carbon The organic materials in tars which is insoluble in carbon disulfide.

Fuel oil equivalent (FOE) The heating value of a standard barrel of fuel oil, equal to 6.05×10^6 Btu (LHV). On a yield chart, dry gas and refinery fuel gas are usually expressed in FOE barrels.

Gas oil Any distillate stream having molecular weights and boiling points higher than heavy naphtha (>400°F, or 205°C). Frequently, any distillate stream heavier than kerosine. Originally was added to manufactured or city gas to make it burn with a luminous flame. Hence, the name “gas oil.”

GHV Gross heating value of fuels. The heat produced by complete oxidation of material at 60°F (25°C) to carbon dioxide and liquid water at 60°F (25°C).

HCO Heavy FCC cycle gas oil.

HCGO Heavy coker gas oil.

Heart cut recycle That unconverted portion of the catalytically cracked material which is recycled to the catalytic cracker. This recycle is usually in the boiling range of the feed and, by definition, contains no bottoms. Recycle allows less severe operation and suppresses the further cracking or desirable products.

Hempel distillation U.S. Bureau of Mines (now Department of Energy) Routine Method Distillation. Results are frequently used interchangeably with TBP Distillation.

HSR Heavy straight-run. Usually a naptha sidestream from the atmospheric distillation tower.

HVG0 Heavy vacuum gas oil. A sidestream from the vacuum distillation tower.

Hydrocarbon Organic molecules containing only hydrogen and carbon.

IBP Initial boiling point of a cut, usually on an ASTM basis.

IPTBE Isopropyl tertiary butyl ether. An oxygenate used in motor fuels.

Isomerate The product of an isomerization process.

Isomerization The rearrangement of straight-chain hydrocarbon molecules to form branched-chain products. Pentanes and hexanes, which are difficult to reform, are isomerized using aluminum chloride or precious metal catalysts to form gasoline blending components of fairly high octane value. Normal butane may be isomerized to provide a portion of the isobutane feed needed for alkylation processes.

IVT Initial vaporization temperature of a cut, usually based on a crude assay distillation.

Kerosine A middle distillate product composed of material of 300 to 550°F boiling range. The exact cut is determined by various specifications of the finished kerosine.

Lamp sulfur The total amount of sulfur present per unit of liquid product. The analysis is made by burning a sample so that the sulfur content will be converted to sulfur dioxide, which can be quantitatively measured. Lamp sulfur is a critical specification of all motor, tractor, and burner fuels; ASTM D-1266.

LCO Light FCC cycle gas oil.

LCGO Light coker gas oil.

Lead susceptibility The variation of the octane number of a gasoline as a function of the tetraethyl lead content.

LHSV Liquid hour space velocity; volume of feed per hour per volume of catalyst.

LHV Lower heating value of fuels (net heat of combustion). The heat produced by complete oxidation of materials at 60°F (25°C) to carbon dioxide and water vapor at 60°F (25°C).

Light ends Hydrocarbon fractions in the butane and lighter boiling range.

Liquefied petroleum gas (LPG) Liquefied light ends gases used for home heating and cooking. This gas is usually 95% propane, the remainder being split between ethane and butane. It can be any one of several specified mixtures of propane and butane which are sold as liquids under pressure at ambient temperatures.

LNG Liquefied natural gas or methane.

Long resid The bottoms stream from the atmospheric distillation tower.

LSR Light straight-run. The low-boiling naptha stream from the atmospheric distillation, usually composed of pentanes and hexanes.

LVGO Light vacuum gas oil; a sidestream from the vacuum distillation tower.

MABP Molal average boiling point:

$$\text{MABP} = \sum_{i=1}^n X_i T_{bi}$$

MeABP Mean average boiling point:

$$\text{MeABP} = \frac{(\text{MABP} + \text{CABP})}{2}$$

MHC Mild hydrocracking.

Mid-boiling point That temperature, usually based on a crude assay distillation, at which one-half of the material of a cut has been vaporized.

Mid-percent point The vapor temperature at which one-half of the material of a cut has been vaporized. Mid-percent point is used to characterize a cut in place of temperature limits.

Middle distillates Atmospheric pipe still cuts boiling in the range of 300 to 700°F vaporization temperature. The exact cut is determined by the specifications of the product.

MONC Motor octane number clear (unleaded).

Motor octane number (MON, ASTM ON, F2) A measure of resistance to self-ignition (knocking) of a gasoline under laboratory conditions which correlates with road performance during highway driving conditions. The percentage by volume of iso-octane in a mixture of iso-octane and n-heptane that knocks with the same intensity as the fuel being tested. A standardized test engine operating under standardized conditions (900 rpm) is used. This test approximates cruising conditions of an automobile; ASTM D-2723.

MPHC Medium pressure hydrocracking or partial conversion hydrocracking.

MTBE Methyl tertiary butyl ether. A high octane oxygenate gasoline blending stock produced by reacting methanol with isobutylene.

Naphtha A pipe still cut in the range of C₅ to 420°F (216°C). Naphthas are subdivided, according to the actual pipe still cuts, into light, intermediate, heavy, and very heavy virgin naphthas. A typical pipestill operation would be:

C₅–160°F(C₅–71°C): light virgin naphtha

160–280°F(71–138°C): intermediate virgin naphtha

280–380°F(138–193°C): heavy virgin naphtha

Naphthas, the major constituents of gasoline, generally need processing to make suitable quality gasoline.

Naphthalene A double-ring aromatic compound in the jet fuel boiling range.

Naphthene A cycloparaffin compound which is a paraffin with a ring structure.

Neutralization number The quantity of acid or base which is required to neutralize all basic or acidic components present in a specified quantity of sample. This is a measure of the amount of oxidation of a product in storage or in service; ASTM D-664, D-974.

Neutral oils Pale or red oils of low viscosity produced from dewaxed oils by distillation.

Olefin An unsaturated hydrocarbon molecule which has a double bond between two of the carbon atoms in the molecule.

Olefin space velocity Volume of olefin charged per hour to an alkylation reactor.

Oxygenate Any organic compound containing oxygen. Specifically for the petroleum industry, this term refers to oxygen containing organic compounds, such as ethers and alcohols, added to fuels to reduce carbon monoxide in the engine exhausts.

Paraffin A saturated hydrocarbon compound in which all carbon atoms in the molecule are connected by single bonds.

Performance rating A method of expressing the quality of a high octane gasoline relative to iso-octane. This rating is used for fuels which are of better quality than iso-octane.

Petrolatum Microcrystalline wax.

Pipe still A heater or furnace containing tubes through which oil is pumped while being heated or vaporized. Pipe stills are fired with waste gas, natural gas,

or heavy oils, and, by providing for rapid heating under conditions of high pressure and temperature, are useful for thermal cracking as well as distillation operations.

Polymerization The combination of two or more unsaturated molecules to form a molecule of higher molecular weight. Propylenes and butylenes are the primary feed material for refinery polymerization processes which use solid or liquid phosphoric acid catalysts.

PON Posted octane number: $(R + M)/2$.

Posted octane number Arithmetic average of research octane number and motor octane number. In the United States, this is the octane number that by federal law must be posted on gasoline dispensing pumps.

Pour point The lowest temperature at which a petroleum oil will flow or pour when it is chilled without disturbance at a controlled rate. Pour point is a critical specification of middle distillate products used in cold climates; ASTM D-99.

Pour blending index (PBI) An empirical quantity related to pour point, which allows volumetric blending of pour points of various blend components. This method of blending is most accurate for blending of similar fractions of the same crude.

Raffinate The residue recovered from an extraction process. An example is the furfural extraction of aromatics from high molecular weight distillates. The raffinate is relatively free of aromatics which have poor viscosity-temperature characteristics (low VI; a high rate of change of viscosity with temperature).

Ramsbottom carbon residue A measure of the carbon forming potential (amount of coke formed) of a petroleum fraction. This is determined by a standard laboratory test procedure which subjects the sample to severe thermal cracking conditions. Recommended to replace Conradson carbon; ASTM D-524. Carbon residue expressed in wt% of the original sample.

Reconstituted crude A crude to which has been added a specific crude fraction for the purpose of meeting some product volume unattainable with the original crude.

Reduced crude A crude whose API gravity has been reduced by distillation of the lighter lower-boiling constituents.

Reformate A reformed naphtha which is upgraded in octane by means of catalytic or thermal reforming.

Reforming The conversion of naphtha fractions to products of higher octane value. Thermal reforming is essentially a light cracking process applied to heavy naphthas to produce increased yields of hydrocarbons in the gasoline boiling range. Catalytic reforming is applied to various straight-run and cracked naphtha fractions and consists primarily of dehydrogenation of naphthenes to aromatics. A number of catalysts, including platinum and platinum-rhenium supported on alumina, are used. A high partial pressure of hydrogen is maintained to prevent the formation of excessive coke.

Reid vapor pressure (RVP) The vapor pressure at 100°F of a product determined in a volume of air four times the liquid volume. Reid vapor pressure is an indication of the ease of starting and vapor-lock tendency of a motor gasoline as well as explosion and evaporation hazards; ASTM D-323. It is usually expressed in kPa or psig.

Research octane number (RON, CFRR, F-1) The percentage by volume of iso-octane in a blend of iso-octane and n-heptane that knocks with the same intensity as the fuel being tested. A standardized test engine operating under standardized conditions (600 rpm) is used. Results are comparable to those obtained in an automobile engine operated at low speed or under city driving conditions; ASTM D-2722.

Resid, residuum An undistilled portion of a crude oil. Usually the atmospheric or vacuum tower bottoms.

Road octane number The percentage by volume of iso-octane which would be required in a blend of iso-octane and n-heptane to give incipient knock in an automobile engine operating under the same conditions of engine load, speed, and degree of spark advance as that of the fuel being tested.

RONC Research octane number clear (unleaded).

Salt content Crude oil usually contains salts in solution in water that is emulsified with the crude. The salt content is expressed as sodium chloride equivalent in pounds per thousand barrels (PTB) of crude oil. Typical values range from 1 to 20 PTB. Although there is no simple conversion from PTB to parts per million by weight (ppm), 1 PTB is roughly equivalent to 3 ppm.

Saponification number An indication of the fraction of fat or fatty oils in a given product. The numer of milligrams of potassium hydroxide required to saponify one gram of the sample.

SCF Volume of gas expressed as standard cubic feet. Standard conditions in petroleum and natural gas usage refer to a pressure base of 14.696 psia and a temperature base of 60°F (15°C).

Selectivity The difference between the research octane number and the motor octane number of a given gasoline. Alkylate is an excellent low-sensitivity and reformatte a high-sensitivity gasoline component.

Service factor A quantity which relates the actual on-stream time of a process unit to the total time available for use. Service factors include both expected and unexpected unit shutdowns.

Severity The degree of intensity of the operating conditions of a process unit. Severity may be indicated by clear research octane number of the product (reformer), percent disappearance of the feed (catalytic cracking), or operating conditions alone.

Short resid Vacuum tower bottoms.

Slack wax Wax produced in the dewaxing of lube oil base stocks. This wax still contains some oil and must be de-oiled to produce a finished waxproduct.

Smoke point A test measuring the burning quality of jet fuels, kerosine, and illuminating oils. It is defined as the height of the flame in millimeters beyond which smoking takes place; ASTM D-1322.

Slurry oil The oil, from the bottoms of the FCC unit fractionating tower, containing a concentration of FCC catalyst particles carried over from the reactor cyclones. The remainder of the FCC bottoms is the decanted oil.

Sour or sweet crude A rather general method for classifying crudes according to sulfur content. Various definitions are available:

Sour crude: A crude which contains sulfur in amounts greater than 0.5 to 1.0 wt%, or whch contains 0.05 ft³ or more of hydrogen sulfide (H₂S) per 100 gal, except West Texas crude, which is always considered sour regardless of its hydrogen sulfide content. Arabian crudes are high-sulfur

crudes which are not always considered sour because they do not contain highly active sulfur compounds.

Sweet crude: As evident from the above definitions, a sweet crude contains little or no dissolved hydrogen sulfide and relatively small amounts of mercaptans and other sulfur compounds.

Space velocity The volume (or weight) of gas and/or liquid passing through a given catalyst or reactor space per unit time, divided by the volume (or weight) of catalyst through which the fluid passes. High space velocities correspond to short reaction times. See LHSV and WHSV.

Straight-run gasoline An uncracked gasoline fraction distilled from crude. Straight-run gasolines contain primarily paraffinic hydrocarbons and have lower octane values than cracked gasolines from the same crude feedstock.

Sweetening The removal or conversion to innocuous substances of sulfur compounds in a petroleum product by any of a number of processes (doctor treating, caustic and water washing, etc.).

Synthetic crude Wide boiling-range product of catalytic cracking, coking, hydrocracking, or some other chemical structure change operation.

TA Total alkylate or true alkylate ($C_5 +$ alkylate).

TAAE Tertiary amyl ethyl ether. A high octane oxygenate blending stock produced by reacting isoamylene (isopentylene) with ethanol.

TAME Tertiary amyl methyl ether. A high octane oxygenate gasoline blending compound, produced by reacting isoamylene (isopentylene) with methanol.

Tail gas Light gases (C_1 to C_3 and H_2) produced as by-products of refinery processing.

TBP distillation See Fifteen-five distillation.

Tetraethyl lead An antiknock additive for gasoline which is no longer used in the United States.

Theoretical plate A theoretical contacting unit useful in distillation, absorption, and extraction calculations. Vapors and liquid leaving any such unit are required to be in equilibrium under the conditions of temperature and pressure which apply. An actual fractionator tray or plate is generally less effective than

a theoretical plate. The ratio of a number of theoretical plates required to perform a given distillation separation to the number of actual plates used gives the overall tray efficiency of the fractionator.

Topping Removal by distillation of the light products from crude oil, leaving in the still bottoms all of the heavier constituents.

Treat gas Light gases, usually high in hydrogen content, which are required for refinery hydrotreating processes such as hydrosulfurization. The treat gas for hydrosulfurization is usually the tail gas from catalytic reforming or the product from a hydrogen unit.

Tube still See Pipe still.

U.S. Bureau of Mines Routine Method of Distillation See Hempel distillation.

Vapor lock index A measure of the tendency of a gasoline to generate excessive vapors in the fuel line thus causing displacement of a liquid fuel and subsequent interruption of normal engine operation. The vapor lock index generally is related to RVP and percent distilled at 158°F (70°C).

VGO Vacuum gas oil. A sidestream from the vacuum distillation tower.

Virgin stocks Petroleum oils which have not been cracked or otherwise subjected to any treatment which would produce appreciable chemical change in their components.

Viscosity Internal resistance to flow of liquids is expressed as viscosity. The property of liquids under flow conditions which causes them to resist instantaneous change of shape or instantaneous rearrangement of their parts due to internal friction. Viscosity is generally measured as the number of seconds, at a definite temperature, required for a standard quantity of oil to flow through a standard apparatus. Common viscosity scales in use are Saybolt Universal, Saybolt Furol, poises, and kinematic [Stokes or centiStokes (cSt)].

Volatility factor An empirical quantity which indicates good gasoline performance with respect to volatility. It involves actual automobile operating conditions and climatic factors. The volatility factor is generally defined as a function of RVP, percent off. at 158°F (70°C), and percent off. at 212°F (100°C). This factor is an attempt to predict the vapor lock tendency of a gasoline.

vppm Parts per million by volume.

VRC Vacuum reduced crude; vacuum tower bottoms.

WABP Weight average boiling point:

$$WABP = \sum_{i=1}^n X_{wi} T_{bi}$$

where

X_{wi} = weight fraction of component i

T_{bi} = average boiling point of component i

WHSV Weight hour space velocity; weight of feed per hour per weight of catalyst.

Wick char A test used as an indication of the burning quality of a kerosine or illuminating oil. It is defined as the weight of deposits remaining on the wick after a specified quantity of sample is burned.

wppm Parts per million by weight.

Appendix B

Physical Properties

Table B.1 Density Conversion Table

Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day	Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day
	°API	lb/bbl	lb/gal			°API	lb/bbl	lb/gal	
1.165	-10.0	407.8	9.71	16.99	1.092	-2.0	382.6	9.11	15.94
1.163	-9.8	407.1	9.69	16.95	1.090	-1.8	382.0	9.09	15.92
1.161	-9.6	406.5	9.68	16.94	1.089	-1.6	381.4	9.08	15.89
1.159	-9.4	405.8	9.66	16.91	1.087	-1.4	380.8	9.07	15.87
1.157	-9.2	405.1	9.65	16.88	1.085	-1.2	380.3	9.05	15.85
1.155	-9.0	404.5	9.63	16.85	1.084	-1.0	379.7	9.04	15.82
1.153	-8.8	403.8	9.61	16.82	1.082	-0.8	379.1	9.03	15.80
1.151	-8.6	403.2	9.60	16.80	1.080	-0.6	378.5	9.01	15.77
1.149	-8.4	402.5	9.58	16.77	1.079	-0.4	377.9	9.00	15.75
1.147	-8.2	401.9	9.57	16.74	1.077	-0.2	377.4	8.98	15.72
1.145	-8.0	401.2	9.55	16.72	1.076	0.0	376.8	8.97	15.70
1.143	-7.8	400.6	9.54	16.69	1.074	.2	376.2	8.96	15.67
1.142	-7.6	399.9	9.52	16.66	1.073	.4	375.6	8.94	15.65
1.140	-7.4	399.3	9.51	16.64	1.071	.6	375.1	8.93	15.63
1.138	-7.2	398.6	9.49	16.61	1.070	.8	374.5	8.92	15.60
1.136	-7.0	398.0	9.48	16.58	1.068	1.0	373.9	8.90	15.53
1.134	-6.8	397.3	9.46	16.55	1.066	.2	373.4	8.89	15.56
1.132	-6.6	396.7	9.45	16.53	1.065	.4	372.8	8.88	15.53
1.131	-6.4	396.1	9.43	16.50	1.063	.6	372.3	8.86	15.51
1.129	-6.2	395.4	9.42	16.47	1.062	.8	371.7	8.85	15.49
1.127	-6.0	394.8	9.40	16.45	1.060	2.0	371.1	8.84	15.46
1.125	-5.8	394.2	9.39	16.42	1.053	.2	370.6	8.82	15.44
1.123	-5.6	393.6	9.37	16.40	1.057	.4	370.0	8.81	15.42
1.122	-5.4	392.9	9.36	16.37	1.055	.6	369.5	8.80	15.40
1.120	-5.2	392.3	9.34	16.35	1.054	.8	368.9	8.78	15.37
1.118	-5.0	391.7	9.33	16.32	1.052	3.0	368.4	8.77	15.35
1.116	-4.8	391.1	9.31	16.30	1.051	.2	367.8	8.76	15.32
1.115	-4.6	390.5	9.30	16.27	1.049	.4	367.3	8.75	15.30
1.113	-4.4	389.8	9.23	16.24	1.047	.6	366.8	8.73	15.28
1.111	-4.2	389.2	9.27	16.22	1.046	.8	366.2	8.72	15.26
1.109	-4.0	388.6	9.25	16.19	1.044	4.0	365.7	8.71	15.24
1.108	-3.8	388.0	9.24	16.17	1.043	.2	365.1	8.69	15.21
1.106	-3.6	387.4	9.22	16.14	1.041	.4	364.6	8.68	15.19
1.104	-3.4	386.8	9.21	16.12	1.040	.6	364.0	8.67	15.17
1.102	-3.2	386.2	9.19	16.09	1.038	.8	363.5	8.66	15.15
1.101	-3.0	385.6	9.18	16.07	1.037	5.0	363.0	8.64	15.12
1.099	-2.8	385.0	9.16	16.04	1.035	.2	362.4	8.63	15.10
1.097	-2.6	384.4	9.15	16.02	1.034	.4	361.9	8.62	15.08
1.096	-2.4	383.8	9.14	15.99	1.032	.6	361.4	8.60	15.06
1.094	-2.2	383.2	9.12	15.97	1.031	.8	360.9	8.59	15.04

Table B.1 Continued

Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day	Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day
	°API	lb/bbl	lb/gal			°API	lb/bbl	lb/gal	
1.029	6.0	360.3	8.58	15.01	0.973	14.0	340.5	8.11	14.19
1.028	.2	359.8	8.57	14.99	0.971	.2	340.1	8.10	14.17
1.026	.4	359.3	8.55	14.97	0.970	.4	339.6	8.09	14.15
1.025	.6	358.8	8.54	14.95	0.969	.6	339.1	8.08	14.13
1.023	.8	358.3	8.53	14.93	0.967	.8	338.7	8.06	14.11
1.022	7.0	357.7	8.52	14.90	0.966	15.0	338.2	8.05	14.09
1.020	.2	357.2	8.51	14.88	0.965	.2	337.8	8.04	14.07
1.019	.4	356.7	8.49	14.86	0.963	.4	337.3	8.03	14.05
1.017	.6	356.2	8.48	14.84	0.962	.6	336.8	8.02	14.03
1.016	.8	355.7	8.47	14.82	0.961	.8	336.4	8.01	14.02
1.014	8.0	355.2	8.46	14.80	0.959	16.0	335.9	8.00	14.00
1.013	.2	354.7	8.44	14.78	0.958	.2	335.5	7.99	13.98
1.011	.4	354.2	8.43	14.76	0.957	.4	335.0	7.98	13.96
1.010	.6	353.7	8.42	14.74	0.955	.6	334.6	7.96	13.94
1.009	.8	353.2	8.41	14.72	0.954	.8	334.1	7.95	13.92
1.007	9.0	352.7	8.40	14.70	0.953	17.0	333.7	7.94	13.90
1.006	.2	352.2	8.38	14.67	0.952	.2	333.2	7.93	13.88
1.004	.4	351.7	8.37	14.65	0.950	.4	332.8	7.92	13.87
1.003	.6	351.2	8.36	14.63	0.949	.6	332.3	7.91	13.85
1.001	.8	350.7	8.35	14.61	0.948	.8	331.9	7.90	13.83
1.000	10.0	350.2	8.34	14.59	0.947	18.0	331.4	7.89	13.81
0.999	10.2	349.7	8.33	14.57	0.945	.2	331.0	7.88	13.79
0.997	10.4	349.2	8.31	14.55	0.944	.4	330.5	7.87	13.77
0.996	10.6	348.7	8.30	14.53	0.943	.6	330.1	7.86	13.75
0.994	10.8	348.2	8.29	14.51	0.942	.8	329.7	7.85	13.74
0.993	11.0	347.7	8.28	14.49	0.940	19.0	329.2	7.84	13.72
0.992	.2	347.2	8.27	14.47	0.939	.2	328.0	7.83	13.70
0.990	.4	346.7	8.26	14.45	0.938	.4	328.4	7.82	13.68
0.989	.6	346.2	8.24	14.43	0.937	.6	327.9	7.81	13.66
0.987	.8	345.8	8.23	14.41	0.935	.8	327.5	7.80	13.65
0.986	12.0	345.3	8.22	14.39	0.934	20.0	327.1	7.79	13.63
0.985	.2	344.8	8.21	14.37	0.933	.2	326.6	7.78	13.61
0.983	.4	344.3	8.20	14.35	0.932	.4	326.2	7.77	13.59
0.982	.6	343.8	8.19	14.33	0.930	.6	325.8	7.76	13.57
0.981	.8	343.4	8.18	14.31	0.929	.8	325.3	7.75	13.55
0.979	13.0	342.9	8.16	14.29	0.928	21.0	324.9	7.74	13.54
0.978	.2	342.4	8.15	14.27	0.927	.2	324.5	7.73	13.52
0.977	.4	341.9	8.14	14.25	0.925	.4	324.0	7.72	13.50
0.975	.6	341.5	8.13	14.23	0.924	.6	323.6	7.71	13.48
0.974	.8	341.0	8.12	14.21	0.923	.8	323.2	7.70	13.47

Table B.1 Continued

Specific gravity 60/60° F	Density in vacuo			lb/hr* from bbl/day	Specific gravity 60/60° F	Density in vacuo			lb/hr* from bbl/day
	°API	lb/bbl	lb/gal			°API	lb/bbl	lb/gal	
0.922	22.0	322.8	7.69	13.45	0.876	30.0	306.8	7.30	12.78
0.921	.2	322.4	7.68	13.43	0.875	.2	306.4	7.30	12.77
0.919	.4	321.9	7.67	13.41	0.874	.4	306.0	7.29	12.75
0.918	.6	321.5	7.66	13.40	0.873	.6	305.7	7.28	12.74
0.917	.8	321.1	7.65	13.38	0.872	.8	305.3	7.27	12.72
0.916	23.0	320.7	7.64	13.36	0.871	31.0	304.9	7.26	12.70
0.915	.2	320.3	7.63	13.35	0.870	.2	304.5	7.25	12.69
0.914	.4	319.9	7.62	13.33	0.869	.4	304.2	7.24	12.67
0.912	.6	319.5	7.61	13.31	0.868	.6	303.8	7.23	12.66
0.911	.8	319.0	7.60	13.29	0.867	.8	303.4	7.22	12.64
0.910	24.0	318.6	7.59	13.27	0.865	32.0	303.0	7.21	12.62
0.909	.2	318.2	7.58	13.26	0.864	.2	302.7	7.20	12.61
0.908	.4	317.8	7.57	13.24	0.863	.4	302.3	7.19	12.60
0.907	.6	317.4	7.56	13.22	0.862	.6	301.9	7.19	12.58
0.905	.8	317.0	7.55	13.21	0.861	.8	301.6	7.18	12.57
0.904	25.0	316.6	7.54	13.19	0.860	33.0	301.2	7.17	12.55
0.903	.2	316.2	7.53	13.17	0.859	.2	300.8	7.16	12.53
0.902	.4	315.8	7.52	13.16	0.858	.4	300.5	7.15	12.52
0.901	.6	315.4	7.51	13.14	0.857	.6	300.1	7.14	12.50
0.900	.8	315.0	7.50	13.12	0.856	.8	299.7	7.14	12.49
0.898	26.0	314.6	7.49	13.11	0.855	34.0	299.4	7.13	12.47
0.897	.2	314.2	7.48	13.09	0.854	.2	299.0	7.12	12.46
0.896	.4	313.8	7.47	13.07	0.853	.4	298.7	7.11	12.45
0.895	.6	313.4	7.46	13.06	0.852	.6	298.3	7.10	12.43
0.894	.8	313.0	7.45	13.04	0.851	.8	297.9	7.09	12.41
0.893	27.0	312.6	7.44	13.02	0.850	35.0	297.6	7.09	12.40
0.892	.2	312.2	7.43	13.01	0.849	.2	297.2	7.08	12.38
0.891	.4	311.8	7.42	12.99	0.848	.4	296.9	7.07	12.37
0.889	.6	311.4	7.41	12.97	0.847	.6	296.5	7.06	12.35
0.888	.8	311.0	7.40	12.96	0.846	.8	296.2	7.05	12.34
0.887	28.0	310.6	7.40	12.95	0.845	36.0	295.8	7.04	12.32
0.886	.2	310.3	7.39	12.93	0.844	.2	295.4	7.04	12.31
0.885	.4	309.9	7.38	12.91	0.843	.4	295.1	7.03	12.30
0.884	.6	309.5	7.37	12.90	0.842	.6	294.8	7.02	12.28
0.883	.8	309.1	7.36	12.88	0.841	.8	294.4	7.01	12.27
0.882	29.0	308.7	7.35	12.86	0.840	37.0	294.0	7.00	12.25
0.881	.2	308.3	7.34	12.85	0.839	.2	293.7	6.99	12.24
0.879	.4	307.9	7.33	12.83	0.838	.4	293.4	6.99	12.21
0.878	.6	307.6	7.32	12.82	0.837	.6	293.0	6.98	12.21
0.877	.8	307.2	7.31	12.80	0.836	.8	292.7	6.97	12.20

Table B.1 Continued

Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day	Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day
	°API	lb/bbl	lb/gal			°API	lb/bbl	lb/gal	
0.835	38.0	292.3	6.96	12.18	0.797	46.0	279.1	6.64	11.63
0.834	.2	292.0	6.95	12.17	0.796	.2	278.3	6.64	11.62
0.833	.4	291.6	6.94	12.15	0.795	.4	278.5	6.63	11.60
0.832	.6	291.3	6.94	12.14	0.795	.6	278.2	6.63	11.59
0.831	.8	291.0	6.93	12.12	0.794	.8	277.9	6.62	11.58
0.830	39.0	290.6	6.92	12.11	0.793	47.0	277.6	6.61	11.57
0.829	.2	290.3	6.91	12.10	0.792	.2	277.3	6.60	11.55
0.828	.4	290.0	6.90	12.08	0.791	.4	277.0	6.59	11.54
0.827	.6	289.6	6.89	12.07	0.790	.6	276.7	6.59	11.53
0.826	.8	289.2	6.89	12.05	0.789	.8	276.3	6.58	11.51
0.825	40.0	288.9	6.88	12.04	0.788	48.0	276.0	6.57	11.50
0.824	.2	288.6	6.87	12.02	0.787	.2	275.7	6.56	11.49
0.823	.4	288.2	6.86	12.01	0.787	.4	275.4	6.56	11.47
0.822	.6	287.9	6.85	12.00	0.786	.6	275.1	6.55	11.46
0.821	.8	287.6	6.84	11.93	0.785	.8	274.1	6.54	11.45
0.820	41.0	287.2	6.84	11.97	0.784	49.0	274.5	6.54	11.44
0.819	.2	286.9	6.83	11.95	0.783	.2	274.2	6.53	11.42
0.818	.4	286.6	6.82	11.94	0.782	.4	273.9	6.52	11.41
0.817	.6	286.2	6.81	11.92	0.781	.6	273.6	6.51	11.40
0.817	.8	285.9	6.81	11.91	0.781	.8	273.3	6.51	11.39
0.816	42.0	285.6	6.80	11.90	0.780	50.0	273.0	6.50	11.37
0.815	.2	285.3	6.79	11.89	0.779	.2	272.7	6.49	11.36
0.814	.4	284.9	6.79	11.87	0.778	.4	272.4	6.49	11.35
0.813	.6	284.6	6.78	11.86	0.777	.6	272.1	6.48	11.34
0.812	.8	284.3	6.77	11.85	0.776	.8	271.8	6.47	11.32
0.811	43.0	283.9	6.76	11.83	0.775	51.0	271.5	6.46	11.31
0.810	.2	283.6	6.75	11.82	0.775	.2	271.2	6.46	11.30
0.809	.4	283.3	6.74	11.80	0.774	.4	270.9	6.45	11.29
0.808	.6	283.0	6.74	11.79	0.773	.6	270.6	6.44	11.27
0.807	.8	282.6	6.73	11.77	0.772	.8	270.3	6.44	11.26
0.806	44.0	282.3	6.72	11.76	0.771	52.0	270.0	6.43	11.25
0.805	.2	282.0	6.71	11.75	0.770	.2	269.7	6.42	11.24
0.804	.4	281.7	6.70	11.74	0.769	.4	269.4	6.41	11.22
0.804	.6	281.4	6.70	11.72	0.769	.6	269.1	6.41	11.21
0.803	.8	281.0	6.69	11.71	0.768	.8	268.8	6.40	11.20
0.802	45.0	280.7	6.69	11.70	0.767	53.0	268.5	6.39	11.19
0.801	.2	280.4	6.68	11.68	0.766	.2	268.3	6.39	11.18
0.800	.4	280.1	6.67	11.67	0.765	.4	268.0	6.38	11.17
0.799	.6	279.8	6.66	11.66	0.764	.6	267.7	6.37	11.15
0.798	.8	279.5	6.65	11.65	0.764	.8	267.4	6.37	11.14

Table B.1 Continued

Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day	Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day
	°API	lb/bbl	lb/gal			°API	lb/bbl	lb/gal	
0.763	54.0	267.1	6.36	11.13	0.731	62.0	256.1	6.10	10.67
0.762	.2	266.8	6.35	11.12	0.730	.2	255.8	6.09	10.66
0.761	.4	266.5	6.34	11.10	0.730	.4	255.5	6.08	10.65
0.760	.6	266.2	6.34	11.09	0.729	.6	255.3	6.08	10.64
0.760	.8	265.9	6.33	11.08	0.728	.8	255.0	6.07	10.62
0.759	55.0	265.7	6.33	11.07	0.728	63.0	254.7	6.07	10.61
0.758	.2	265.4	6.32	11.06	0.727	.2	254.5	6.06	10.60
0.757	.4	265.1	6.31	11.05	0.726	.4	254.2	6.05	10.59
0.756	.6	264.8	6.30	11.03	0.725	.6	254.0	6.05	10.58
0.756	.8	264.5	6.30	11.02	0.724	.8	253.7	6.04	10.57
0.755	56.0	264.3	6.29	11.01	0.724	64.0	253.4	6.03	10.56
0.754	.2	264.0	6.29	11.00	0.723	.2	253.2	6.03	10.55
0.753	.4	263.7	6.28	10.99	0.722	.4	252.9	6.02	10.54
0.752	.6	263.4	6.27	10.97	0.722	.6	252.7	6.02	10.53
0.752	.8	263.1	6.27	10.96	0.721	.8	252.4	6.01	10.52
0.751	57.0	262.9	6.26	10.95	0.720	65.0	252.2	6.00	10.51
0.750	.2	262.6	6.26	10.94	0.719	.2	251.9	6.00	10.50
0.749	.4	262.3	6.24	10.93	0.719	.4	251.6	5.99	10.48
0.748	.6	262.0	6.24	10.92	0.718	.6	251.4	5.98	10.47
0.748	.8	261.7	6.23	10.90	0.717	.8	251.1	5.98	10.46
0.747	58.0	261.5	6.23	10.89	0.716	66.0	250.9	5.97	10.45
0.746	.2	261.2	6.22	10.88	0.716	.2	250.6	5.97	10.44
0.745	.4	260.9	6.21	10.87	0.715	.4	250.4	5.96	10.43
0.744	.6	260.6	6.20	10.86	0.714	.6	250.1	5.95	10.42
0.744	.8	260.4	6.20	10.85	0.714	.8	249.9	5.95	10.41
0.743	59.0	260.1	6.19	10.84	0.713	67.0	249.6	5.94	10.40
0.742	.2	259.8	6.19	10.82	0.712	.2	249.4	5.94	10.39
0.741	.4	259.6	6.18	10.81	0.711	.4	249.1	5.93	10.38
0.740	.6	259.3	6.17	10.80	0.711	.6	248.9	5.93	10.37
0.740	.8	259.0	6.17	10.79	0.710	.8	248.6	5.92	10.36
0.739	60.0	258.7	6.16	10.78	0.709	68.0	248.4	5.91	10.35
0.738	.2	258.5	6.15	10.77	0.709	.2	248.1	5.91	10.34
0.737	.4	258.2	6.15	10.76	0.708	.4	247.9	5.90	10.33
0.737	.6	257.9	6.14	10.75	0.707	.6	247.6	5.90	10.32
0.736	.8	257.7	6.14	10.74	0.706	.8	247.4	5.89	10.31
0.735	61.0	257.4	6.13	10.72	0.706	69.0	247.1	5.88	10.30
0.734	.2	257.1	6.12	10.71	0.705	.2	246.9	5.88	10.29
0.734	.4	256.9	6.12	10.70	0.704	.4	246.6	5.87	10.28
0.733	.6	256.6	6.11	10.69	0.704	.6	246.4	5.87	10.27
0.732	.8	256.3	6.10	10.68	0.703	.8	246.1	5.86	10.26

Table B.1 Continued

Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day	Specific gravity 60/60°F	Density in vacuo			lb/hr* from bbl/day
	°API	lb/bbl	lb/gal			°API	lb/bbl	lb/gal	
0.702	70.0	245.9	5.85	10.25	0.646	.5	226.2	5.39	9.42
0.701	.5	245.3	5.84	10.22	0.645	88.0	225.7	5.38	9.40
0.699	71.0	244.7	5.83	10.20	0.643	.5	225.2	5.36	9.38
0.697	.5	244.1	5.81	10.17	0.642	89.0	224.7	5.35	9.36
0.695	72.0	243.5	5.80	10.15	0.640	.5	224.2	5.34	9.34
0.694	.5	242.9	5.78	10.12	0.639	90.0	223.7	5.33	9.32
0.692	73.0	242.3	5.77	10.10	0.637	.5	223.2	5.31	9.30
0.609	.5	241.7	5.75	10.07	0.636	91.0	222.7	5.30	9.28
0.689	74.0	241.1	5.74	10.05	0.635	.5	222.2	5.29	9.26
0.687	.5	240.5	5.73	10.02	0.633	92.0	221.7	5.28	9.24
0.685	75.0	239.9	5.71	10.00	0.632	.5	221.2	5.27	9.22
0.684	.5	239.4	5.70	9.97	0.630	93.0	220.7	5.26	9.20
0.682	76.0	238.8	5.69	9.95	0.629	.5	220.2	5.24	9.18
0.680	.5	238.2	5.67	9.92	0.628	94.0	219.7	5.23	9.16
0.679	77.0	237.6	5.66	9.90	0.626	.5	219.2	5.22	9.14
0.677	.5	237.1	5.64	9.88	0.625	95.0	218/8	5.21	9.12
0.675	78.0	236.5	5.63	9.85	0.623	.5	218.3	5.20	9.10
0.674	.5	235.9	5.62	9.83	0.622	96.0	217.8	5.19	9.03
0.672	79.0	235.4	5.60	9.81	0.621	.5	217.3	5.17	9.06
0.671	.5	234.8	5.59	9.78	0.619	97.0	216.8	5.16	9.04
0.669	80.0	234.3	5.58	9.76	0.618	.5	216.4	5.15	9.02
0.668	.5	233.7	5.56	9.74	0.617	98.0	215.9	5.14	9.00
0.666	81.0	233.2	5.55	9.72	0.615	.5	215.4	5.13	8.98
0.664	.5	232.6	5.54	9.69	0.614	99.0	215.0	5.12	8.96
0.663	82.0	232.1	5.53	9.67	0.613	.5	214.5	5.11	8.94
0.661	.5	231.5	5.51	9.65	0.611	100.0	214.0	5.10	8.92
0.660	83.0	231.0	5.50	9.62	0.610	.5	213.6	5.09	8.90
0.658	.5	230.4	5.49	9.60	0.609	101.0	213.1	5.07	8.83
0.657	84.0	229.9	5.48	9.58	0.607	.5	212.7	5.06	8.86
0.655	.5	229.4	5.46	9.56	0.606	102.0	212.2	5.05	8.84
0.654	85.0	228.9	5.45	9.54	0.605	.5	211.7	5.04	8.82
0.652	.5	228.3	5.44	9.51	0.603	103.0	211.3	5.03	8.80
0.651	86.0	227.8	5.43	9.49	0.602	.5	210.8	5.02	8.78
0.649	.5	227.3	5.41	9.47	0.601	104.0	210.4	5.01	8.77
0.648	87.0	226.8	5.40	9.45	0.600	.5	209.9	5.00	8.75
					0.598	105.0	209.5	4.99	8.73

Source: From ASTM D-1250.

*Multiply barrels/day by the factor in this column corresponding to the API gravity to obtain pounds/hour.

Table B.2 Physical Constants of Paraffin Hydrocarbons and Other Components of Natural Gas [NGPA Publication 2145-74(1)]

Component	Notes	Methane	Ethane	Propane	Iso-Butane	N-Butane	Iso-Pentane	N-Pentane
Molecular Weight		16.043	30.070	44.097	58.124	58.124	72.151	72.151
Boiling Point @ 14,696 psia, °F		-258.89	-127.48	-43.87	10.90	31.10	82.12	98.92
Freezing Point @ 14,696 psia, °F		-298.46 ^d	-297.89 ^d	-305.84 ^d	-255.29	-217.05	-255.83	-201.51
Vapor Pressure @ 100°F, psia	(5000) (800)	190	72.2	51.6	20.44	15.570		
Density of Liquid @ 60°F & 14,696 psia								
Specific Gravity @ 60°F/60°F	a,b	0.3 ⁱ	0.3584 ^b	0.5077 ^b	0.5631 ^b	0.5844 ^b	0.6247	0.6310
"API	* a,b	340 ^j	265.5 ^j	147.2 ^j	119.8 ^j	110.6 ^j	95.0	92.7
Lb./gal @ 60°F, wt in vacuum	*	2.5 ⁱ	2.97 ^b	4.233 ^b	4.695 ^b	4.872 ^b	5.208	5.261
Lb./gal @ 60°F, wt in air	* c	2.5 ⁱ	2.962 ^b	4.223 ^b	4.686 ^b	4.865 ^b	5.199	5.251
Density of Gas @ 60°F & 14,696 psia								
Specific Gravity, Air = 1.00, ideal gas	*	0.5539	1.0382	1.5225	2.0068	2.0068	2.4911	2.4911
Lb./cu ft, ideal gas	*	42.28	79.24	116.20	153.16	153.16	190.13	190.13
Volume Ratio @ 60°F & 14,696 psia								
Gal./lb mol	*	6.4 ⁱ	10.12 ^b	10.42 ^b	12.38 ^b	11.93 ^b	13.85	13.71
Cu ft gas/gal liquid, ideal gas	*	59 ⁱ	37.5 ^b	36.43 ^b	30.65 ^b	31.81 ^b	27.39	27.67
Gas vol./liquid vol., ideal gas	*	443 ⁱ	280.5 ^b	272.51 ^b	229.30 ^b	237.98 ^b	204.93	207.00
Critical Conditions								
Temperature, °F		-116.63	90.09	206.01	274.98	305.85	369.10	385.7
Pressure, psia		667.8	707.8	816.3	529.1	556.7	490.4	488.6
Gross Heat of Combustion @ 60°F								
Btu/lb liquid	*	—	22,214 ^d	21,513 ^d	21,091 ^d	21,139 ^d	20,889	20,928
Btu/lb gas	*	23,885	22,323	21,665	21,237	21,298	21,040	21,089
Btu/cu ft, ideal gas	* p	1009.7	1768.8	2517.5	3252.7	3262.1	4000.3	4009.6
Btu/gal liquid	*	—	65,998 ^d	91,055 ^d	99,022 ^d	102,989 ^d	108,790	110,102
Cu ft air to burn 1 cu ft gas - ideal gas	*	9.54	16.70	23.86	31.02	31.02	38.18	38.18
Flammability Limit @ 100°F & 14,696 psia								
Lower, vol % in air		5.0	2.9	2.1	1.8	1.8	1.4	1.4
Upper, vol % in air		15.0	13.0	9.5	8.4	8.4	(8.3)	8.3
Heat of Vaporization @ 14,696 psia								
Btu/lb @ boiling point		219.22	210.41	183.05	157.53	185.65	147.13	153.59
Specific Heat @ 60°F & 14,696 psia								
C _p gas — Btu/lb, °F, ideal gas		0.5265	0.4097	0.3881	0.3872	0.3887	0.3827	0.3883
C _v gas — Btu/lb, °F, ideal gas	*	0.4027	0.3436	0.3430	0.3530	0.3525	0.3552	0.3608
N = C _p /C _v	*	1.308	1.192	1.131	1.097	1.097	1.078	1.076
C _p , liquid — Btu/lb, °F	*	—	0.9256	0.5920	0.5695	0.5636	0.5353	0.5441
Octane Number								
Motor clear		—	+ .05 ^f	97.1	97.6	89.6 ^g	90.3	62.6 ^h
Research clear		—	+1.64 ^f	+1.84 ^f	+0.10 ⁱ	93.8 ^g	92.3	61.7 ^h
Refractive Index n_D @ 60°F		—	—	—	—	1.3326 ^k	1.35373	1.35748

NOTES

- a. Air saturated hydrocarbons.
- b. Absolute values from weights in vacuum.
- c. The apparent values for weight in air are shown for users' convenience. All other mass data in this table are on an absolute mass (weight in vacuum) basis.
- d. At saturation pressure (triple point).
- e. The + sign and number following signify the octane number corresponding to that of 2,2,4 trimethylpentane with the indicated number of ml of TEL added.
- f. Saturation pressure and 60°F.
- g. Apparent value for methane at 60°F.
- h. Average value from octane numbers of more than one sample.
- i. Density of liquid, gm/ml at normal boiling point.
- j. Heat of vaporization.
- k. Gross heat values are reported on a dry basis at 60°F and 14,696 psia based on ideal gas calculations. To convert to water saturation basis, multiply by 0.9026.
- l. Extrapolated to room temperature from higher temperature.
- m. Calculated values. 1989 atomic weights used. See "Constants for Use in Calculations."
- () Estimated values.

Table B.2 Continued

N-Hexane	N-Heptane	N-Octane	N-Nonane	N-Decane	Carbon Dioxide	Hydrogen Sulfide	Nitrogen	Oxygen	Air	Water
86.178	100.205	114.232	128.259	142.286	44.010	34.076	28.013	31.999	28.984	18.015
155.72	209.17	256.22	303.47	345.48	-109.3°	-76.6° ⁽²⁾	-320.4° ⁽²⁾	-297.4° ⁽²⁾	-317.6° ⁽²⁾	212.0
-139.58	-131.05	-70.18	-64.28	-21.36	-	-117.2° ⁽²⁾	-346.0° ⁽²⁾	-381.8° ⁽²⁾	-	32.0
4.956	1.620	0.537	0.179	0.0597	-	394.0° ⁽²⁾	-	-	-	0.9492 ⁽¹⁾
0.8640	0.6882	0.7088	0.7217	0.7342	0.827 ⁽¹⁾	0.79 ⁽¹⁾	0.808m ⁽³⁾	1.14m ⁽³⁾	0.858m ⁽¹⁾	1.000
81.6	74.1	68.7	64.6	61.2	39.6°	47.6°	43.6°	-7.4°	33.8°	10.0
5.534	5.738	5.893	6.017	6.121	6.89°	6.59°	6.74°	9.50°	7.14°	8.337
5.526	5.728	5.883	6.008	6.112	6.89°	6.58°	6.73°	9.50°	7.13°	8.328
2.9753	3.4598	3.9439	4.4282	4.9125	1.5195	1.1785	0.9872	1.1048	1.0000	0.6220
227.09	284.05	301.01	337.98	374.94	115.97	89.79	73.82	84.32	76.32	47.47
15.57	17.46	19.39	21.32	23.24	6.38°	5.17°	4.16°	3.37°	4.06°	2.16
24.38	21.73	19.58	17.80	16.33	59.5°	73.3°	91.3°	112.7°	93.5°	175.6
182.37	182.56	146.45	133.18	122.13	444.8°	548.7°	682.7°	843.2°	699.5°	1313.8
453.7	512.8	364.22	610.68	652.1	87.9° ⁽²⁾	212.7° ⁽²⁾	-232.4° ⁽²⁾	-181.1° ⁽²⁾	-221.3° ⁽²⁾	705.6° ⁽²⁾
436.8	398.8	380.6	332	304	1071° ⁽²⁾	1306° ⁽²⁾	493.0° ⁽²⁾	736.9° ⁽²⁾	547° ⁽²⁾	3208° ⁽²⁾
20.784	20.681	20.604	20.544	20.494	-	-	-	-	-	-
20.944	20.840	20.762	20.701	20.649	-	-	-	-	-	-
4756.2	5502.8	6249.7	6996.5	7742.1	-	637° ⁽¹⁾	-	-	-	-
115.060	118.668	121.419	123.613	125.444	-	-	-	-	-	-
45.34	52.50	59.65	66.81	73.97	-	7.16	-	-	-	-
1.2	1.0	0.96	0.87*	0.78*	-	4.30 ⁽²⁾	-	-	-	-
7.7	7.0	-	2.9	2.6	-	45.50	-	-	-	-
143.95	136.01	129.53	123.76	118.68	238.2° ⁽¹⁾	235.6° ⁽²⁾	87.8° ⁽¹⁾	91.6° ⁽¹⁾	92° ⁽²⁾	970.3° ⁽²⁾
0.3864	0.3875	(0.3876)	0.3840	0.3835	0.1991° ⁽²⁾	0.238° ⁽²⁾	0.2462° ⁽²⁾	0.2188° ⁽²⁾	0.2400° ⁽²⁾	0.4446° ⁽²⁾
0.3633	0.3677	0.3702	0.3685	0.3695	0.1539	0.1797	0.1773	0.1567	0.1714	0.3343
1.063	1.054	1.047	1.042	1.038	1.293	1.325	1.400	1.396	1.400	1.330
0.5332	0.5283	0.5239	0.5228	0.5208	-	-	-	-	-	1.0009 ⁽²⁾
26.0	0.0	-	-	-	-	-	-	-	-	-
24.8	0.0	-	-	-	-	-	-	-	-	-
1.37486	1.38764	1.39743	1.40542	1.41189	-	-	-	-	-	1.3330 ⁽²⁾

REFERENCES

- Values for hydrocarbons were selected or calculated from API Project 44 which is identical to or equivalent with ASTM DS 4A "Physical Constants of Hydrocarbons," C10.2, 1971, American Society for Testing Materials, 1916 Race Street, Philadelphia.
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CONSTANTS FOR USE IN CALCULATIONS

Atomic weights [based on 1969 values, Pure Applied Chemistry 20(4) (1969)]:

C: 12.011 H: 1.0080 N: 14.0067 O: 15.9994 S: 32.06

Ideal gas:

1 mol = 379.49 ft³ at 14.696 psia and 60°F

1 mol = 22.414 liters at 14.696 psia and 32°F

Conversion factors:

1 ft³ = 28.317 liters 1 gal = 3785.41 milliliters 1 ft³ = 7.4805 gal

760 mmHg = 14.696 lb/in² = 1 atm

1 lb = 453.59 gms 0°F = 459.67° Rankine

Density of water at 60°F = 8.3372 lb/gal = 0.999015 g/cc (weight in vacuum)

Specific gravity at 60°F/60°F × 0.999015 = density at 60°F, g/cc

$$^{\circ}\text{F} = \frac{9}{5} ^{\circ}\text{C} + 32 \quad ^{\circ}\text{API} = \frac{141.5}{\text{sp gr at } 60^{\circ}\text{F}/60^{\circ}\text{F}} - 131.5$$

CALCULATED VALUES

Density of liquid at 60°F and 14.696 psia:

$$\begin{aligned} \text{lb/gal at } 60^{\circ}\text{F (weight-in-vacuum)} &= \text{sp gr at } 60^{\circ}\text{F}/60^{\circ}\text{F (weight-in-vacuum)} \\ &\times 8.3372 \text{ lb/gal (wt-in-vacuum)} \end{aligned}$$

lb/gal at 60°F (weight-in-air) (see ASTM DS 4A, p. 61):

$$\text{gal/lb mol at } 60^{\circ}\text{F} = \frac{\text{mol wt}}{\text{lb/gal at } 60^{\circ}\text{F (weight-in-vacuum)}}$$

Density of gas at 60°F and 14.696 psia (ideal gas):

$$\text{sp gr at } 60^{\circ}\text{F} = \frac{\text{mol wt}}{28.964}$$

$$\text{lb/M cu ft} = \frac{(\text{mol wt} \times 1000)}{379.49}$$

$$\text{ft}^3 \text{ vap/gal liq} = \frac{\text{lb/gal at } 60^\circ\text{F (wt-in-vac)} \times 379.49}{\text{mol wt}}$$

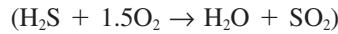
Ratio gas vol/liq vol:

$$\text{Gas vol/liq vol} = \frac{\text{lb/gal at } 60^\circ\text{F (wt-in-vac)} \times 379.49 \times 7.4805}{\text{mol wt}}$$

Heat of combustion at 60°F: The heat of combustion in Btu/gal was calculated as follows: The gross heat of combustion in Btu/lb gas less the heat of vaporization at 60°F is the calculated heat of combustion for the liquid state in Btu/lb. The heat of vaporization at 60°F was calculated from the normal boiling point, critical temperature, and the heat of vaporization at the normal boiling point using the method of Fishtine (see Reid and Sherwood, *The Properties of Gases and Liquids*, 2nd Ed., page 148). The heat of combustion in Btu/lb liquid multiplied by the weight in vacuum, lb/gal, yields the heat of combustion in Btu/gal at the saturation pressure and 60°F.

Cubic feet of air to burn 1 ft³ gas (ideal gas)—C_aH_b (see ASTM DS 4A, p. 63):

$$\frac{\text{ft}^3 \text{ air}}{\text{ft}^3 \text{ gas}} = \frac{(a + b/4)}{0.2095}$$



Specific Heat at 60°F and 14.696 psia (ideal gas):

$$C_v(\text{gas}) = C_p(\text{gas}) - \left(\frac{1.98719}{\text{mol wt}} \right) \text{ (for hydrocarbons)}$$

C_v values for nonhydrocarbon components are calculated from C_p and N values.

Table B.3 Heats of Combustion of Residual Fuel Oils

°API at 60°F	Specific at 60°/60°F	Gravity	Density, lb per gal	Total heat of combustion at constant volume, Qv			Net heat of combustion at constant pressure, Qp		
				Btu			Btu		
				Cal per g	per lb	per gal	Cal per g	per lb	per gal
0	1.0760	8.962	9,970	17,950	160,900	9,470	17,050	152,800	
1.0	1.0679	8.895	10,010	18,010	160,200	9,500	17,100	152,100	
2.0	1.0599	8.828	10,040	18,070	159,500	9,530	17,150	151,400	
3.0	1.0520	8.762	10,080	18,140	158,900	9,560	17,210	150,800	
4.0	1.0443	8.698	10,110	18,200	158,300	9,590	17,260	150,100	
5.0	1.0366	8.634	10,140	18,250	157,600	9,620	17,320	149,500	
6.0	1.0291	8.571	10,180	18,320	157,000	9,650	17,370	148,900	
7.0	1.0217	8.509	10,210	18,380	156,400	9,670	17,410	148,200	
8.0	1.0143	8.448	10,240	18,430	155,700	9,690	17,450	147,400	
9.0	1.0071	8.388	10,270	18,490	155,100	9,720	17,500	146,800	
10.0	1.0000	8.328	10,300	18,540	154,400	9,740	17,540	146,100	
11.0	0.9930	8.270	10,330	18,590	153,700	9,770	17,580	145,500	
12.0	0.9861	8.212	10,360	18,640	153,000	9,790	17,620	144,800	
13.0	0.9792	8.155	10,390	18,690	152,400	9,810	17,670	144,100	
14.0	0.9725	8.099	10,410	18,740	151,800	9,840	17,710	143,500	
15.0	0.9659	8.044	10,440	18,790	151,100	9,860	17,750	142,800	
16.0	0.9593	7.989	10,470	18,840	150,500	9,880	17,790	142,200	
17.0	0.9529	7.935	10,490	18,890	149,900	9,900	17,820	141,500	
18.0	0.9465	7.882	10,520	18,930	149,200	9,920	17,860	140,800	
19.0	0.9402	7.830	10,540	18,980	148,600	9,940	17,900	140,200	
20.0	0.9340	7.778	10,570	19,020	147,900	9,960	17,930	139,500	
21.0	0.9279	7.727	10,590	19,060	147,300	9,980	17,960	138,900	
22.0	0.9218	7.676	10,620	19,110	146,600	10,000	18,000	138,200	
23.0	0.9159	7.627	10,640	19,150	146,000	10,020	18,030	137,600	
24.0	0.9100	7.578	10,660	19,190	145,400	10,040	18,070	137,000	
25.0	0.9024	7.529	10,680	19,230	144,800	10,050	18,100	136,300	
26.0	0.8984	7.481	10,710	19,270	144,100	10,070	18,130	135,700	
27.0	0.8927	7.434	10,730	19,310	143,500	10,090	18,160	135,100	
28.0	0.8871	7.387	10,750	19,350	142,900	10,110	18,190	134,500	
29.0	0.8816	7.341	10,770	19,380	142,300	10,120	18,220	133,800	
30.0	0.8762	7.305	10,790	19,420	141,800	10,140	18,250	133,300	
31.0	0.8708	7.260	10,810	19,450	141,200	10,150	18,280	132,700	
32.0	0.8654	7.215	10,830	19,490	140,600	10,170	18,310	132,100	
33.0	0.8602	7.171	10,850	19,520	140,000	10,180	18,330	131,500	
34.0	0.8550	7.128	10,860	19,560	139,400	10,200	18,360	130,900	

Table B.3 Continued

Gravity		Density, lb per gal	Total heat of combustion at constant volume, Qv			Net heat of combustion at constant pressure, Qp		
°API	Specific at 60°F		Btu per gal	Btu per lb	Btu per gal	Cal per g	Btu per lb	Btu per gal
35.0	0.8498	7.085	10,880	19,590	138,800	10,210	18,390	130,300
36.0	0.8448	7.043	10,900	19,620	138,200	10,230	18,410	129,700
37.0	0.8398	7.001	10,920	19,650	137,600	10,240	18,430	129,100
38.0	0.8348	6.960	10,940	19,680	137,000	10,260	18,460	128,500
39.0	0.8299	6.920	10,950	19,720	136,400	10,270	18,840	127,900
40.0	0.8251	6.879	10,970	19,750	135,800	10,280	18,510	127,300
41.0	0.8203	6.839	10,990	19,780	135,200	10,300	18,530	126,700
42.0	0.8155	6.799	11,000	19,810	134,700	10,310	18,560	126,200
43.0	0.8109	6.760	11,020	19,830	134,100	10,320	18,580	125,600
44.0	0.8063	6.722	11,030	19,860	133,500	10,330	18,600	125,000
45.0	0.8017	6.684	11,050	19,890	132,900	10,340	18,620	124,400
46.0	0.7972	6.646	11,070	19,920	132,400	10,360	18,640	123,900
47.0	0.7927	6.609	11,080	19,940	131,900	10,370	18,660	123,300
48.0	0.7883	6.572	11,100	19,970	131,200	10,380	18,680	122,800
49.0	0.7839	6.536	11,110	20,000	130,700	10,390	18,700	122,200

Source: K. M. Guthrie, ed., "Petroleum Products Handbook." Copyright 1960, McGraw-Hill Book Company. Used with permission of McGraw-Hill Book Company.

Appendix C

U.S. Bureau of Mines Routine Analyses of Selected Crude Oils

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 55151

IDENTIFICATION

Ten Section field
Stevens, Upper Miocene
7,800-8,400 feet

California
Kern County

GENERAL CHARACTERISTICS

Gravity, specific, .0.854	Gravity, ° API, 34.2	Pour point, ° F., below 5
Sulfur, percent, 0.45		Color, brownish black
Viscosity, Saybolt Universal at 100° F., 43 sec.		Nitrogen, percent, 0.289

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, .756 mm. Hg
First drop, 82° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test. ° F.
1	122	2.6	2.6	0.644	88.2					
2	167	2.3	4.9	.683	75.7	14	1.38469	122.3		
3	212	5.0	9.9	.725	63.7	24	1.40300	124.0		
4	257	7.9	17.8	.751	56.9	27	1.41569	128.6		
5	302	6.2	24.0	.772	51.8	29	1.42785	133.6		
6	347	4.9	28.9	.791	47.4	32	1.43863	135.5		
7	302	4.6	33.5	.808	43.6	33	1.44778	140.5		
8	437	5.2	38.7	.825	40.0	36	1.45638	144.7		
9	482	4.9	43.6	.837	37.6	36	1.46441	152.5		
10	527	6.2	49.8	.852	34.6	39	1.47262	151.8		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	4.3	54.1	0.867	31.7	42	1.47941	156.0	41	10
12	437	5.2	59.3	.872	30.8	40	1.48461	163.8	49	30
13	482	5.3	64.6	.890	27.5	46	1.49418	170.9	66	55
14	527	3.2	67.8	.897	26.3	46			105	70
15	572	5.4	73.2	.915	23.1	51			200	80
Residuum		25.0	98.2	.984	12.3					

Carbon residue, Conradson: Residuum, 10.5 percent; crude, 3.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	9.9	0.694	72.4	
Total gasoline and naphtha	33.5	0.752	56.7	
Kerosine distillate	5.2	.825	40.0	
Gas oil	18.5	.855	34.0	
Nonviscous lubricating distillate	8.5	.873-.896	30.6-26.4	50-100
Medium lubricating distillate	4.8	.896-.915	26.4-23.1	100-200
Viscous lubricating distillate	2.7	.915-.926	23.1-21.3	Above 200
Residuum	25.0	.984	12.3	
Distillation loss				

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Laramie Laboratory
Sample PC-65-28

IDENTIFICATION

Elk Hills field (Naval Reserve No. 1)
Sub-Scales No. 1 sandstone - Pliocene
3,333-3,370 feet

California
Kern County
SE1/4SW1/4, sec. 8,
T 31 S, R 24 E

GENERAL CHARACTERISTICS

Gravity, specific, .896	Gravity, ° API, 26.4	Pour point, ° F., below 5
Sulfur, percent, .51	Color, greenish black	Nitrogen, percent, 0.398
Viscosity, Saybolt Universal at 100°F., 61 sec; at 77°F., 83 sec.		

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 760 mm. Hg
First drop, 154 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	0.6	0.6	0.697	71.5		1.39020	118.3		
2	167	3.3	3.9	.739	60.0	30	1.40622	121.1		
3	212	5.8	9.7	.762	54.2	32	1.41838	122.5		
4	257	5.2	14.9	.782	49.5	34	1.42933	125.8		
5	302	5.1	20.0	.805	44.3	38	1.44218	137.8		
6	347	4.4	24.4	.825	40.0	41	1.45419	141.2		
7	392	5.7	30.1	.840	37.0	43	1.46360	145.8		
8	437	7.4	37.5	.855	34.0	45	1.47338	155.8		
9	482	5.5	43.0	.871	31.0	48	1.48395	170.5		
10	527									

STAGE 2—Distillation continued at 40 mm. Hg

11	392	1.5	44.5	.890	27.5	53	1.49180	166.4	41	below 5
12	437	5.8	50.3	.892	27.1	50	1.49533	174.4	47	below 5
13	482	5.3	55.6	.906	24.7	53	1.49684	171.6	63	below 5
14	527	4.8	60.4	.931	20.5	62			110	below 5
15	572	5.3	65.7	.938	19.4	62			280	below 5
Residuum		33.8	99.5	.984	12.3					

Carbon residue, Conradson: Residuum, 11.6 percent; crude, 4.3 percent.

APPROXIMATE SUMMARY

		Percent	Sp. gr.	° API	Viscosity
Light gasoline		3.9	0.733	61.5	
Total gasoline and naphtha		24.4	.782	49.5	
Kerosine distillate					
Gas oil		23.9	.863	32.5	
Nonviscous lubricating distillate		8.6	.894-.926	26.8-21.3	50-100
Medium lubricating distillate		3.8	.926-.935	21.3-19.8	100-200
Viscous lubricating distillate		5.0	.935-.942	19.8-18.7	Above 200
Residuum		33.8	.984	12.3	
Distillation loss5			

U. S. GOVERNMENT PRINTING OFFICE 10-57843-3

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
 Sample 55126

IDENTIFICATION

Torrance Field California
 Del Amo, Miocene Los Angeles County
 3,100-5,000 feet

GENERAL CHARACTERISTICS

Gravity, specific, .0.911.....	Gravity, ° API, 23.8.....	Pour point, ° F., below 5.....
Sulfur, percent, 1.84.....	Color, brownish black.....	
Viscosity, Saybolt Universal at 100° F., 160 sec.; 130° F., 96 sec.....		Nitrogen, percent, 0.555.....

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 746 mm. Hg
 First drop, 81 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _d at 20° C.	Specific dispersion	S. U. vis., 100° F.	Cloud test, ° F.
1.....	122	0.3	0.3	0.675	78.1					
2.....	167	1.1	1.4	.683	75.7	14	1.39514	126.2		
3.....	212	2.2	3.6	.725	63.7	24	1.41771	130.2		
4.....	257	3.7	7.3	.755	55.9	29	1.42842	134.5		
5.....	302	3.8	11.1	.777	50.6	32	1.43986	138.3		
6.....	347	3.3	14.4	.796	46.3	34	1.44908	141.7		
7.....	392	3.5	17.9	.813	42.6	36	1.45776	142.1		
8.....	437	4.3	22.2	.830	39.0	38	1.46618	148.3		
9.....	482	4.6	26.8	.843	36.4	39	1.47548	151.0		
10.....	527	7.4	34.2	.861	32.8	43				

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	1.6	35.8	0.872	30.8	44	1.48248	—	43	10
12.....	437	5.4	41.2	.884	28.6	46	1.48731	150.6	49	30
13.....	482	6.0	47.2	.901	25.6	51	1.49769	—	70	45
14.....	527	5.5	52.7	.910	24.0	52	1.50544	—	125	65
15.....	572	4.6	57.3	.927	21.1	57			250	80
Residuum.....		41.9	99.2	1.004	9.4					

Carbon residue, Conradson: Residuum, 13.2 percent; crude, 6.1 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	3.6	0.708	68.4	
Total gasoline and naphtha	17.9	0.769	52.5	
Kerosine distillate	—	—	—	
Gas oil	21.0	.855	34.0	
Nonviscous lubricating distillate	8.5	.855-.906	28.4-24.7	50-100
Medium lubricating distillate	5.7	.906-.921	24.7-22.1	100-200
Viscous lubricating distillate	4.2	.921-.934	22.1-20.0	Above 200
Residuum	41.9	1.004	9.4	
Distillation loss	8			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 58010

IDENTIFICATION

Rangely field
Weber, Pennsylvanian
5,960-6,459 feet

Colorado
Rio Blanco County

GENERAL CHARACTERISTICS

Gravity, specific, ... 0.851	Gravity, ° API, ... 34.8	Pour point, ° F., ... 10
Sulfur, percent, ... 0.56		Color, greenish black
Viscosity, Saybolt Universal at 100° F., 48 sec.		Nitrogen, percent, 0.073

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, ... 754 mm. Hg
First drop, ... 88 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index n_{D}^{20} at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	1.4	1.4	0.647	87.2					
2	167	2.6	4.0	.670	79.7	7.5	1.37406	125.6		
3	212	2.9	6.9	.709	68.1	16	1.39574	128.0		
4	257	5.2	12.1	.731	62.1	18	1.40817	128.2		
5	302	3.9	16.0	.752	56.7	20	1.41885	131.4		
6	347	5.3	21.3	.772	51.8	23	1.42916	135.2		
7	392	4.8	26.1	.792	47.2	26	1.43936	137.1		
8	437	4.7	30.8	.810	43.2	29	1.44801	138.8		
9	482	5.6	36.4	.824	40.2	30	1.45630	140.5		
10	527	6.6	43.0	.843	36.4	34	1.46581	147.3		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	2.9	45.9	0.854	34.2	36	1.47399	150.5	40	10
12	437	7.6	53.5	.861	32.8	35	1.47765	162.0	46	24
13	482	6.9	60.4	.880	29.3	41	1.48676	156.8	61	50
14	527	5.8	66.2	.891	27.3	43	1.49293	-	86	60
15	572	5.8	72.0	.902	25.4	45			160	74
Residuum		26.5	98.5	.962	15.6					

Carbon residue, Conradson: Residuum, 7.6 percent; crude, 2.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	6.9	0.682	76.0	
Total gasoline and naphtha	26.1	0.741	59.5	
Kerosine distillate	10.3	.818	41.5	
Gas oil	15.3	.852	34.6	
Nonviscous lubricating distillate	12.7	.865-.893	32.1-27.0	50-100
Medium lubricating distillate	7.6	.893-.907	27.0-24.5	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	26.5	.962	15.6	
Distillation loss	1.5			

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CRUDE PETROLEUM ANALYSIS

Bureau of Mines ... Bartlesville Laboratory
 Sample ... 57069

IDENTIFICATION

Bridgeport field
 Bridgeport, Pennsylvanian
 906-938 feet

Illinois
 Lawrence County

GENERAL CHARACTERISTICS

Gravity, specific, .847.....	Gravity, ° API, 35.6.....	Pour point, ° F., below 5.....
Sulfur, percent, 0.21.....	Color, brownish green.....	Nitrogen, percent, 0.138.....
Viscosity, Saybolt Universal at 100° F., 46 sec.....		

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, mm. Hg

First drop, ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1.....	122	2.3	2.3	0.638	90.3	8.0	1.37182	121.0		
2.....	167	2.2	4.5	.671	79.4					
3.....	212	4.6	9.1	.712	67.2	18	1.39622	116.9		
4.....	257	5.7	14.8	.738	60.2	21	1.40852	123.8		
5.....	302	5.3	20.1	.756	55.7	22	1.41885	128.7		
6.....	347	5.3	25.4	.776	50.9	24	1.42922	129.4		
7.....	392	4.4	29.8	.792	47.2	26	1.43930	135.2		
8.....	437	4.7	34.5	.809	43.4	28	1.44784	133.7		
9.....	482	4.8	39.3	.823	40.4	30	1.45582	134.3		
10.....	527	5.9	45.2	.837	37.6	32	1.46433	142.6		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	3.7	48.9	0.852	34.6	35	1.47330	150.0	40	10
12.....	437	5.7	54.6	.858	33.4	34	1.47744	--	47	25
13.....	482	4.5	59.1	.873	30.6	37	1.48469	--	61	50
14.....	527	4.7	63.8	.885	28.4	40	1.49563	--	89	65
15.....	572	5.5	69.3	.901	25.6	45			170	75
Residuum.....		28.3	97.6	.960	15.9					

Carbon residue, Conradson: Residuum, 8.4 percent; crude, 2.7 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	9.1	0.683	75.7	
Total gasoline and naphtha	29.8	0.739	60.0	
Kerosine distillate	9.5	.816	41.9	
Gas oil	13.7	.847	35.6	
Nonviscous lubricating distillate	9.2	.861-.887	32.8-27.7	50-100
Medium lubricating distillate	6.4	.887-.907	27.7-24.5	100-200
Viscous lubricating distillate7	.907-.909	24.5-24.2	Above 200
Residuum	28.3	.960	15.9	
Distillation loss	2.4			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 61084

IDENTIFICATION

Marcotte field
Arbuckle, Cambro-Ordovician
3,757-3,761 feet

Kansas
Rooks County

GENERAL CHARACTERISTICS

Gravity, specific, .0.897.....	Gravity, ° API, 26.3.....	Pour point, ° F., ...15.....
Sulfur, percent, ..0.77.....	Color, brownish black.....	
Viscosity, Saybolt Universal at 100° F., 242 sec.; 130° F., 122 sec.....	Nitrogen, percent, 0.19.....	

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 746 mm. Hg
First drop, 185 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1.....	122
2.....	167
3.....	212
4.....	257	2.3	2.3	0.730	62.3	-	1.40764	126.2
5.....	302	2.5	4.8	.749	57.4	18	1.41629	124.0
6.....	347	3.4	8.2	.770	52.3	22	1.42613	126.1
7.....	392	3.6	11.8	.790	47.6	25	1.43574	127.7
8.....	437	4.6	16.4	.804	44.5	26	1.44520	129.3
9.....	482	4.5	20.9	.821	40.9	29	1.45305	132.8
10.....	527	6.1	27.0	.836	37.8	31	1.46130	139.3

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	2.7	29.7	0.848	35.4	33	1.46983	143.7	39	below 5
12.....	437	6.4	36.1	.860	33.0	35	1.47567	148.0	46	15
13.....	482	8.2	44.3	.876	30.0	39	1.48456	155.4	61	30
14.....	527	4.6	48.9	.893	27.0	44	1.49161	161.2	98	60
15.....	572	6.7	55.6	.897	26.3	43	1.49562	168.5	155	75
Residuum.....		43.6	99.2	.974	13.8					

Carbon residue, Conradson: Residuum, 8.5 percent; crude, 4.1 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	-	-	-	-
Total gasoline and naphtha.....	11.8	0.764	53.7	
Kerosine distillate.....	9.1	.812	42.8	
Gas oil.....	14.9	.847	35.6	
Nonviscous lubricating distillate.....	11.0	.866-.893	31.9-27.0	50-100
Medium lubricating distillate.....	8.8	.893-.899	27.0-25.9	100-200
Viscous lubricating distillate.....	-	-	-	Above 200
Residuum.....	43.6	.974	13.8	
Distillation loss.....	.8	-	-	

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 60052

IDENTIFICATION

Black Bay, West field
9200¹, Miocene
9,178-9,185 feet

Louisiana
Piaquemines Parish

GENERAL CHARACTERISTICS

Gravity, specific, ...0.853.....	Gravity, ° API, ..34.4.....	Pour point, ° F., below 5.....
Sulfur, percent,0.19.....	Color, brownish green.....	
Viscosity, Saybolt Universal at ...100° F., .46 sec.....	Nitrogen, percent, .0.04.....	

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 758 mm. Hg
First drop, 113 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1.....	122									
2.....	167									
3.....	212	2.6	2.6	0.706	68.9	-	1.39971	129.4		
4.....	257	3.1	5.7	.739	60.0	21	1.41235	132.0		
5.....	302	3.7	9.4	.762	54.2	25	1.42308	135.4		
6.....	347	4.2	13.6	.780	49.9	26	1.43298	137.1		
7.....	392	5.8	19.4	.796	46.3	28	1.44076	138.4		
8.....	437	4.9	24.3	.807	43.8	27	1.44701	139.1		
9.....	482	7.6	31.9	.820	41.1	28	1.45389	140.8		
10.....	527	9.1	41.0	.834	38.2	30	1.46161	143.0		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	6.0	47.0	0.846	35.8	32	1.46906	148.8	40	below 5
12.....	437	8.3	55.3	.854	34.2	32	1.47238	147.4	46	20
13.....	482	6.8	62.1	.866	31.9	34	1.47868	144.0	58	50
14.....	527	5.8	67.9	.881	29.1	38	1.48434	-	81	60
15.....	572	6.1	74.0	.892	27.1	40			135	70
Residuum.....		24.5	98.5	.940	19.0					

Carbon residue, Conradson: Residuum, 4.6 percent; crude, 1.2 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	2.6	0.706	68.9	
Total gasoline and naphtha	19.4	0.765	53.5	
Kerosine distillate	12.5	.815	42.1	
Gas oil	21.9	.843	36.4	
Nonviscous lubricating distillate	12.9	.858-.884	33.4-28.6	50-100
Medium lubricating distillate	7.3	.884-.898	28.6-26.1	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	24.5	.940	19.0	
Distillation loss	1.5			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines ... Bartlesville Laboratory
Sample ... 54060

IDENTIFICATION

Bayou des Allemands field
MioceneLouisiana
Lafourche Parish

GENERAL CHARACTERISTICS

Gravity, specific, .0.845.....	Gravity, ° API, 36.0.....	Pour point, ° F., 35.....
Sulfur, percent, .0.20.....		Color, ...brownish green.....
Viscosity, Saybolt Universal at 100° F., 49 sec.....		Nitrogen, percent, 0.040.....

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 743... mm. Hg
First drop, 66 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc. 100° F.	Cloud test, ° F.
1.....	122	.0.5	.0.5	.670	79.7	11				
2.....	167	1.2	1.7	.675	78.1					
3.....	212	1.6	3.3	.722	64.5	23	1.39163	137.0		
4.....	257	2.7	6.0	.748	57.7	26	1.41725	141.7		
5.....	302	3.1	9.1	.765	53.5	26	1.42648	142.3		
6.....	347	3.9	13.0	.778	50.4	25	1.43374	140.7		
7.....	392	4.7	17.7	.789	47.8	24	1.43962	138.0		
8.....	437	5.7	23.4	.801	45.2	24	1.44529	137.6		
9.....	482	8.0	31.4	.814	42.3	25	1.45193	137.4		
10.....	527	10.7	42.1	.825	40.0	26	1.45884	142.9		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	5.0	47.1	0.845	36.0	31	1.46614	142.6	40	15
12.....	437	10.0	57.1	.854	32	32	1.46870	139.9	45	30
13.....	482	7.8	64.9	.863	32.5	33	1.47403	140.4	56	50
14.....	527	7.0	71.9	.874	30.4	35			81	65
15.....	572	6.5	78.4	.889	27.7	39			145	85
Residuum.....		20.8	99.2	.931	20.5					

Carbon residue, Conradson: Residuum, .3.7. percent; crude, .0.8. percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	3.3	0.697	71.5	
Total gasoline and naphtha	17.7	0.759	54.9	
Kerosine distillate	24.4	.816	41.9	
Gas oil	14.2	.850	35.0	
Nonviscous lubricating distillate	14.1	.858-.878	33.4-29.7	50-100
Medium lubricating distillate	8.0	.878-.895	29.7-26.6	100-200
Viscous lubricating distillate	-	-	-	Above 200
Residuum	20.8	.931	20.5	
Distillation loss8			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 54064

IDENTIFICATION

Sho-Vel-Tum field
Camp area Oklahoma
Springer, Pennsylvanian Carter County
6,295-6,305 feet

GENERAL CHARACTERISTICS

Gravity, specific, .0.887.....	Gravity, ° API, ...28.0.....	Pour point, ° F., ...10.....
Sulfur, percent, ..1.41.....	Color, brownish black.....	
Viscosity, Saybolt Universal at 100° F., 115 sec.; 130° F., 81 sec.....		Nitrogen, percent, 0.318.....

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 745 mm. Hg
First drop, 84 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1.....	122	1.3	1.3	0.648	86.9					
2.....	167	1.5	2.8	.674	78.4	9.4				
3.....	212	3.3	6.1	.712	67.2	18	1.39123	127.3		
4.....	257	4.3	10.4	.739	60.0	21	1.40995	127.9		
5.....	302	4.0	14.4	.758	55.2	23	1.42105	130.1		
6.....	347	4.1	18.5	.779	50.1	26	1.43181	134.3		
7.....	392	3.7	22.2	.798	45.8	29	1.44175	136.9		
8.....	437	4.1	26.3	.814	42.3	31	1.45087	141.2		
9.....	482	4.8	31.1	.831	39.8	33	1.46025	145.7		
10.....	527	6.0	37.1	.848	35.4	37	1.46939	155.6		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	1.1	38.2	0.862	32.7	39	1.47778	153.8	43	10
12.....	437	4.7	42.9	.873	30.6	41	1.48216	156.6	46	25
13.....	482	4.6	47.5	.882	28.9	42	1.48952	161.8	58	40
14.....	527	5.3	52.8	.898	26.1	46			88	52
15.....	572	5.3	58.1	.911	23.8	49			175	70
Residuum.....		40.9	99.0	.982	12.6					

Carbon residue, Conradson: Residuum, 11.4 percent; crude, 5.2 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	6.1	0.689	73.9	
Total gasoline and naphtha.....	22.2	0.746	58.2	
Kerosine distillate.....	4.1	.814	42.3	
Gas oil.....	16.0	.844	36.2	
Nonviscous lubricating distillate.....	8.6	.854-.871	34.2-31.0	50-100
Medium lubricating distillate.....	6.1	.871-.891	31.0-27.3	100-200
Viscous lubricating distillate.....	1.1	.891-.894	27.3-26.8	Above 200
Residuum.....	40.9	.982	12.6	
Distillation loss.....	1.0			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 59172

IDENTIFICATION

Sho-Vel-Tum field
Tatums area
Pennsylvanian

Oklahoma
Garvin County

GENERAL CHARACTERISTICS

Gravity, specific, .0.928	Gravity, ° API, 21.0	Pour point, ° F., below 5
Sulfur, percent, 1.68	Color, brownish black	
Viscosity, Saybolt Universal at 100°F., 550 sec.; 130°F., 440 sec.	Nitrogen, percent, 0.482	

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 743 mm. Hg
First drop, 147 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_0 at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122									
2	167									
3	212	2.6	2.6	0.695	72.1	-	1.38886	124.3		
4	257	2.8	5.4	.737	60.5	20	1.40876	124.0		
5	302	2.9	8.3	.758	55.2	23	1.41971	128.8		
6	347	3.5	11.8	.778	50.3	25	1.43164	131.0		
7	392	2.7	14.5	.799	45.6	29	1.44187	135.5		
8	437	3.1	17.6	.817	41.7	32	1.45080	138.7		
9	482	4.4	22.0	.832	38.6	-	1.46062	143.8		
10	527									

STAGE 2—Distillation continued at 40 mm. Hg

11	392	6.1	28.1	0.859	33.2	-	1.47659	156.3	38	below 5
12	437	4.5	32.6	.878	29.7	43	1.48547	160.2	47	do
13	482	3.9	36.5	.890	27.5	46	1.49374	157.4	62	do
14	527	4.8	41.3	.909	24.2	-	1.50253	161.8	105	do
15										
Residuum.		55.9	97.2	1.012	8.3					

Carbon residue, Conradson: Residuum, 8.2 percent; crude, 5.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	2.6	0.695	72.1	
Total gasoline and naphtha	14.5	0.755	55.9	
Kerosine distillate	3.1	.817	41.7	
Gas oil	13.6	.854	34.2	
Nonviscous lubricating distillate	7.3	.880-.907	29.3-24.5	50-100
Medium lubricating distillate	2.8	.907-.919	24.5-22.5	100-200
Viscous lubricating distillate			-	Above 200
Residuum	55.9	1.012	8.3	
Distillation loss	2.8			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 64036

Sho-Vel-Tum field
Sholem Alechem area
Pennsylvanian
3,468-3,488 feet

IDENTIFICATION

Oklahoma
Stephens County

GENERAL CHARACTERISTICS

Gravity, specific, .0.893	Gravity, ° API, 27.0	Pour point, ° F., below 5
Sulfur, percent, 1.34	Color, greenish black	
Viscosity, Saybolt Universal at 100°F., 131 sec.; 130°F., 84 sec.	Nitrogen, percent, 0.243	

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 732 mm. Hg
First drop, 77 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index n_d^{20} at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122									
2	167									
3	212	3.2	3.2	0.704	69.5	-	1.39260	128.2		
4	257	3.5	6.7	.732	60.5	20	1.40952	131.7		
5	302	3.7	10.4	.759	54.9	23	1.42062	133.4		
6	347	3.8	14.2	.778	50.4	25	1.43156	135.0		
7	392	3.5	17.7	.798	45.8	29	1.44148	137.7		
8	437	4.0	21.7	.814	42.3	31	1.45105	140.0		
9	482	4.7	26.4	.832	38.6	34	1.46032	148.1		
10	527	5.1	31.5	.847	35.6	36	1.46909	154.9		

STAGE 2—Distillation continued at 40 mm. Hg

11	392	3.2	35.2	0.870	31.1	43	1.47931	158.1	42	5
12	437	4.7	39.9	.877	29.8	43	1.48496	164.2	50	25
13	482	5.6	45.5	.895	26.6	48	1.49389	-	73	50
14	527	3.8	49.3	.905	24.9	49			115	60
Residuum		48.9	98.2	.972	14.1					

Carbon residue, Conradson: Residuum, 9.2 percent; crude, 4.9 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	3.2	0.704	69.5	
Total gasoline and naphtha	17.7	0.757	55.5	
Kerosine distillate	4.0	.814	42.3	
Gas oil	15.8	.852	34.6	
Nonviscous lubricating distillate	8.2	.877-.901	29.8-25.5	50-100
Medium lubricating distillate	3.6	.901-.909	25.5-24.2	100-200
Viscous lubricating distillate				Above 200
Residuum	48.9	.972	14.1	
Distillation loss	1.8			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines ... Bartlesville Laboratory
 Sample ... 62066

IDENTIFICATION

Hastings, East field
 Frio, Oligocene
 6,020-6,050 feet

Texas
 Brazoria County

GENERAL CHARACTERISTICS

Gravity, specific, 0.871	Gravity, ° API, 31.0	Pour point, ° F, below 5
Sulfur, percent, 0.15	Color, greenish black	Nitrogen, percent, 0.02
Viscosity, Saybolt Universal at 77° F., 62 sec.	100° F., 55 sec.	

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 743 mm. Hg
 First drop, 145 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr., 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1.....	122									
2.....	167	1.1	1.1	0.748	57.7	-	1.40061	126.1		
3.....	212	1.8	2.9	.753	56.4	37	1.40946	129.6		
4.....	257	1.7	4.6	.757	55.4	30	1.41686	131.3		
5.....	302	2.7	7.3	.770	52.3	28	1.42613	139.7		
6.....	347	3.4	10.7	.789	47.8	31	1.43860	142.8		
7.....	392	5.1	15.8	.813	42.6	36	1.45011	147.6		
8.....	437	5.9	21.7	.829	39.2	38	1.45805	149.8		
9.....	482	9.8	31.5	.846	35.8	41	1.46806	153.5		
10.....	527	10.7	42.2	.860	33.0	42	1.47690	158.6		

STAGE 2—Distillation continued at 40 mm. Hg

11.....	392	4.4	46.6	0.871	31.0	44	1.48289	158.7	42	Below 5
12.....	437	8.7	55.3	.880	29.3	44	1.48436	156.3	49	do.
13.....	482	6.7	62.0	.891	27.3	46	1.48938	155.1	68	do.
14.....	527	5.9	67.9	.904	25.0	49	1.49414	153.0	110	do.
15.....	572	6.6	74.5	.910	24.0	49			225	10
Residuum.....		23.0	97.5	.942	18.7					

Carbon residue, Conradson: Residuum, 4.3 percent; crude, 1.1 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	2.9	0.751	56.9	
Total gasoline and naphtha	15.8	0.783	49.2	
Kerosine distillate	-	-	-	
Gas oil	35.6	.855	34.0	
Nonviscous lubricating distillate	12.1	.880-.901	29.3-25.6	50-100
Medium lubricating distillate	6.4	.901-.908	25.6-24.3	100-200
Viscous lubricating distillate	4.6	.908-.913	24.3-23.5	Above 200
Residuum	23.0	.942	18.7	
Distillation loss	2.5			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Bartlesville Laboratory
Sample 51051

IDENTIFICATION

Cedar Lake Field
San Andres, Permian
4,580-4,765 feet

Texas
Gaines County

GENERAL CHARACTERISTICS

Gravity, specific, .0.863 Gravity, ° API, 32.5 Pour point, ° F., below 5
Sulfur, percent, 2.12 Color, greenish black
Viscosity, Saybolt Universal at 100° F., 45 sec. Nitrogen, percent, 0.09

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

STAGE 1—Distillation at atmospheric pressure, 746 mm. Hg
First drop, 88 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum, percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n_d^{20} at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1	122	1.8	1.8	0.656	84.2	20	1.39023	.139.5		
2	167	6.4	8.2	.697	71.5	—	—	—		
3	212	3.1	11.3	.740	69.5	31	1.42215	.146.8		
4	257	4.7	16.0	.761	54.4	32	1.43240	.150.7		
5	302	6.4	22.4	.777	50.6	32	1.43892	.147.8		
6	347	4.6	27.0	.790	47.6	31	1.44401	.145.3		
7	392	4.8	31.8	.801	45.2	30	1.45084	.145.9		
8	437	4.3	36.1	.815	42.1	31	1.46039	.151.1		
9	482	5.4	41.5	.831	38.8	33	1.47221	.162.4		
10	527	6.8	48.3	.849	35.2	37				

STAGE 2—Distillation continued at 40 mm. Hg

11	392	1.4	49.7	0.862	32.7	39			40	15
12	437	5.7	55.4	.873	30.6	41			44	30
13	482	5.6	61.0	.889	27.7	45			56	50
14	527	5.3	66.3	.899	25.9	47			82	.65
15	572	5.5	71.8	.916	23.0	55			150	85
Residuum.		27.0	98.8	.987	11.9					

Carbon residue, Conradson: Residuum, 10.7 percent; crude, 3.3 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline	11.3	0.702	70.1	
Total gasoline and naphtha	31.8	0.754	56.2	
Kerosine distillate	4.3	.815	42.1	
Gas oil	19.5	.852	34.6	
Nonviscous lubricating distillate	9.5	.881-.903	29.1-25.2	50-100
Medium lubricating distillate	6.7	.903-.925	25.2-21.9	100-200
Viscous lubricating distillate	—	—	—	Above 200
Residuum	27.0	.987	11.9	
Distillation loss	1.2			

CRUDE PETROLEUM ANALYSIS

Bureau of Mines Marionville Laboratory
 Sample 56112

IDENTIFICATION

Corsicana field
Wolf City, Upper Cretaceous
1,088-1,116 feet

Texas
Navarro County

GENERAL CHARACTERISTICS

Gravity, specific, .0.834.....	Gravity, ° API, 38.2.....	Pour point, ° F.,below 5.....
Sulfur, percent, .0.24.....	Color, brownish green.....	Nitrogen, percent, .0.000.....
Viscosity, Saybolt Universal at 100°F., 43. sec.....		

DISTILLATION, BUREAU OF MINES ROUTINE METHOD

Stage 1—Distillation at atmospheric pressure, 751 mm. Hg
 First drop, 106 ° F.

Fraction No.	Cut temp. ° F.	Percent	Sum. percent	Sp. gr. 60/60° F.	° API, 60° F.	C. I.	Refractive index, n _D at 20° C.	Specific dispersion	S. U. visc., 100° F.	Cloud test, ° F.
1.....	122									
2.....	167	1.7	1.7	0.666	81.0					
3.....	212	3.2	4.9	.701	70.4	12	1.38738	.127.2		
4.....	257	6.2	11.1	.724	63.9	14	1.40466	.128.3		
5.....	302	5.9	17.0	.742	59.2	15	1.41441	.122.9		
6.....	347	7.6	24.6	.762	54.2	18	1.42379	.132.2		
7.....	392	6.8	31.4	.778	50.4	19	1.43298	.128.6		
8.....	437	5.7	37.1	.795	46.5	22	1.44101	.125.8		
9.....	482	7.1	44.2	.809	43.4	23	1.44869	.130.9		
10.....	527	7.4	51.6	.826	39.8	26	1.45727	.134.7		

Stage 2—Distillation continued at 40 mm. Hg

11.....	392	4.5	56.1	0.844	36.2	31	1.46666	.136.0	41	10
12.....	437	6.2	62.3	.854	34.2	32	1.47119	.139.4	47	25
13.....	482	5.1	67.4	.866	31.9	34	1.47746	.141.3	59	45
14.....	527	4.8	72.2	.884	28.6	40	1.48359	.147.2	84	60
15.....	572	5.5	77.7	.894	26.8	41	1.49112	.142.5	155	75
Residuum.....		21.6	99.3	.951	17.2					

Carbon residue, Conradson: Residuum, .8.3. percent; crude, .2.0. percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	° API	Viscosity
Light gasoline.....	4.9	0.689	73.9	
Total gasoline and naphtha.....	31.4	0.743	58.9	
Kerosine distillate.....	12.8	.803	44.7	
Gas oil.....	16.5	.839	37.2	
Nonviscous lubricating distillate.....	10.3	.857-.886	33.6-28.2	50-100
Medium lubricating distillate.....	6.7	.886-.889	28.2-25.9	100-200
Viscous lubricating distillate.....	-	-	-	Above 200
Residuum.....	21.6	.951	17.3	
Distillation loss.....	.7			

Appendix D

Economic Evaluation Example Problem

UNDERSTANDING “TRUE RATE OF RETURN”

The continuous inflation of our economy and escalation of prices makes imperative the consideration of the “time-value” of money when evaluating new investments. The easily understood simple payout and simple percent return, which were the yardsticks of engineers and management 10 to 15 years ago, have been replaced with new evaluation techniques which account for the time-value of money.

These widely used procedures have many sophisticated names and definitions. All too frequently, the managerial and technical people who use these tools do not clearly understand the actual physical significance of the terms.

A brief review of these definitions, explained with a numerical example, is the best method of providing a clear understanding of the “true rate of return” (TRR). The terms listed below are all synonymous with true rate of return.

- Average annual rate of return (AARR)
- Internal rate of return (IRR)
- Interest rate of return (IRR)
- Discounted cash flow rate of return (DCFRR)
- Investors method rate of return (IMRR)
- Profitability index (PI)

A common definition of the terms listed above is: “The true rate of return is the [highest, constant] percentage of the outstanding investment which can be realized as a profit [or saving] each year [for the life of the facility] and at the same time provide funds [from the operating income] that will exactly amortize [recover] the investment over the useful life of the facility.” This definition is easier to understand if the bracketed words are omitted.

This rate can be calculated for the case of a single lump investment and constant annual cash flow by the following equation:

$$i = \frac{S}{I} - \frac{i}{(1 + i)^T - 1} \quad (1)$$

where

i = annual rate of return (as a fraction)

S = annual cash flow (net after-tax income plus depreciation)

I = investment

T = life of facility (years)

An example will provide tangible significance of the above definition.

Example

Initial (and only) investment (I): \$1,000,000

Useful life of facility (T): 3 years

Annual cash flow (S): \$500,000 (after-tax income plus depreciation allowed for tax calculation)

Calculate i by solution of the equation, given $S/I = 0.5$ and $T = 3$:

$$i = 0.5 - \frac{i}{(1 + i)^3 - 1} = 0.234 \quad (2)$$

Year	Amt. outstanding on investment	Cash flow	Profit realized (23.4% × A)	Cash flow used to amortize investment		Remaining investment (A - D)
				(B - C)	E	
	A	B	C	D		
1	\$1,000,000	\$500,000	\$234,000	\$266,000	\$734,000	
2	734,000	500,000	172,000	328,000	406,000	
3	406,000	500,000	94,000	406,000	—	
Total		\$1,500,000	\$500,000	\$1,000,000		

From the above example, it can be seen that the total cash flow minus the total profit, taken at a constant percentage (23.4) of outstanding investment, is equal to a total cash allowance which will exactly recover the investment over the project life.

$$\Sigma B - \Sigma C = \Sigma D = \text{investment} \quad (3)$$

The above statement simply says that over the life of the project, the total of the annual net income minus the investment is equal to the total profit. The value of this obvious statement is that it makes the bankers' and accountants' definition of TRR, AARR, IRR, DCFRR, IMRR, and PI understandable. This definition is: "The TRR is the particular interest rate that equates the total present value cash investments to the total present values cash flow incomes."

This definition leads to the more common way of determining the TRR. Our previous example can be solved by determining the discount rate at which total cash flows for three years will equal the investment.

Year	Cash flow	Discounted factor (23.4%)	Discounted cash flow
1	\$500,000	1/1.234	\$406,000
2	500,000	1/(1.234) ²	328,000
3	500,000	1/(1.234) ³	266,000
Total			\$1,000,000

A third approach defines the TRR as: "The interest rate required for an annuity fund started with the same sum of capital to make the same payments at the same time as the proposed investment." Illustrating this definition with our example, we have the following values:

Year	Principal + interest	Less payments	Balance investment
1	1,000,000 × 1.234 = 1,234,000	500,000	734,000
2	734,000 × 1.234 = 906,000	500,000	406,000
3	406,000 × 1.234 = 500,000	500,000	—

The above procedure is suitable for evaluation of projects which have varying cash flows and distributed investments.

The examples are based on periodic interest rates and the assumption that the annual cash flow all occurs at the end of the year. For most evaluations, these conditions are sufficiently accurate. A review of alternative procedures to allow for continuous interest and continuous cash flow has been given by Souders [3].

For those cases where cash flow is constant and the investment is all made at the start of the project, a simple graphical solution for the TRR is possible [2].

A recent article by Reul [1] reviews the relative merits of the several types of investment evaluation techniques. As very clearly illustrated, there is really no acceptable alternative to the true rate of return for comparing the economic performance of various investments.

NOTES

1. R. Reul, Chem. Eng. 22 Apr., p. 212 (1968).
2. R. Salmon, Chem. Eng. 1 Apr., p. 79 (1963).
3. M. Souders, Chem. Eng. Progr. 62(3), 79 (1966).

Appendix E

Photographs

- Photo 1 Overall refinery view.
- Photo 2 Crude oil distillation unit. Left: atmospheric distillation tower; right: vacuum distillation tower.
- Photo 3 Delayed coking unit.
- Photo 4 2000-BPD platformer. (Photo courtesy of UOP LLC.)
- Photo 5 Powerformer catalytic reforming unit.
- Photo 6 UOP LLC CCR catalytic reforming unit. (Photo courtesy of UOP LLC.)
- Photo 7 20,000-BPD fluid catalytic cracking unit. (Photo courtesy of UOP LLC.)
- Photo 8 Exxon Flexicracking IIIR fluid catalytic cracking unit. (Photo courtesy of Exxon Research and Engineering Company.)
- Photo 9 Fluid catalytic cracker. (Photo courtesy of Fluor Engineers and Constructors, Inc.)
- Photo 10 12,000-BPD TCC unit. (Photo by Ray Manley, courtesy of the Stearns Roger Corp.)
- Photo 11 24,000-BPD H-Oil unit. (Photo courtesy of Fluor Engineers and Constructors, Inc.)
- Photo 12 10,000-BPD hydrofluoric acid alkylation unit. (Photo by Ray Manley, courtesy of the Stearns Roger Corp.)
- Photo 13 Sulfuric acid alkylation unit.
- Photo 14 Strateco sulfuric acid alkylation unit. (Photo courtesy of Stratco, Inc.)
- Photo 15 Light ends distillation units.

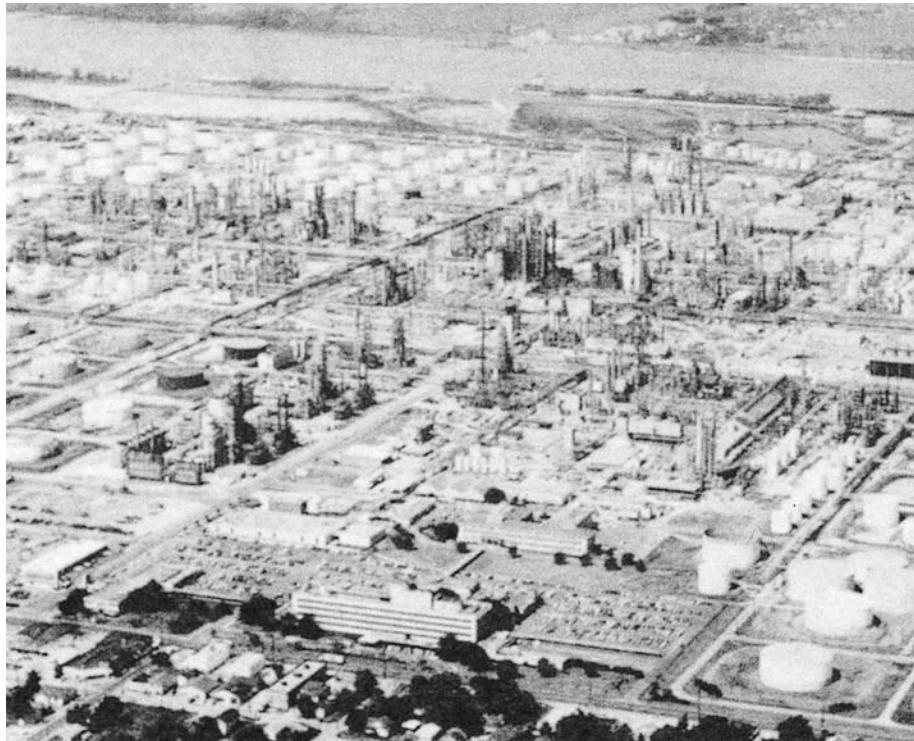


Photo 1 Overall refinery view.

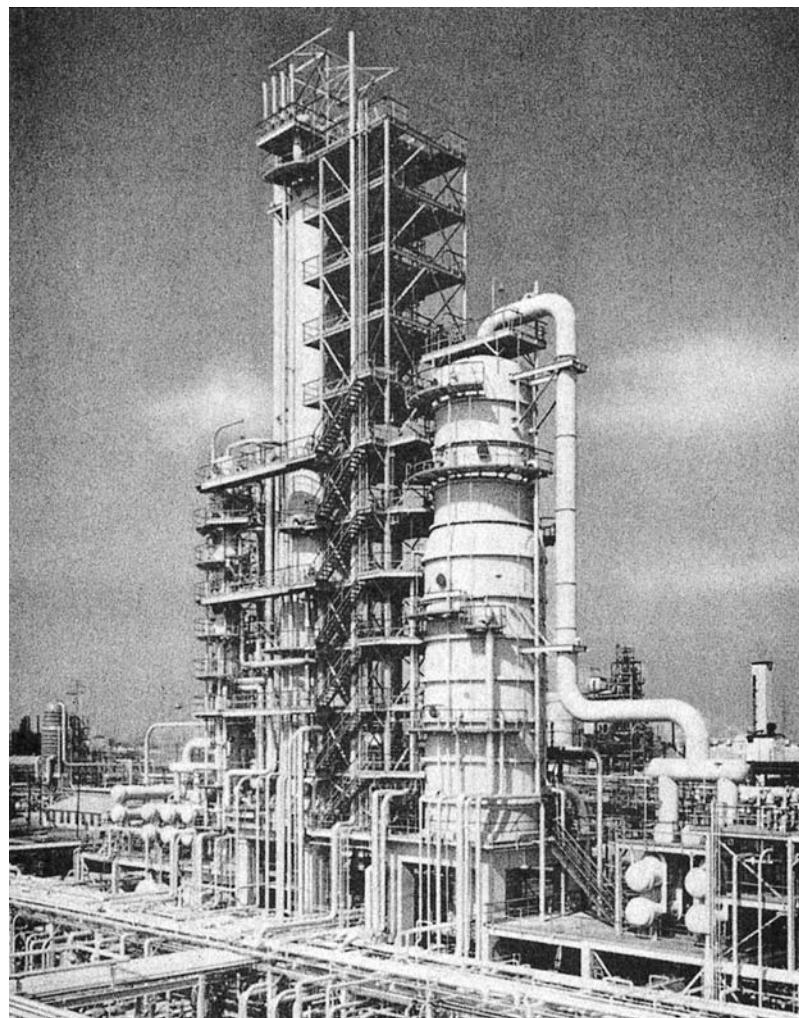


Photo 2 Crude oil distillation unit. Left: atmospheric distillation tower; right: vacuum distillation tower.

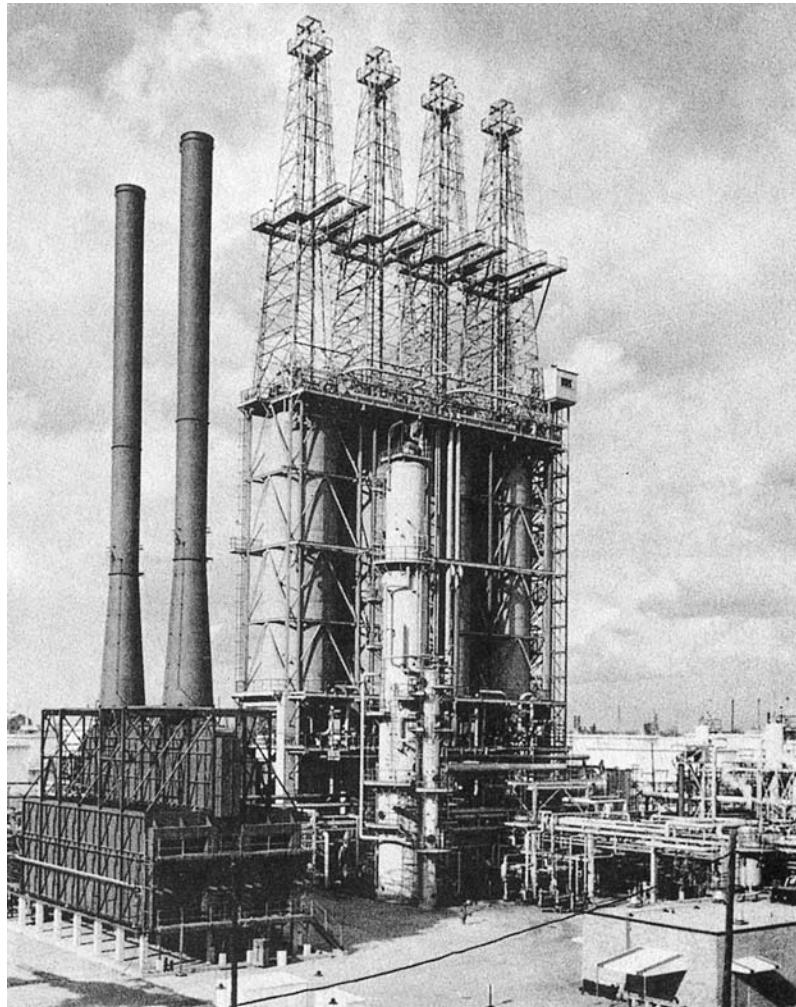


Photo 3 Delayed coking unit.

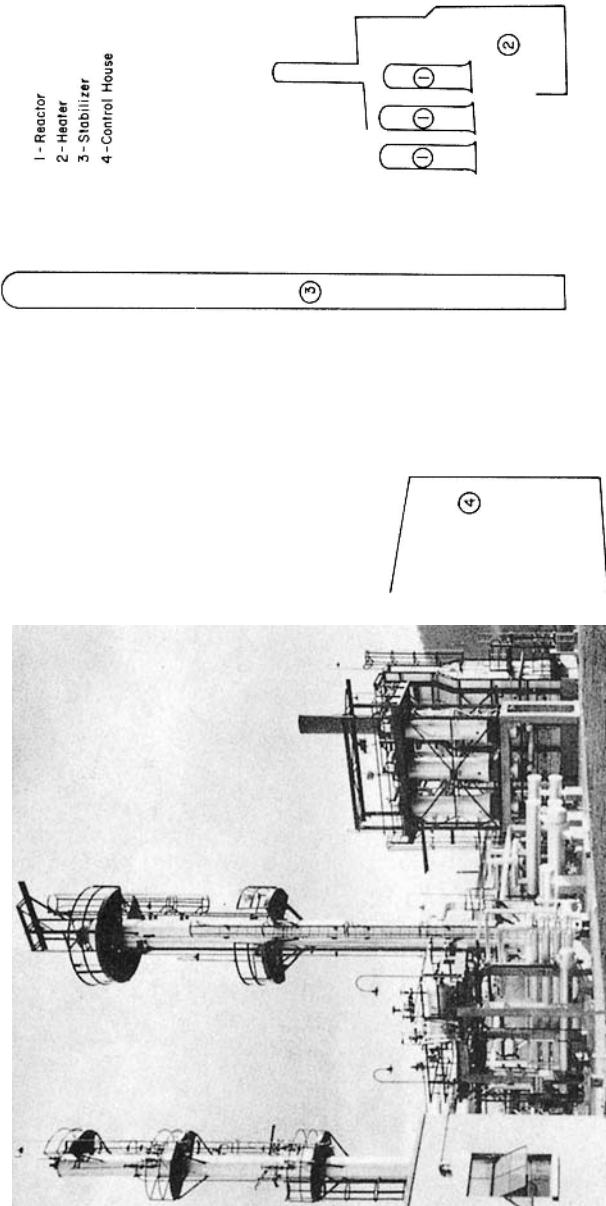


Photo 4 2,000-BPD platermer. (Photo courtesy of the UOP LLC.)

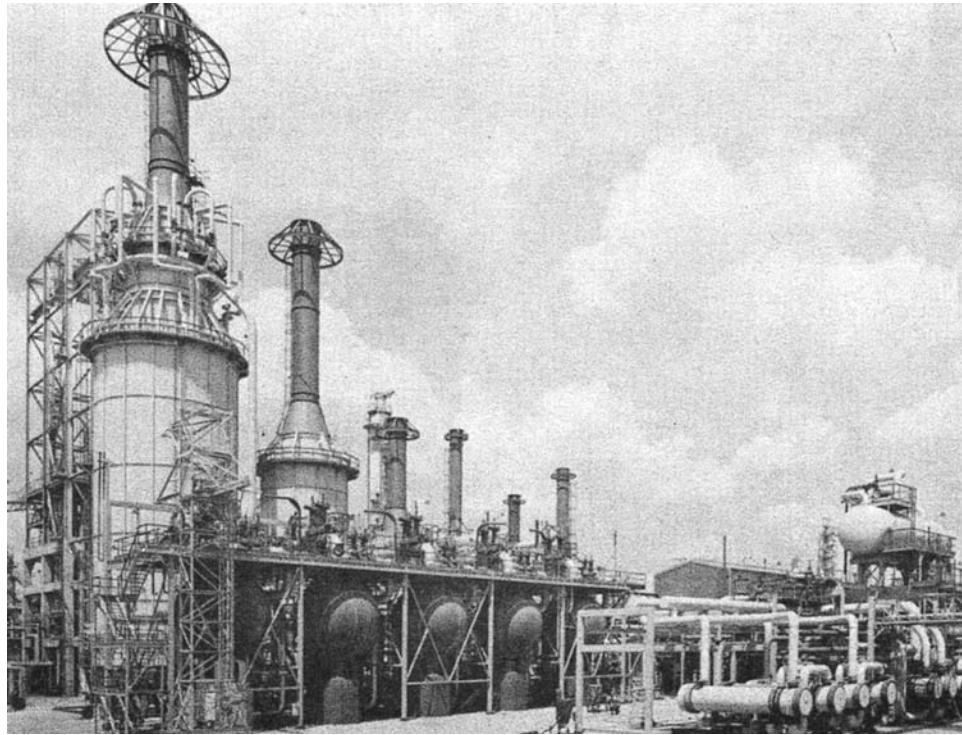


Photo 5 Powerformer catalytic reforming unit.

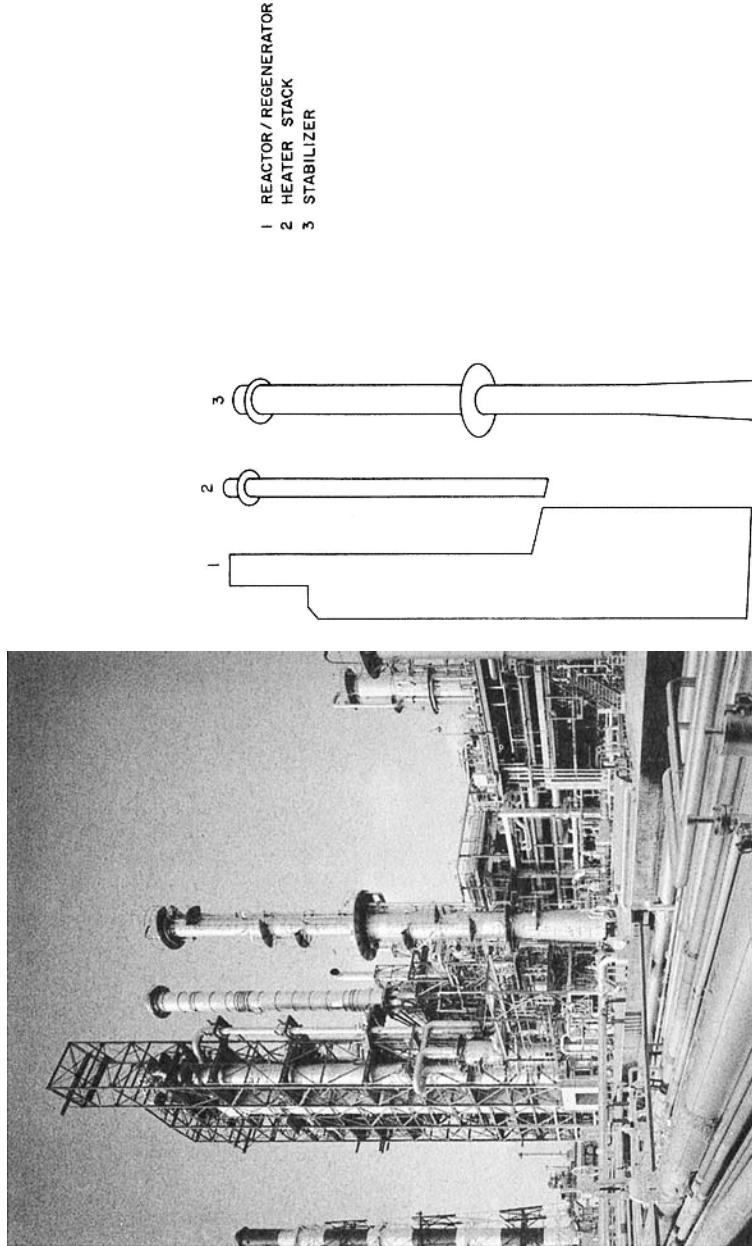


Photo 6 UOP LLC CCR catalytic reforming unit. (Photo courtesy of UOP LLC.)

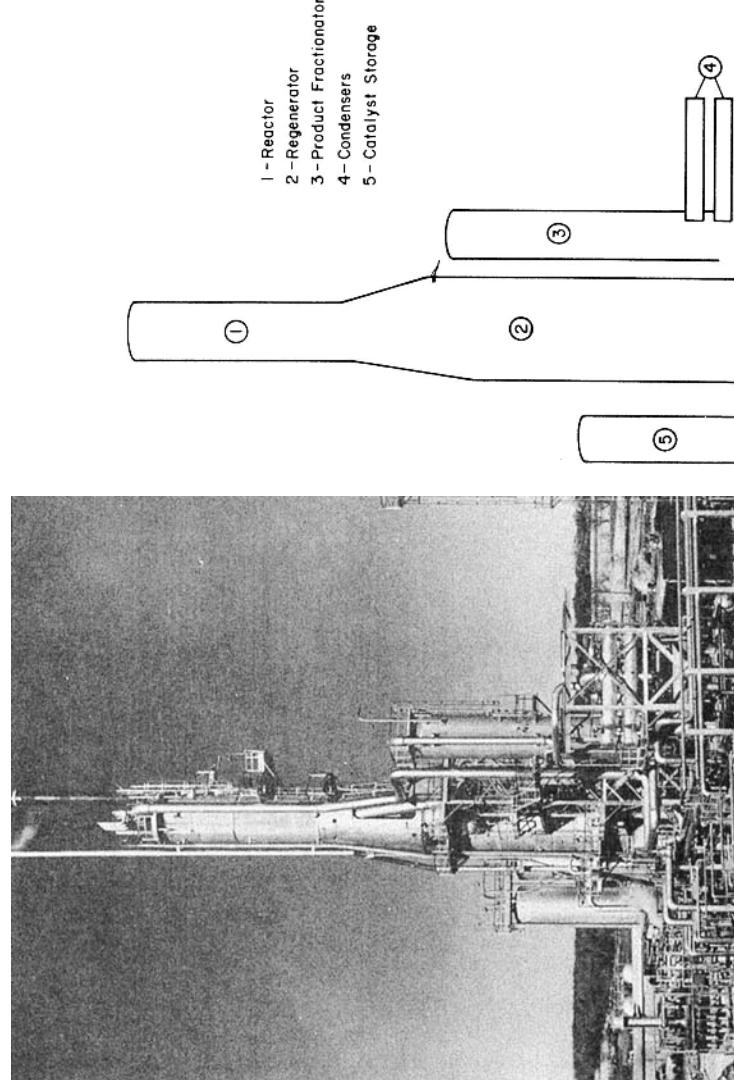


Photo 7 20,000-BPD fluid catalytic cracking unit. (Photo courtesy of UOP LLC.)

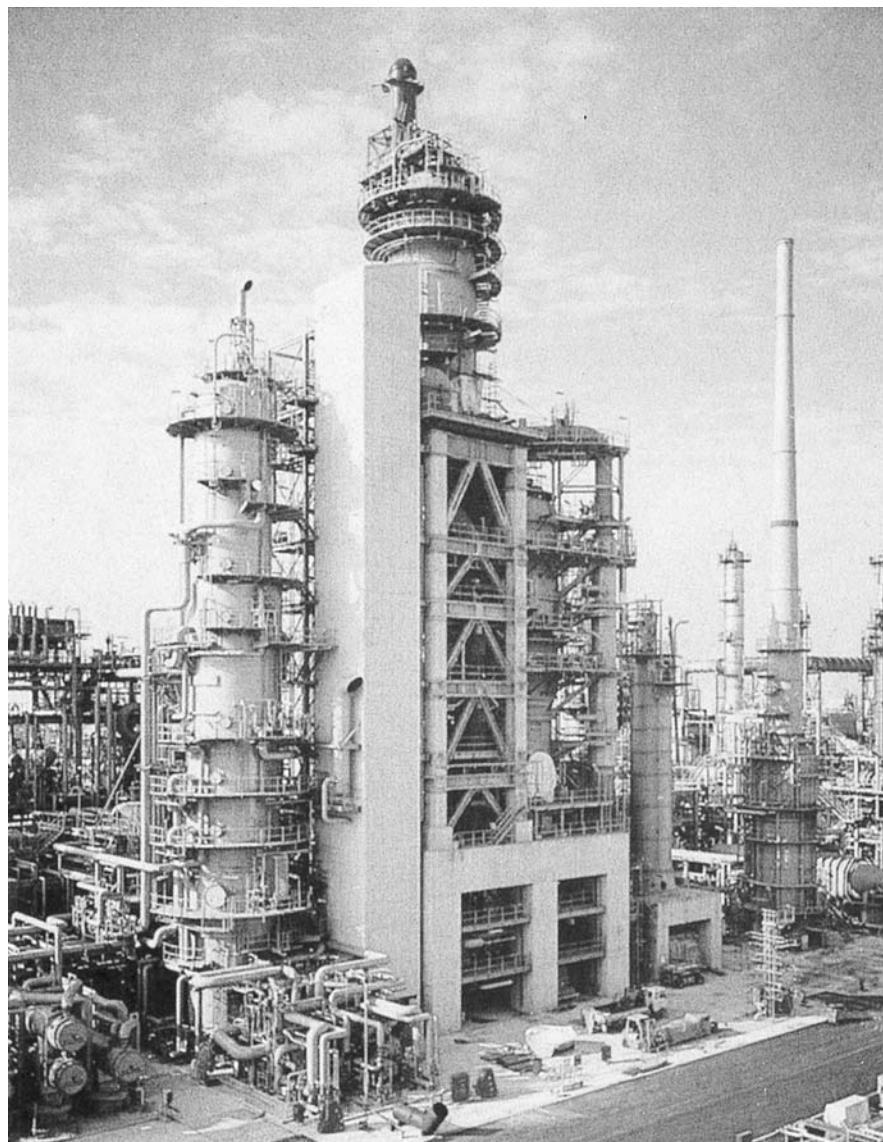


Photo 8 Exxon Flexicracking IIIR fluid catalytic cracking unit. (Photo courtesy of Exxon Research and Engineering Company.)

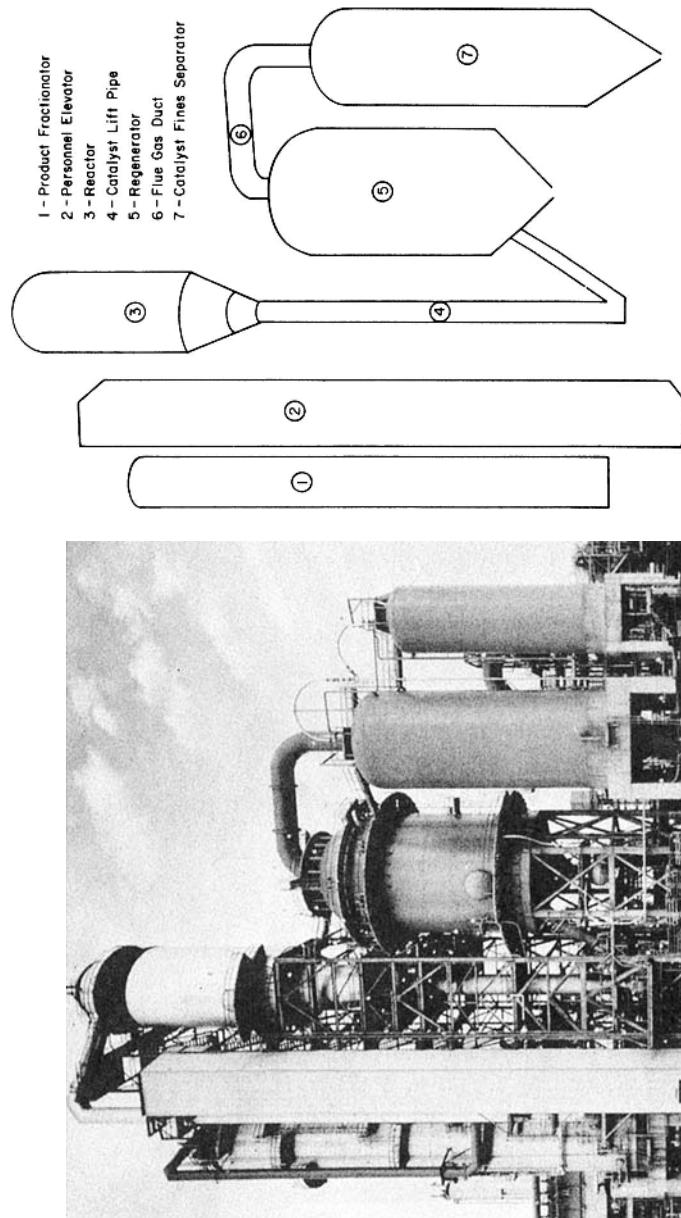


Photo 9 Fluid catalytic cracker. (Photo courtesy of Fluor Engineers and Constructors, Inc.)

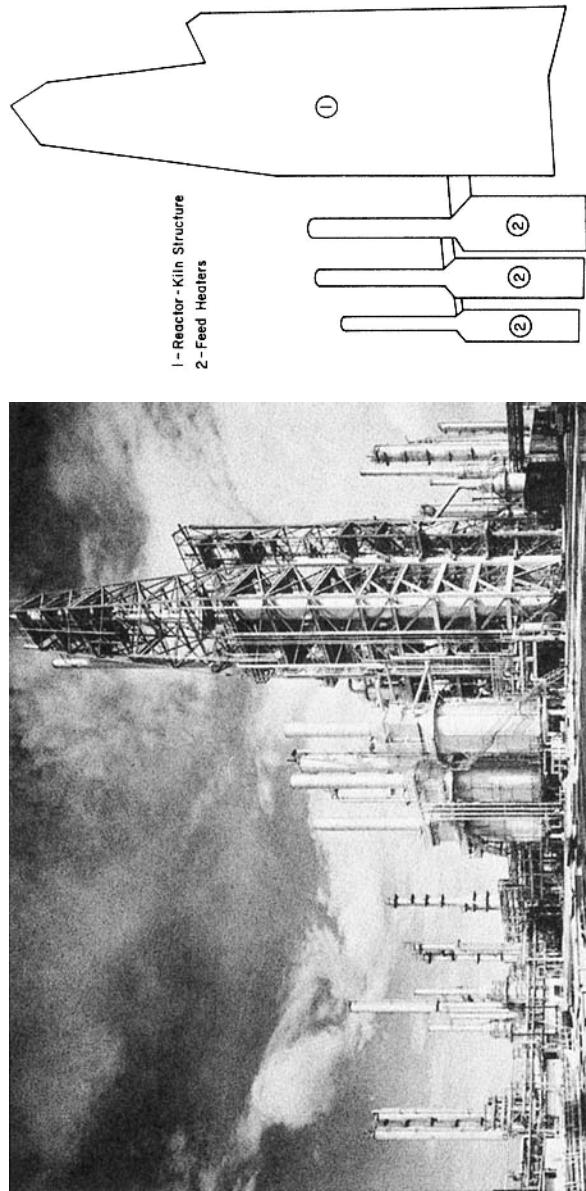


Photo 10 12,000-BPD TCC unit. (Photo by Ray Manley, courtesy of the Stearns Roger Corp.)



Photo 11 24,000-BPD H-Oil unit. (Photo courtesy of Fluor Engineers and Constructors, Inc.)

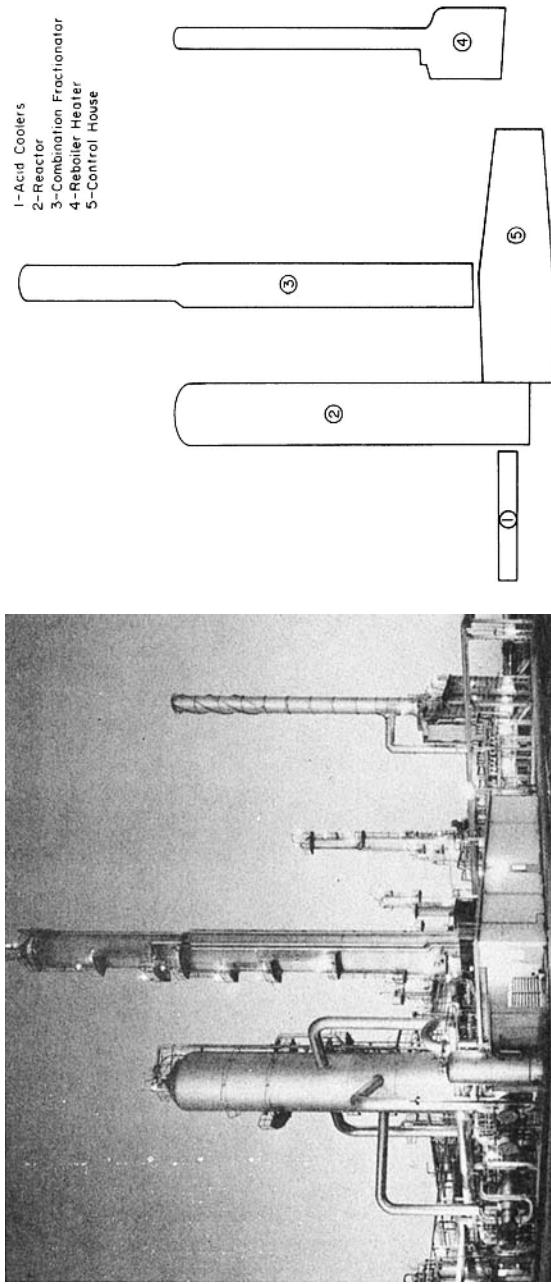


Photo 12 10,000-BPD hydrofluoric acid alkylation unit. (Photo by Ray Manley, courtesy of the Steams Roger Corp.)

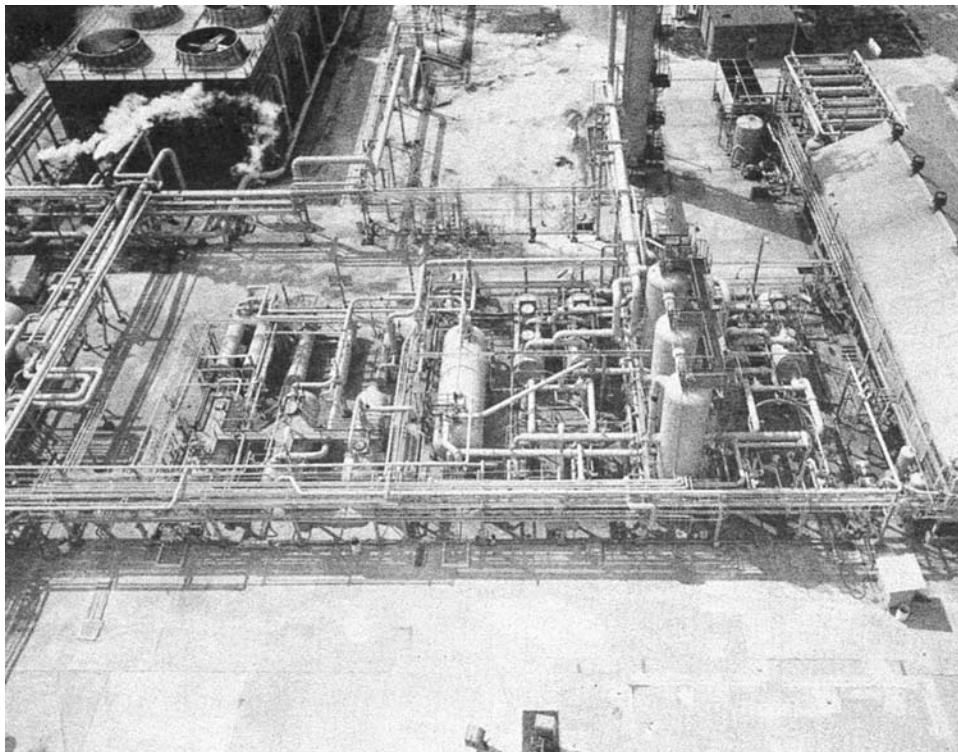


Photo 13 Sulfuric acid alkylation unit.

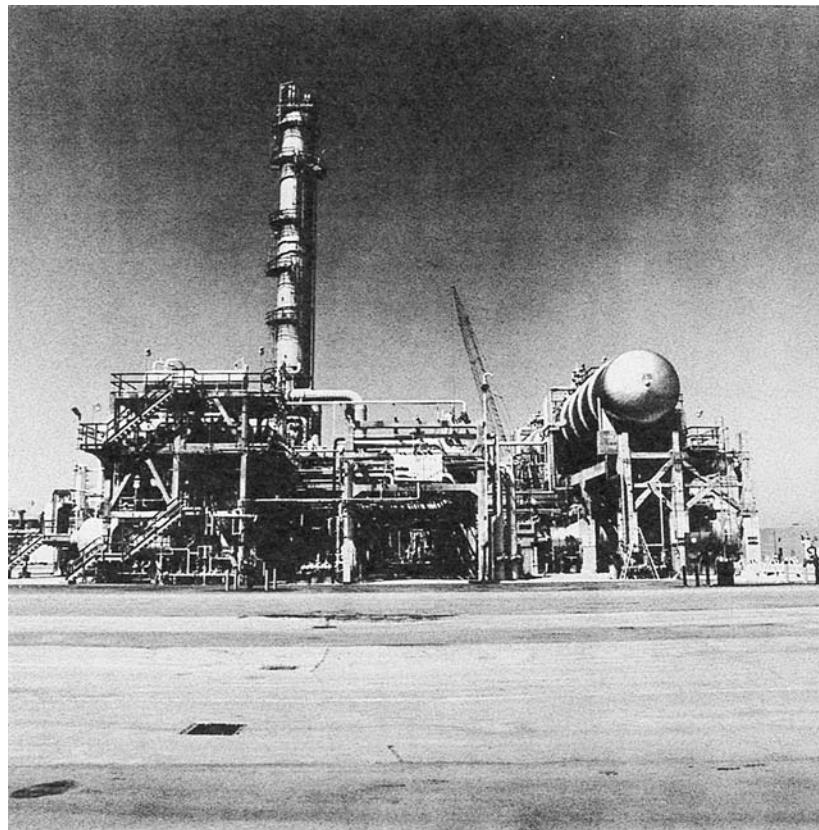


Photo 14 Stratco sulfuric acid alkylation unit. (Photo courtesy of Stratco, Inc.)

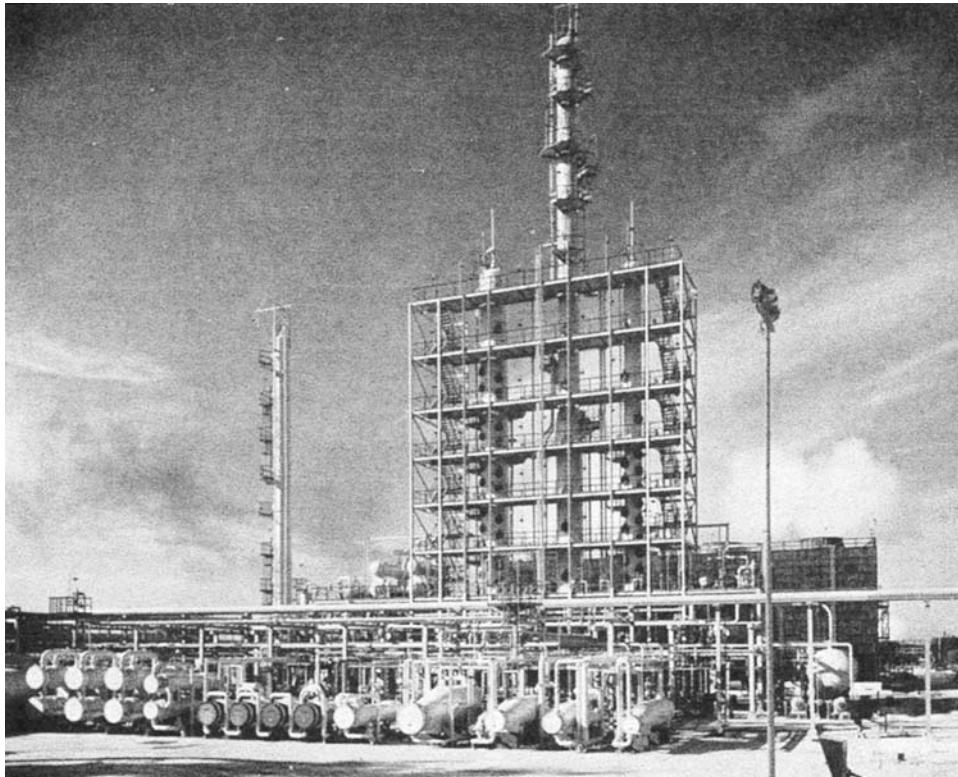


Photo 15 Light ends distillation units.

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