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Petroleum and Its Products

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THE NATURE OF PETROLEUM

Petroleum is a diverse mixture of hydrocarbons—chemical combinations of primarily hydrogen and carbon. Complete combustion of hydrocarbons yields the end products of carbon dioxide (CO_2) and water (H_2O). However, incomplete combustion results in a composite mixture of other products such as CO_2, H_2O, carbon monoxide (CO), and various oxygenated hydrocarbons. Since burning petroleum consumes air, nitrogen compounds are also formed. In addition, other elements are associated with hydrocarbon compounds such as sulfur, nickel, and vanadium.

Petroleum is found at great depths underground or below seabeds. It can exist as a gas, liquid, solid, or a combination of these three states, which is very common. Drilling efforts are used to reach and extract gaseous and liquid deposits. These products are brought to the surface via piping. Once found in a reservoir, gas usually flows under its own pressure. Conversely, discovered liquid hydrocarbons may flow on their own due to pressure from the reservoir or may be forced to the surface by submerged pumps. Also injection of fluids and gases provides a driving force to push liquid hydrocarbon through rock strata. Solid or semisolid petroleum is brought to the surface though several methods: by digging with conventional mining techniques, by gasifying or liquefying with high-temperature steam, or by burning a portion of the material in the ground so that the remainder can flow to the surface.

Hydrocarbon Forms

As mentioned earlier, petroleum is any product that is primarily composed of hydrogen and carbon bonded compounds. These compounds can be further categorized by their characteristics.

Natural gas is the gaseous form of petroleum. It is mostly the single-carbon molecule—methane (CH_4). When natural gas is associated with liquid petroleum underground, the methane will come to the surface in admixture with some heavier hydrocarbons. The gas is considered a wet gas; the heavier hydrocarbons

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are isolated and purified in natural-gas processing plants. Gas processing yields ethane (an important petrochemical feedstock), propane [liquefied petroleum gas (LPG)], butane (refinery blending stock), and hydrocarbon liquids (natural gas condensate). When the underground natural gas is associated with solid hydrocarbons such as tar or coal, the methane will have few other hydrocarbons and is considered a dry gas.

Crude oil is the common name for liquid petroleum. In some literature, one will see reference to "petroleum and natural gas," suggesting petroleum and crude oil are used as synonymous terms. Some crude oils have such great density that they are referred to as heavy oils and tars.

Tar sands are small particles of sandstone surrounded by an organic material called bitumen. The bitumen is a highly viscous hydrocarbon that clings tenaciously to the sandstone; thus, it is easy to think of the mixture as a solid form of petroleum. Yet, it is a mixture of high-density liquid on a supporting solid.

Oil sands are true petroleum solids. Curiously, oil sands do not contain petroleum crude oil; it is an organic material called kerogen. The kerogen can be heated to yield a liquid called shale oil, which can be refined into conventional petroleum products.

Largest Energy Supplier

In Chapter 19 the point is made that coal offers an abundant primary energy source. Yet, present and proposed environmental legislation deters future coal usage. Due to stringent stack-emission restrictions for power generation, utilities are seeking "cleaner fuel" options to replace coal. Utility companies view natural gas as the "cleaner fuel" option. Petroleum feedstocks contain sulfur, which is strictly regulated on emission permits. Natural gas usage is growing within the power/utility industry. Yet, petroleum remains the major fuel source used in transportation, manufacturing, and home heating.

Primary energy sources are defined as those sourced to natural raw materials. Electricity is not included because it is a secondary energy source; it is generated by consuming one or more of the other natural energy sources. To put petroleum consumption into perspective, the primary energy sources considered here are: petroleum crude oil, natural gas, coal, hydropower (water to generate electricity), and nuclear energy. The quantities reported here will exclude energy from wood, peat, animal waste, and other sources, despite their importance to some localities.

The common practice is to relate energy units to a common product, in this case, to petroleum liquid. For example, world consumption of crude oil and liquids (condensates) from natural gas in 1999 reached 149.72 Quadrillion (10^{15} BTUs)—Quad. If the amount of energy from other sources were converted to equivalent barrels of oil, the total world energy consumption in 1999 would be 380 Quads.[1] The relative distribution of these sources is shown in Fig. 18.1. More energy comes from oil than from any other single source.

Another view to consumption is that the world consumption of crude oil and liquids from natural gas in 2001 reached 76 million barrels per day (MMbpd). North America is the largest energy consumer at 24.1 MMbpd. The Asia–Pacific regional demand is steadily increasing. In 2001, Asia–Pacific comprised 27.2 percent of the world's oil demand, up from 20 percent in 1990.[2] Crude oil's share of primary energy consumption was 39.4 percent in 2001. Thus, petroleum oil and natural gas remain the steadfast energy sources globally, as shown in Fig. 18.1.[2]

From Well to Refinery

Crude oil production for various countries is shown in Fig. 18.2.[2] The Middle Eastern countries produce more oil than they consume; the extra production is gated for export. Conversely, the United States and Western Europe consume much more crude oil than they produce (Fig. 18.3).[2] This condition demonstrates the great importance of worldwide petroleum movements. The difference between production and consumption for any

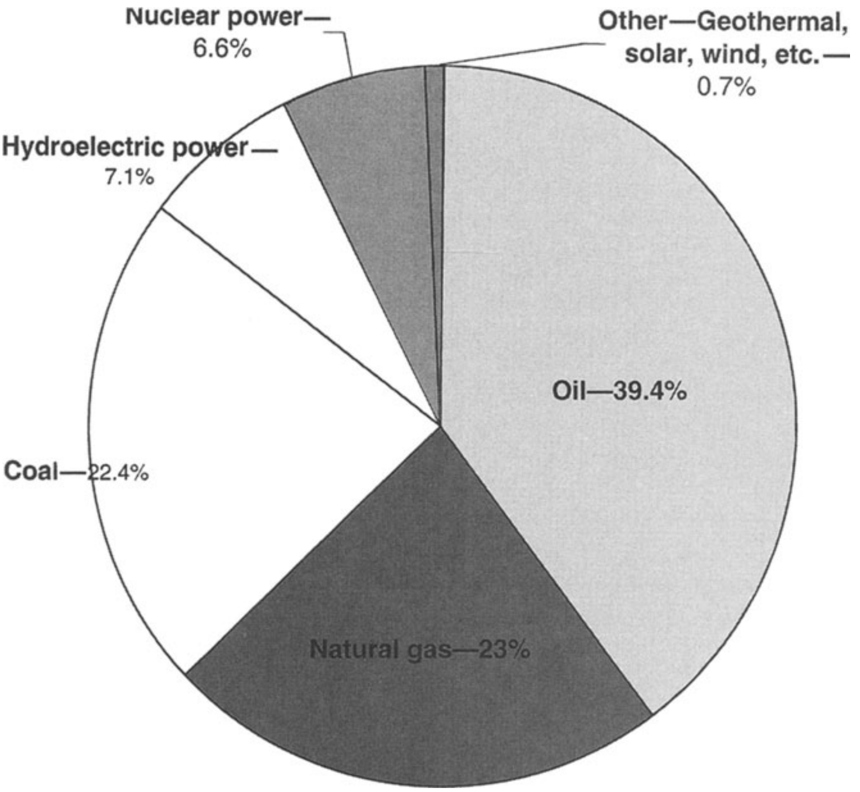


Fig. 18.1. World production of primary energy selected by groups.

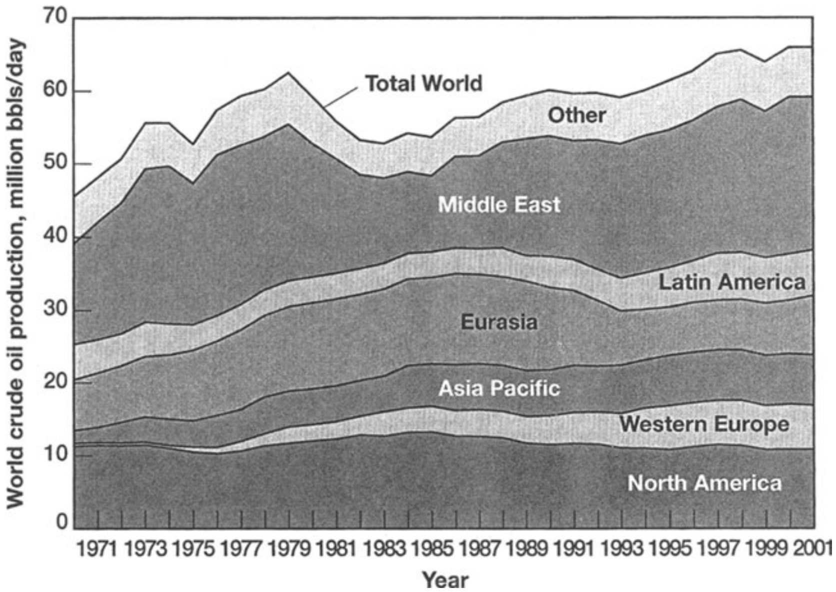


Fig. 18.2. World crude oil production by producing region. (Data from industry sources.)

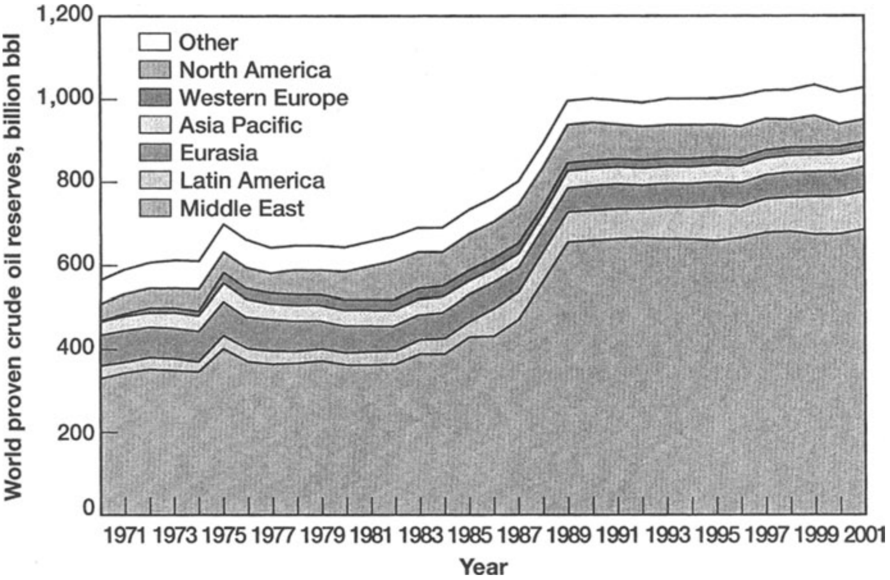


Fig. 18.3. World proven crude oil reserves. (Data from industry sources.)

one period is balanced by oil being added to or removed from extensive areas around the world.

The growth of world refining capacity attempts to keep pace with rising demand for petroleum-based products.[2] Curiously, refining capacity has surged ahead in some regions, notably the Middle East and the Asia–Pacific region, over the last 30 years. However, in developed markets, refinery throughput was almost flat during the 1980s and 1990s. New and larger state-of-the-art refining facilities were more energy efficient and had lower operating costs per barrel of refined products. Consequently, smaller refiners could not compete against new facilities and subsequently had to shut down operations. Another factor in refining growth is the time to construct processing units. In highly industrialized countries such as the United States, Japan, and Western Europe, mounting environmental regulations and stiff emission and performance laws have all but stifled the construction of new grassroots refineries. Construction of new refining capacity must overcome a long list of federal, state, and local governmental requirements. In the United States, the last grassroots refinery was constructed in 1974, before the onslaught of the Clean Air Act of 1970. New governmental regulations are focused on strict reductions on emissions (air, water, and solids) to improve air quality for high-density populated areas and high-density industrial regions. Consequently, construction of new facilities in developed markets is negligible.

In industrialized nations, new refining capacity will be realized by the expansion of existing facilities that are permitted by the local regulatory agencies. Even expanding existing facilities is exempted from environmental constraints. With new construction and capacity expansion, operating companies must cut emissions below present permitted levels. Thus, operating companies must install more intrusive emission reduction/control technologies and equipment to eliminate release from new and existing plant equipment.

Refiners have become particularly adept in using technology to find incremental capacity from existing processing equipment. Thus, the refining industry can process more crude oil with present equipment. In spite of this, the number of refineries is decreasing; yet, capacity increases incrementally.

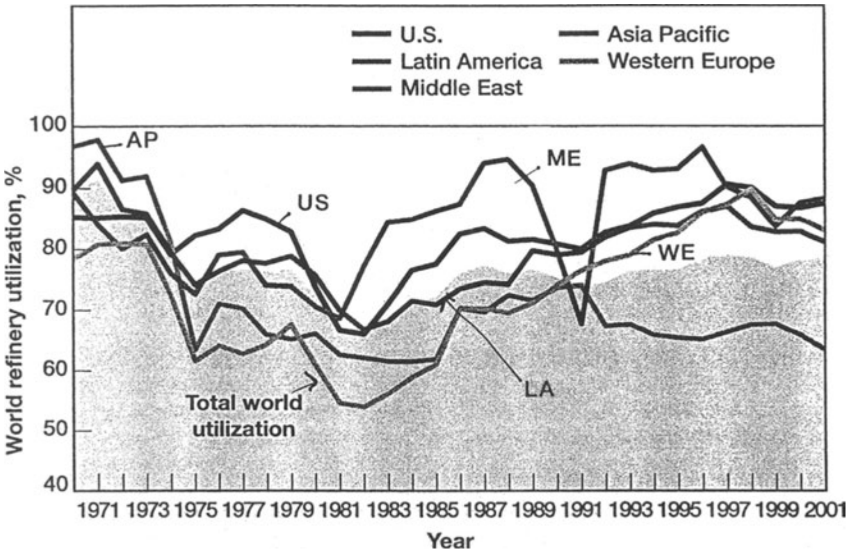


Fig. 18.4. World refinery utilization as percent. (Data from industry sources.)

Advancements and innovations in processing methods and catalyst systems have enabled construction of large, highly integrated, and complex refining complexes. New materials of construction have aided in building larger facilities; thus, smaller, older refineries cannot compete with newer, larger facilities. The number of operating facilities continues to decrease; yet capacity rises. Less efficient facilities shut down their operations since they are handicapped in producing refined products (Fig. 18.4).

In 1984, the number of refineries operating in the United States peaked at 318 facilities with a refining capacity of 18.62 MMbpd.[3] Technological advancements in processing methods and catalytic systems have enabled refiners to increase the capacity of existing units incrementally. Newer processing units are larger than the earlier versions. Refiners are applying economies of scale to disperse the product costs of refineries. Since 1981, the number of United States operating refineries has decreased to 155 in 2000 with a total operating capacity of 16.52 MMbpd, as shown in Fig. 18.5. Notably, smaller and less competitive refineries were shut down. Equally important, the utilization of operating United States refineries rose over this same period, from a low of 68.6 percent to 92.6 percent.[3]

Technology helps refiners to push the boundaries of manufacturing, especially in the average-size refinery. In 1975, the averaged United States refinery had an operating capacity of 60,000 barrels per day (bpd). Innovations in catalyst technology and equipment design enabled the construction of larger vessels and reactors, and the introduction of ancillary equipment to support processing operations. Thus in 2000 the average refining capacity for a United States refinery exceeded 100,000 bpd, nearly double the capacity from 1975. In the United States, refiners have avoided constructing grassroots facilities to meet rising demand for products.

As the wave of environmental regulations continues to be levied against the refining industry, more consolidation is anticipated. More companies will leave segments of fuel manufacturing due to capital investments with diminishing returns?

Distribution of Crude Oil and Refined Products. Crude oil and its refined products are viewed as commodity products; thus, they are easily traded and transported to market. Many methods can be used to deliver crude to

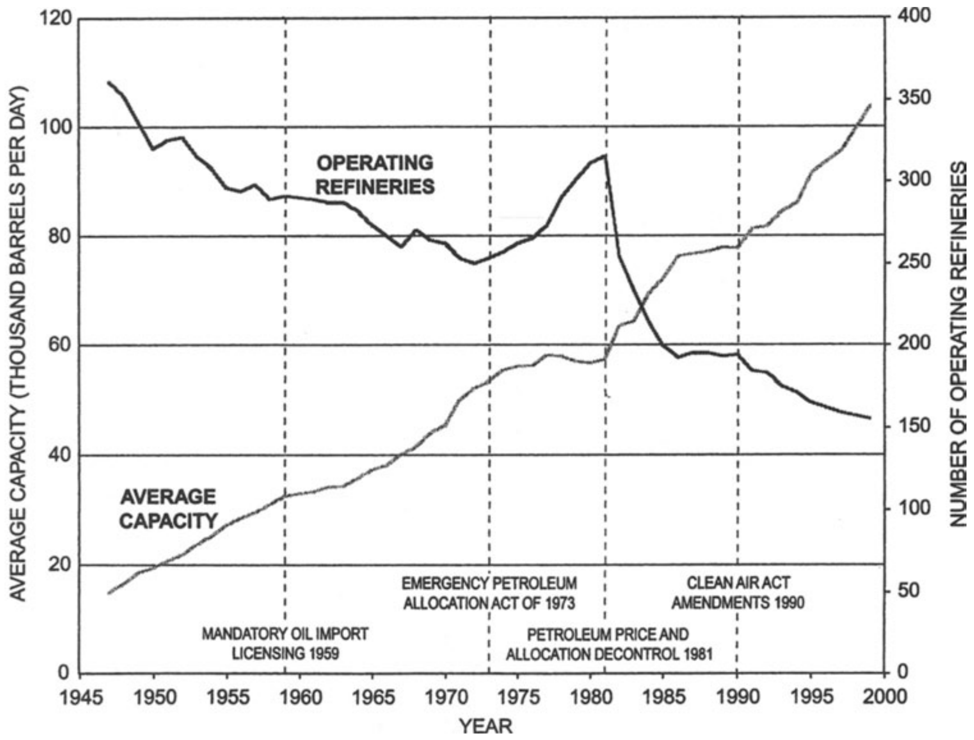


Fig. 18.5. Average capacity and number of U.S. operating refineries. (Data from industry sources.)

oil refineries. For example, United States refinery can receive feedstock crude oil via pipelines, tank trucks, barges, and ocean-going vessels—supertankers. Most refineries are located near port facilities to receive feedstocks from barges and supertankers.

PRODUCT

Refining crude oil involves breaking carbon-to-carbon (C–C) bonds of the complex hydrocarbon compounds and adding hydrogen. Such efforts are done thermally and catalytically. The distinction between refined products and petrochemicals often is subtle. In general, when the product fraction is from crude oil that includes a fairly large group of hydrocarbons, the fraction is classified as a refined product. Examples of refined products are: gasoline, diesel fuel, heating oil, lubricants, waxes, asphalts, and petroleum coke.

By contrast, when the product from crude oil is limited to only one or two specific hydrocarbons of fairly high purity, the fraction is called a petrochemical. Examples of petrochemicals are: ethylene, propylene, benzene, toluene, and styrene. Refined products are defined by the fraction's boiling point and may be composed of various hydrocarbons. Multiple compounds compose refined-product fractions. In contrast, petrochemicals are single-compound fractions, which are required for feedstocks for other petrochemicals and polymers. More processing and separation (distillation, extraction, etc.) operations are used to extract petrochemical products from processing streams. Thus, more identifiable petrochemical products are processed than refined products. Many specific hydrocarbon compounds can be derived from crude oil. However, these hydrocarbons lose their individual identity when they are grouped together as a refined product.

Refined Products

Most refined products at the consumer level are blends of several refinery streams. Product specifications determine which streams are suitable for a specific blend. Part of the difficulty in learning about refining lies in the industry's use of stream names that are different from the names of consumer products.

Refining is considered a "dirty" processing effort. Product separation of refined product streams is not as clean as efforts to process petrochemicals. Refiners have the flexibility to blend final fuel products. Thus, there is no exact recipe used by all refiners to produce consumer products. Multiple crude oils are processed and then blended to meet consumer fuel product specifications. Table 18.1 lists the refining streams that are blended to produce consumer products. The consumer products are familiar. However, within a refinery these products are blended from portions of crude oil fractions from the listed reforming process units. To complicate the situation further, not all refineries are configured identically. Many different processing operations can be used to refine and separate product streams to blend the products listed in Table 18.1.

For example, gasoline at the consumer level may be called benzol or petrol, depending upon the country where it is sold. In the early stages of crude oil processing, most gasoline components are called naphthas. Kerosene is another example. It may be called coal oil to denote that it replaces stove oil (or range oil) once derived from coal. Historically, Kerosene gained significant importance as a replacement for whale oil for lamps. In the early 1900s, refining efforts were directed to supplying Kerosene–lamp oil. However, in the 1920s, a new energy form—electricity—began to displace Kerosene usage. Thus, early refiners sought other products to compensate for this market loss.[4] Today, Kerosene fractions are directed to jet fuel and high-quality No. 1 heating oil.

Product Specifications

Product applications and customer acceptance set detailed specifications for various products properties. In the United States, the American Society for Testing Materials (ASTM) and the American Petroleum Institute (API) are recognized for establishing specifications on both products and methods for testing. Other countries have similar referee organizations. For example, in the United Kingdom, it is the Institute of Petroleum (IP). In Germany, it is the Deutsches Institute suer Normung (DIN). In Japan, it is the Ministry of International Trade and Industry (MITI).

A boiling range is the major distinction among refined products, and many other product properties are related to the products in these boiling ranges. A summary of ASTM

TABLE 18.1 Several Names for the Same Material

Crude Oil Cuts	*Refinery Blends*	*Consumer Products*
Gases	Still gases	Fuel gas
	Propane/Butane	Liquefied petroleum gas (LPG)
Light/heavy naphtha	Motor Fuel	Gasoline
	Aviation turbine, Jet-B	Jet fuel (naphtha type)
Kerosene	Aviation turbine, Jet-A	Jet fuel (kerosene type)
	No. 1 Fuel oil	Kerosene (range oil)
Light gas oil	Diesel	Auto and tractor diesel
	No. 2 fuel oil	Home heating oil
Heavy gas oil	No. 4 fuel oil	Commercial heating oil
	No. 5 fuel oil	Industrial heating oil
	Bright stock	Lubricants
Residuals	No. 6 fuel oil	Bunker C oil
	Heavy residual	Asphalt
	Coke	Coke

specifications for fuel boiling ranges is given in Table 18.2.[5] Boiling range is also used to identify individual refinery streams; in a later section we use the example of crude oil distillation. The temperature that separates one fraction from an adjacent fraction will differ from refinery to refinery. Factors influencing the choice of cut-point temperature include: crude oil feedstocks, type and size of downstream processes, and market demand for products.

Other specifications can involve either physical or chemical properties. Generally, these specifications are stated as minimum or maximum quantities. Once a product qualifies to be in a certain group, it may receive a premium price by virtue of exceeding minimum specifications or by being below maximum specifications. The only advantage of being better than the specifications is an increase in the volume of sales in a competitive market.

TABLE 18.2 Major Petroleum Products and Their Specified Boiling Range[5]

		Specified Temp. for Vol. % Distilled at 1 atm °F		
Product Designation	*ASTM Designation*	*10%*	*50%*	*90%*
Liquefied petroleum gas (LPG)	D 1835			
Commercial propane		—[a]		—[b]
Commercial butane		—[a]		—[c]
Aviation gasoline (Avgas)	D 910	167 max	221 max	275 max[d]
Automotive gasoline	D 439			
Volatility class A		158 max	170–250	374 max[e]
Volatility class B		149 max	170–245	374 max[e]
Volatility class C		140 max	170–240	365 max[e]
Volatility class D		131 max	170–235	365 max[e]
Volatility class E		122 max	170–230	365 max[e]
Aviation turbine fuel	D 1655			
Jet A or A-1		400 max		—[f]
Jet B		—[g]	374 max	473 max
Diesel fuel oil	D 975			
Grade 1-D				550 max
Grade 2-D				540–640
Grade 4-D		—	not specified	—
Gas turbine fuel oil	D 2880			
No. 0-GT		—[h]	not specified	—
No. 1-GT				550 max
No. 2-GT				540–640
No. 3-GT		—	not specified	—
No. 4-GT		—	not specified	—
Fuel oil	D 396			
Grade No. 1		419 max		550 max
Grade No. 2		—[h]		540–640
Grade No. 4		—	not specified	—
Grade No. 5		—	not specified	—
Grade No. 6		—	not specified	—

[a] Vapor pressure specified instead of front end distillation.
[b] 95% point, −37°F max.
[c] 95% point, 36°F max.
[d] Final point, 338°F max.
[e] Final point, all classes, 437°F max.
[f] Final point, 572°F max.
[g] 20% point, 293°F max.
[h] Flash point specified instead of front end distillation.

The evolution of product specifications will, at times, appear sadly behind recent developments in more sophisticated analytical techniques. Certainly, the ultimate specification should be based on how well the product performs. Yet, the industry has grown comfortable with certain comparisons, and these standards are retained for easier comparison with earlier products. Thus, it is not uncommon to find petroleum products sold under an array of tests and specifications, some seemingly measuring similar properties.

It is behind the scenes that sophisticated analytical techniques prove their worth. These techniques can identify the specific hydrocarbons responsible for one property or another. Suitable refining processes are devised to accomplish a desired chemical reaction that will increase production of specific hydrocarbon products.

When discussing refining schemes, major specifications will be identified for each product category. It should be kept in mind that a wide variety of specifications must be met for each product.

Product Yields

As changes occur in product demand and specifications, refiners continuously adjust the configuration of internal processing streams. The challenge remains that increasing the volume of one fraction of crude oil processing will lower volumes of other product fractions. Thus, adjustments of one processing stream, especially major processing units, affect downstream processing streams and end-product volumes.

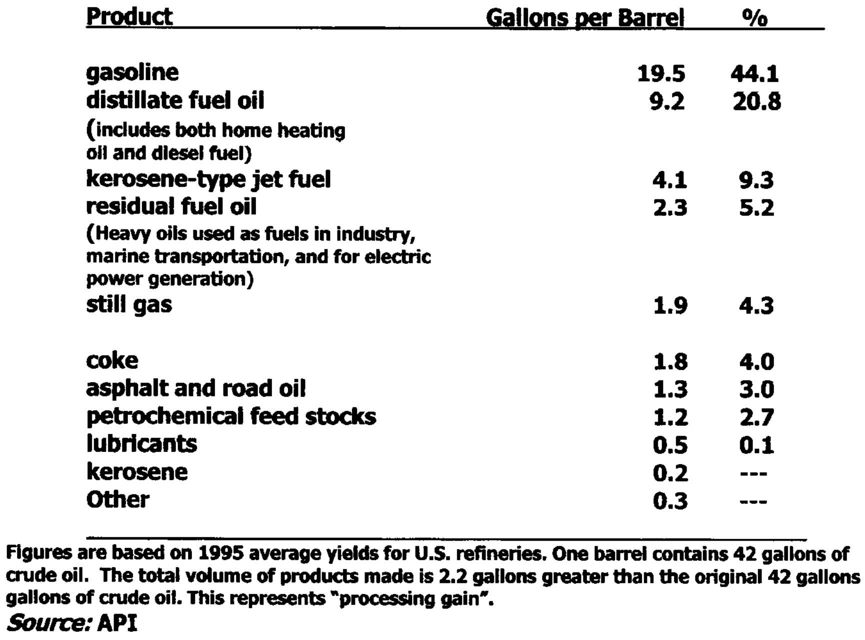
Refined product demand is seasonal. Demand for heating oil is higher during winter than during mid-summer. Equally important, gasoline demand fluctuates from summer highs, known as the driving season, and then declines in fall and winter. Refiners begin ramping up gasoline production over heating oil in early spring to meet anticipated demand and have sufficient gasoline supply in the system for distribution. Refiners try to avoid storing products.

Notably, fuel specifications for industrialized countries mandate blending winter- and summer-grade gasolines. Regions that do not meet air-quality specifications—known as nonattainment areas—are strictly regulated on the sale and distribution of the proper gasoline types. Refiners constantly estimate how much of a particular gasoline type to blend without overprocessing. Linear program (LP) models are extensively used to evaluate how best to use a crude stock to process designated products with the available processing capabilities. LPs are models that refiners can use to predict product yields with the resources available. They are gaining increased importance in assisting refiners in optimizing resources to avoid waste and maximize yields. These models are extensively used to estimate how changes in operating conditions, feeds, and new processing units/equipment will affect facility operations.

A barrel of crude oil has limited value, if any, to consumers. Its true value is the number of value-added products that can be extracted from the crude oil using various chemical reactions and separation methods. Thus, the refining operation is the first step in the transformation of crude petroleum oil into consumer products. So what are the possible products from a barrel of crude oil? Figure 18.6 lists the average breakdown of a barrel of oil by a United States refinery. As shown in Fig. 18.6, over 75 percent of the product yield from a refined barrel of oil is fuel based. In this example, United States refineries are focused on gasoline production, whereas European refineries focus on diesel product. Yet, refineries can also produce value-added petrochemicals for adjacent facilities.

Petrochemicals

The portion of crude oil going to petrochemicals may appear small compared with the volume of fuels yielded by refining operations; however, the variety of petrochemicals is large. Table 18.3 lists the many products derived for petrochemical applications. Many of these products are described in Chapter 10. A few are included here in as much as they compete with the manufacturing of fuels. Despite their variety, all commercially manufactured petrochemicals account for the



Product	**Gallons per Barrel**	**%**
gasoline	**19.5**	**44.1**
distillate fuel oil **(includes both home heating oil and diesel fuel)**	**9.2**	**20.8**
kerosene-type jet fuel	**4.1**	**9.3**
residual fuel oil **(Heavy oils used as fuels in industry, marine transportation, and for electric power generation)**	**2.3**	**5.2**
still gas	**1.9**	**4.3**
coke	**1.8**	**4.0**
asphalt and road oil	**1.3**	**3.0**
petrochemical feed stocks	**1.2**	**2.7**
lubricants	**0.5**	**0.1**
kerosene	**0.2**	**---**
Other	**0.3**	**---**

Figures are based on 1995 average yields for U.S. refineries. One barrel contains 42 gallons of crude oil. The total volume of products made is 2.2 gallons greater than the original 42 gallons gallons of crude oil. This represents "processing gain".

Source: **API**

Fig. 18.6. Product breakdown from one barrel of crude. (Source: API.)

TABLE 18.3 Petrochemical Applications

Absorbents
Activators
Adhesives
Adsorbents
Analgesics
Anesthetics
Antifreezes
Antiknocks
Beltings
Biocides
Bleaches
Catalysts
Chelating agents
Cleaners
Coatings
Containers
Corrosion inhib.
Cosmetics
Cushions
De-emulsifiers
Desiccants
Detergents
Drugs
Drying oils
Dyes
Elastomers
Emulsifiers
Explosives
Fertilizers
Fibers
Films
Finish removers
Fire-proofers
Flavors
Food supplements
Fumigants
Fungicides
Gaskets
Hair conditioners
Heat transfer fluids
Herbicides
Hoses
Humectants
Inks
Insecticides
Insulations
Lacquers
Laxatives
Odorants
Oxidation inhib.
Packagings
Paints
Paper sizings
Perfumes
Pesticides
Pharmaceuticals
Photographic chem.
Pipe
Plasticizers
Preservatives
Refrigerants
Resins
Rigid foams
Rust inhib.
Safety glass
Scavengers
Stabilizers
Soldering flux
Solvents
Surfactants
Sweeteners
Synthetic rubber
Textile sizings
Tire cord

consumption of only a small part of the total crude oil processed.

REFINING SCHEMES

A refinery is a complex processing methodology involving a massive network of vessels, reactors, distillation columns, rotating/compression equipment, heat exchangers, and piping. The total scheme can be subdivided into a number of unit processes. In what follows, only the major flow streams will be shown, and each unit will be depicted by a simple block in the flow diagram.

Refined products establish the order in which each refining unit will be introduced. Only one or two key product(s) specifications are used to explain the purpose of each unit. Nevertheless, the reader is reminded that the choices among several types of units and sizes of these units are complicated economic decisions. The trade-offs among product types, quantity, and quality will be mentioned only to the extent that they influence the choice of one type of processing technology over another.

Feedstock Identification

Each refinery has its own range of preferred crude oil feedstocks from which a desired product portfolio can be obtained. Crude oil typically is identified by its source country, underground reservoir, or some distinguishing physical or chemical property. The three most frequently specified properties are density, chemical characterization, and sulfur content.

API *gravity* is a contrived measure of density:

$$\text{API} = \frac{141.5}{sp\ gr} - 131.5$$

where *sp gr* is the specific gravity, or the ratio of the weight of a given volume of oil to the weight of the same volume of water at a standard temperature, usually 60°F. An oil with a density the same as that of water, or with a specific gravity of 1.0, would then be a 10°API oil. Oils with a higher than 10°API are lighter than water. Because the lighter crude oil fractions are usually more valuable, a crude oil with a higher °API gravity will bring a premium market price.

Heavier crude oils are receiving renewed interest as supplies of lighter crude oil dwindle and increase in price. Heavy crudes are those with an 20°API or less. Generally, heavier crudes fetch a lower price on the market. However, heavier crudes will require more processing to convert the high-boiling-point fractions into desired lighter products. Thus, refiners balance the cost of more expensive light, sweet feedstocks against capital investment to refine cheaper, heavy, sour crude oils.

A *characterization factor* was introduced by Watson and Nelson to use an index of the chemical character of crude oil or its fractions.[6] The Watson characterization factor is defined as

$$\text{Watson } K = \frac{(T_B)^{1/3}}{(sp\ gr)}$$

where T_B is the absolute boiling point in degrees Rankine (°R), and *sp gr* is the specific gravity compared with water at 60°F. For a wide boiling point range of material such as crude oil, the boiling point is taken as an average of five temperatures at which 10, 30, 50, 70, and 90 percent are vaporized.

A highly paraffinic crude oil might have a characterization factor as high as 13, whereas a highly naphthenic crude oil could be as low as 10.5. Highly paraffinic crude oils may also contain heavy waxes, which make the oil viscous and difficult to flow. Thus another test for paraffin content is used to measure how cold a crude oil can be before it fails to flow under specific test conditions. The higher the pour-point temperature, the greater the paraffin content for a given boiling range.

Sweet and *sour* are terms that refer to the sulfur content of the crude oil. In the early days, those terms designated the smell of the oil. A crude oil with a high sulfur content usually contains hydrogen sulfide, the gas associated with rotten eggs. Such crudes with high sulfur levels were called sour. Without this disagreeable odor, the crude was judged as sweet. Today, the distinction between sour and sweet is based on analytical assessment of sulfur content. A sour crude oil is one with more than 0.5 weight percent (wt.%) sulfur, whereas a sweet crude has less than 0.5 wt.% sulfur. It is estimated that 81 percent of the world's crude oil reserves are sour.[7]

ASTM distillation is a test prescribed by the American Society for Testing and Materials to measure the volume percent distilled at various temperatures.[5] The results often are reported the other way around: the temperatures at which given volume percents vaporize.[8] These data indicate the quantity of conventional boiling range products occurring naturally in the crude oil. Analytical tests on each fraction indicate the kind of processing

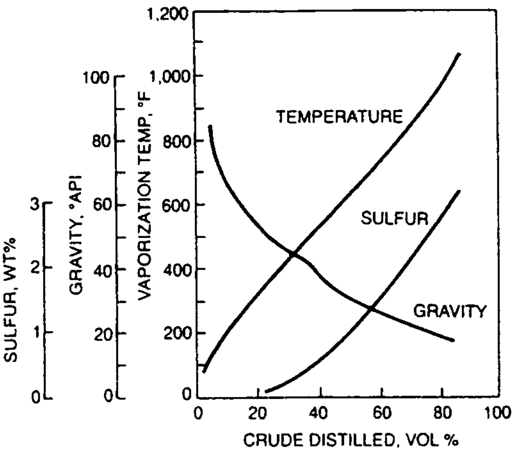


Fig. 18.7. Analysis of light Arabian crude.

that may be needed to make specific products. A plot of boiling point, sulfur content, and API gravity for fractions of Light Arabian crude oil is shown in Fig. 18.7. This crude oil is among those most traded in international crude oil markets.

From Fig. 18.7 it can be seen that the mid-volume range of Light Arabian crude oil has a boiling point of approximately 600°F, a liquid density of nearly 30°API, and an approximate sulfur content of 1.0 wt.% . These data are an average of eight samples. More precise values would be obtained on a specific crude oil if the data were to be used in design work.

Because a refinery stream spans a wide boiling range, the crude oil analysis data would be accumulated throughout that range to provide fraction properties. The intent here is to demonstrate the relationship among volume distilled, boiling point, liquid density, and sulfur content.

Crude Oil Pretreatment

Crude oil comes from the ground admixed with a variety of substances: gases, water, and dirt (minerals). The technical literature devoted to petroleum refining often omits crude oil cleanup steps. It is often assumed that the oil has been previously pretreated before entering the refining process. However, cleanup is important if the crude is to be transported effectively and processed without causing fouling and corrosion. Cleanup occurs in two ways: field separation and crude desalting.

Field separation is the first attempt to remove gases, water, and dirt that accompany crude oil extracted from the ground. As the term implies, field separation is done onsite at the production operation. The field separator is often no more than a large vessel that gives a quieting zone to permit gravity separation of the three phases: gases, crude oil, and water (with entrained dirt).

The crude oil is lighter than water, but heavier than the gases. Therefore, the crude oil appears within the field separator as a middle layer. The water is withdrawn from the bottom and is disposed of at the well site. Gases are withdrawn from the top and piped to a natural-gas processing plant or reinjected back into the reservoir to maintain well pressure. Crude oil from the middle layer is pumped to the refinery or to storage to await transportation by other methods.

Crude desalting is a water-washing operation done at the refinery to further clean up the crude oil before processing. The crude oil pretreated by field separators will still contain water and entrained dirt. Water-washing removes much of the water-soluble minerals and entrained solids.

If these crude-oil contaminants were not removed, they could cause operating problems during the refining process. The solids (dirt and silt) can clog equipment and deposit on heat-transfer surfaces, thereby reducing processing heat-transfer efficiency. Some solids, being minerals, can dissociate at high process temperatures and corrode major equipment. Other solids and minerals can deactivate catalysts used in refining processes.

Crude Oil Fractions

The importance of boiling range for petroleum products has already been discussed in Table 18.2. The simplest form of refining would isolate crude oil into fractions having boiling ranges that would coincide with the temperature ranges for consumer products. Some treatment steps might be added to

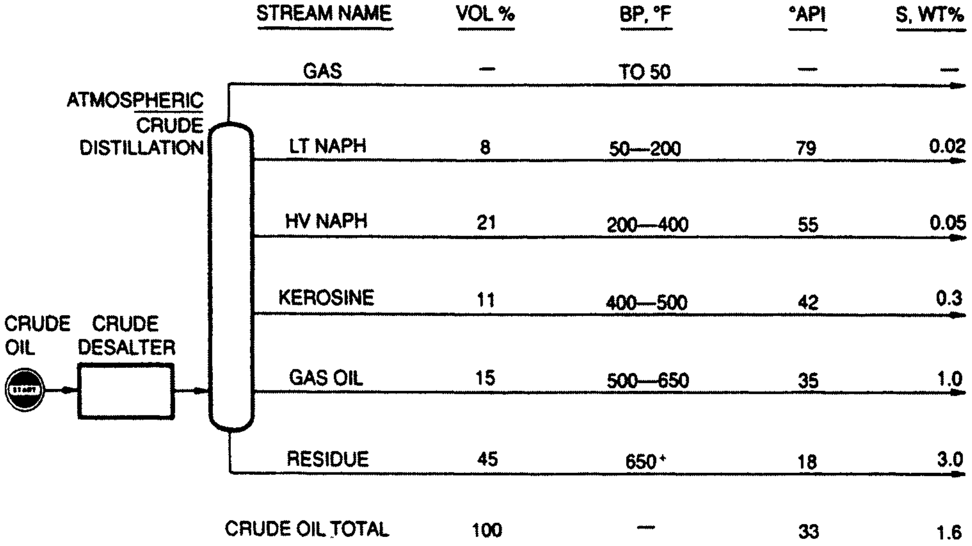


Fig. 18.8. Separating desalted crude oil into fractions.

remove or alter undesirable compounds, and a very small quantity of various chemical additives would be included to enhance final properties.

Crude oil distillation separates the desalted crude oil into fractions of different boiling ranges. Instead of trying to match final product boiling ranges, the fractions are defined by the number and type of downstream processes.

The desalting and distillation units are shown in Figs. 18.8–18.10 along with the crude fractions from the crude distillation column. The relationships between some finished products and downstream processing steps will be expanded upon later in the chapter.

GASOLINE

Gasoline is blended from several refining processes, as shown in Fig. 18.8. Depending on the individual refinery configuration, gasoline blending streams are separated and refined. Figure 18.9 depicts a light-fraction processing scheme.[9] A straight-run gasoline stream is separated from the top portion of the atmospheric crude distillation column, which has a boiling range of 90–200°F and is very paraffinic.

The next cut gasoline stream from the crude distillation column is the naphtha cut. This stream has a boiling range of 200–365°F and contains a significant portion of naphthenes, aromatics, and paraffins. Thus, the naphtha cut is hydrotreated and reformed to upgrade this stream into a gasoline blending stock.[9]

In present-day refineries, the fluid catalytic cracking (FCC) unit has become the major gasoline-producing unit. The FCC's major purpose is to upgrade heavy fractions, that is, gas oil from the atmospheric and vacuum distillation columns and delayed coker, into light products. Atmospheric gas oil has a boiling range of between 650–725°F.[9]

The crude oil feedstock heavily influences the product slate for the refinery and the downstream processing required to meet the refinery's product goals. Fuels are blended to meet product specifications of volatility, sulfur content, and octane number. Most important, refiners constantly seek to optimize their blending programs to meet product goals without giving up product.

The automobile engine's drive train sets the specifications for gasoline. Notably, as automobile manufacturers design more sophisticated engines, in response refiners must adjust their operation to refine and blend fuels that are compatible with newer engines.

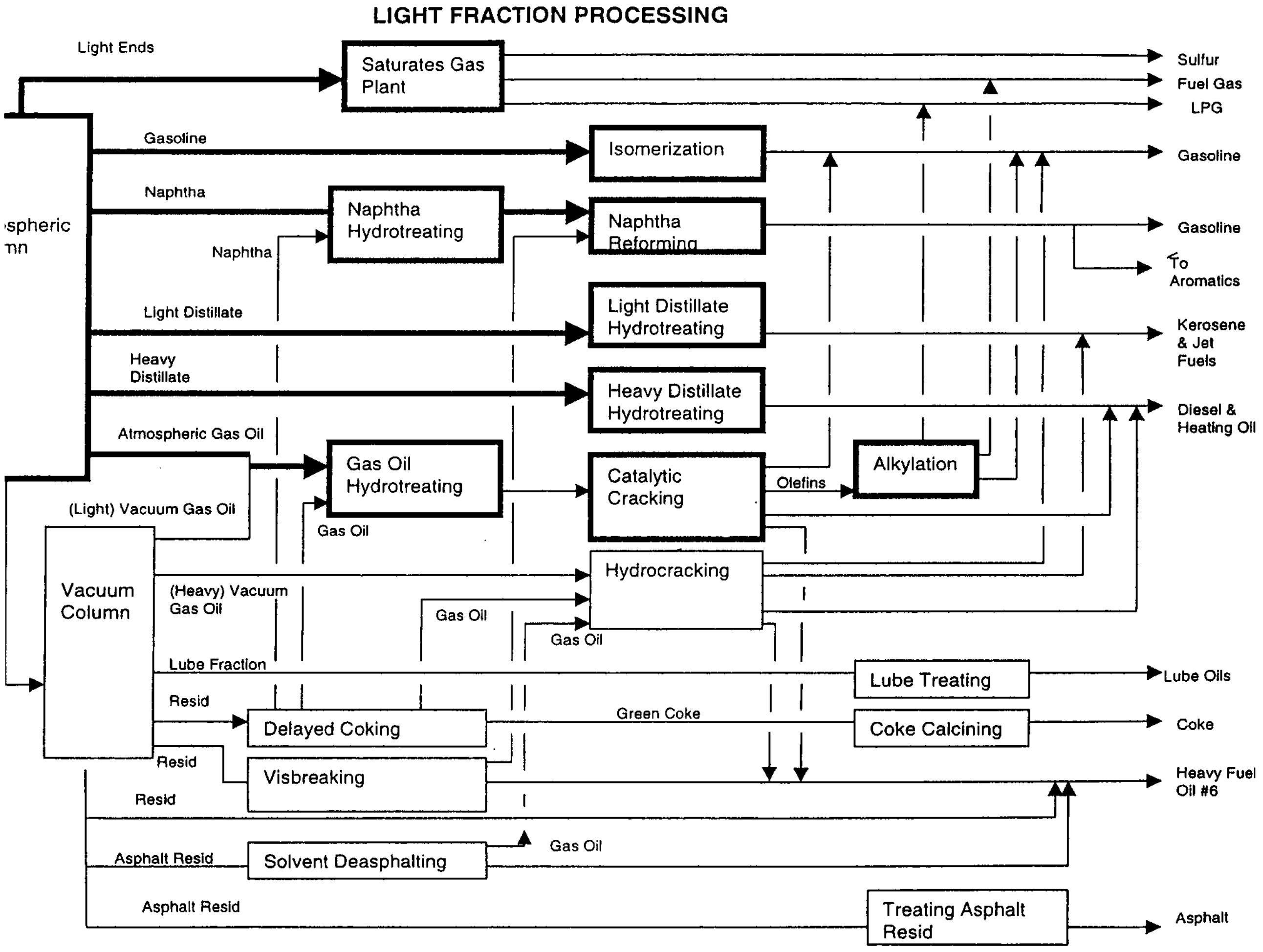


Fig. 18.9. Process flow diagram for a modern integrated refinery. (Reprinted with permission of Ed Ekholm, Copyright 1999 by Ed Ekholm; all rights reserved.)

TABLE 18.4 Anticipated Fuel Specifications Under Auto Oil Program and U.S. Requirements[10]

Period	*Up to 1999*	*2000*	*2005*	*2008 (Expected Values)*	*2000 (U.S. only)*	*2006*
Gasoline						
Sulfur content	<500 ppm	<150 ppm	<50 ppm[b]		<170 ppm	30 ppm
Benzene content	<5% v/v	<1% v/v	<1% v/v[a]		<1% v/v	—
Aromatics content	—	<42% v/v	<35% v/v		<25 v/v	—
Diesel fuel						
Sulfur content, ppm	<500	<350	<50	<30	<500	<10
Cetane number, min	49	51	53[a]	54–58	40	—
Polynuclear aromatics	—	<11% w/w	<6% w/w[a]	<4–1% w/w	—	—
Density, kg/l max	<0.86	<0.845	<0.845[a]	<0.830–0.825	—	—
Distillation T95, °C	<370	<360	<360[a]	<350–340	—	—

% v/v: percent by volume; % w/w: percent by weight; [a]Expected values; [b]Germany is promoting 10 ppm sulfur for gasoline by 2003.
Source: Linde Technische Gase GmbH.

Worldwide, new environment legislation has set product specifications for fuels. Table 18.4 lists the quality standards for automotive gasoline and diesel.[10] These mandates are geared to lower tailpipe emission from vehicles. Sulfur content and volatility will be strictly limited in future fuel requirements.

Volatility

A gasoline's boiling point is important during its aspiration into the combustion chamber of a gasoline-powered engine. Vapor pressure is a function of the fuel's boiling point. Boiling range and vapor pressures are combined as the concept, *volatility*.[11]

The lighter components in gasoline are used as a compromise between two extremes: enough light components so that adequate vaporization of the fuel–air mixture provides an easy engine start in cold weather, but too many light components can cause the fuel to vaporize within the fuel pump and cause vapor lock.

Environmental studies suggest that light gasoline components are detectable in the atmospheres of large metropolitan areas. New environmental laws limit the volatility of gasoline, so refiners must use other processing streams to meet volatility requirements. However, the fuel must provide performance to consumers, for example, by minimizing chamber deposits and spark-plug fouling in the engine.

Sulfur Content

Sulfur compounds are corrosive and foul-smelling. When burned in an engine these compounds form sulfur dioxide and other oxides referred to as SO_x in engine exhaust. These compounds recombine and form sulfur trioxide and sulfuric acid mist, which is released as engine exhaust. Efforts to improve air quality are targeted at reducing vehicle engine exhaust of toxins and SO_x compounds. Thus, many new environmental regulations (Table 18.4) are focused on reducing the sulfur content of fuels. All crude oils contain some sulfur concentration. How much desulfurization is needed is dependent on the feedstock and product slate.

Caustic wash or other enhanced solvent-washing methods are a sufficient pretreatment to remove sulfur compounds from light naphtha. The sulfur compounds in light naphtha are mercaptans and organic sulfides that are readily removed by these washing processes. Heavy naphtha is harder to desulfurize. This stream has a higher sulfur content, and, equally important, the sulfur is embedded in complex hydrocarbon compounds and rings. Washing efforts are more effective on mercaptans, which are not usually present in heavy

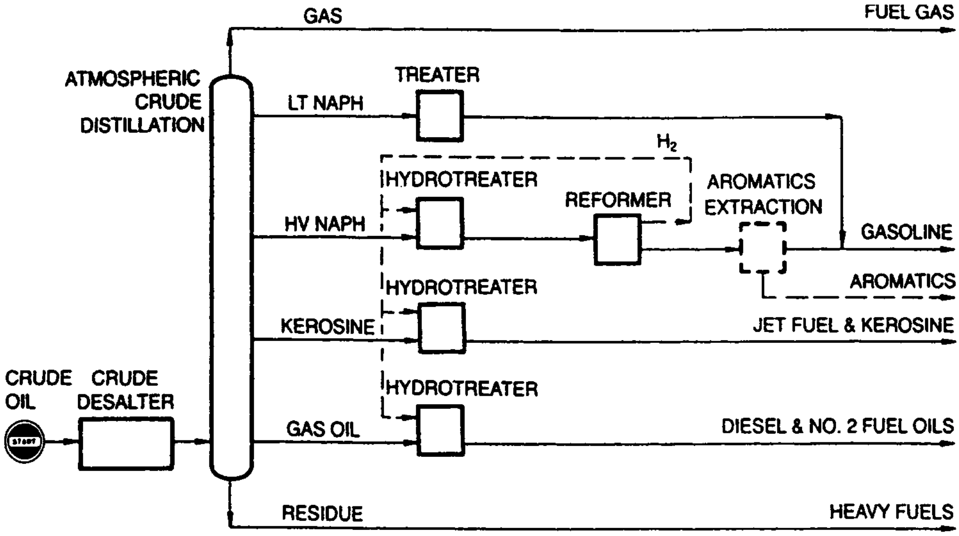


Fig. 18.10. Low-investment route to modern products.

naphtha. More aggressive methods are needed to break the compound structures and release the sulfur. Hydrotreating is one effective method to reduce sulfur content in hydrocarbon streams.[12]

Hydrotreating is a catalytic process that converts sulfur-containing hydrocarbons, that is, sulfides, disulfides, and ring compounds such as thiopenes, into low-sulfur liquids and hydrogen sulfide. This technology is widely used throughout the refinery, as shown in Figs. 18.9 and 18.10.[9] This process is operated under a hydrogen-rich blanket at elevated temperatures and pressure. The process is a hydrogen-consuming step, because the hydrogen replaces sulfur on the hydrocarbon molecule.[9]

Nitrogen and oxygen compounds are also dissociated by hydrotreating. Consequently, hydrotreating provides additional benefits of hydrodenitrification, which improves downstream operations. For nitrogen and oxygen compounds, the products from hydrotreating are ammonia and water, respectively. Thus, these contaminants will be separated in the off-gas and are easily removed by conventional gas-treating processes.

Octane Number

Another condition to keep gasoline engines running smoothly is that the fuel–air mixture starts burning at a precise time in the combustion cycle. An electrical spark starts the ignition. The remainder of the fuel–air mix should be consumed by a flame front moving out from the initial spark.

Under some conditions, a portion of the fuel–air mix will ignite spontaneously instead of waiting for the flame front from the spark. The extra pressure pulses that occur from spontaneous combustion are usually audible above the background sounds of the engine running and give rise to a condition know as "engine knock." The engine pings and rumbles when under "knock conditions." This condition is undesirable; it is a waste of available power.

The *octane number* is a measure of a fuel's ability to avoid knocking. The octane number of gasoline is determined in a special single-cylinder engine where various combustion conditions can be controlled.[5] The test engine is adjusted to trace the knock from the fuel being rated. Various mixtures of iso-octane and normal heptane (*n*-heptane) are used to find the ratio of the two reference fuels that will give the same intensity of knock as that from an unknown fuel. Defining iso-octane as 100 octane number and *n*-heptane as 0 octane number, the volumetric percentage of iso-octane in heptane that matches knock from the unknown fuel is reported as the octane number of the fuel. For example, 90 vol.% of iso-octane and 10 vol.% *n*-heptane establishes a 90 octane number reference fuel.

Two types of octane number ratings are specified, although other methods are often used for engine and fuel development. Both methods use the same reference fuels for essentially the same test engine. Engine operating conditions are the difference. In the *research method*, the spark advance is fixed, the air inlet temperature is 125°F, and the engine speed is 600 rpm. The other method is called the *motor method*; it uses variable spark timing, a higher mixture temperature (300°F), and a faster engine speed (900 rpm).

The more severe conditions of the motor method have a greater influence on commercial blends than they do on the reference fuels. Thus, a motor octane number (MON) of a commercial blend often has a lower research octane number (RON). Consequently, blended fuels use an arithmetic average of both ratings—MON and RON—and can be abbreviated as (R + M)/2.

Catalytic reforming is the principal process used to upgrade the octane number of naphtha for gasoline blending.[13] Reforming uses catalysts to reshape the molecular structure of hydrocarbons to raise the octane number of the process stream. Naphthenes are converted to aromatics; paraffins are isomerized to isomeric forms.[9] Reforming efforts are most effective when used on heavier molecules; a greater increase in octane number can be attained by reforming heavy naphtha cuts.

Reforming catalysts typically contain platinum or a mixture of platinum and other metal promoters on a silica–alumina support. Only a concentration of platinum is used, averaging about 0.4 wt.%. The reforming process is a highly endothermic process. Desulfurized feeds are preheated to 900°F, and the reactions are done at various pressures (50–300 psig), which are dependent on the licensed process used.[12] At elevated temperatures and pressures, the catalyst is susceptible to coking, which decreases catalyst efficiency. Thus, refiners must regenerate the catalyst to maintain process efficiency. Reforming catalyst can be regenerated in situ by burning off the coke from the catalyst. Newer developments now use continuous regeneration of the reforming catalyst in which three reforming reactors are stacked one on top of the other. Gravity flow moves the catalyst from the top to the bottom and sends it to a regeneration step in which a dry burn removes the coke. The regenerated catalyst is then returned to process. Also, reforming feeds are pretreated to remove poisons that can kill precious-metal catalysts.

Hydrotreating is an effective method to pretreat reforming feedstocks (Fig. 18.10). Combining hydrotreating with reforming is most effective. Due to cyclization and dehydrogenation of hydrocarbon molecules in the reformer, hydrogen is a by-product of this operation.[14] Notably, by-product hydrogen from the reform can be directed to the hydrotreating operations. Thus, the reformer can provide the refinery with the hydrogen supply for hydrotreating. A rule of thumb is that the catalytic reformer produces 800–1200 scf/bbl = standard cubic feet per barrel (scf/bbl) for naphtha. The excess hydrogen is available for hydrotreating other fractions in separate hydrotreaters.

DISTILLATES

Jet fuel, kerosene (range oil), No. 1 fuel oil, No. 2 fuel oil, and diesel fuel are all popular distillate products from the 365–650°F fractions of crude oil.[9] Distillates are further classified as light distillates with a true boiling point range of 365–525°F, and heavy distillate cuts have a true boiling point range from 525–650°F. Light distillates are blended into kerosene and jet fuels. Heavy distillate cuts are used to blend diesel fuels and home heating oils.[9]

Some heating oil (generally No. 2 heating oil) and diesel fuel are very similar and are sometimes substituted for each other. Home heating oil is intended to be burned in a furnace for space heating. Diesel fuel is intended for compression–ignition engines.

Distillates are lower cuts from the atmospheric crude distillation column (Fig. 18.10); thus, these refinery streams may have high sulfur concentrations due to the feedstock that is processed. Newer product specifications limit sulfur concentrations in consumer products, especially diesel. Consequently, distillate streams must be upgraded. Hydrotreating improves the product properties of distillate products; notably it reduces sulfur content. More important, hydrotreating hydrogenates unsaturated hydrocarbons so that they will not contribute to smoke and particulate emissions, whether the fuel is burned in a furnace or used in an engine.

Residuals

Crude oil is seldom distilled at temperatures above 650°F. At higher temperatures, coke will form and plug the lower section of the crude oil distillation tower. This bottom fraction from the atmospheric crude column has a true boiling point range of 650–725°F and is often referred to as *atmospheric gas oil* or *residuals*. This fraction is traditionally not vaporized. Atmospheric gas oil must be upgraded extensively; it can be severely hydrotreated to break apart the complex ring compounds and saturate them into lighter products. This stream can be sent to a catalytic cracker to further upgrade this heavy fraction into gasoline, diesel, and home heating fuel.[9] The heaviest cut of the atmospheric crude distillation is often referred to as the *long residuum*. This fraction is further processed via a vacuum distillation column.

PRODUCING MORE LIGHT PRODUCTS

The refining scheme shown in Fig. 18.9 is a simplified view of an integrated refinery. More processing steps can be added and are dependent upon the product slate of the refinery and the cracking slate anticipated for its design. If the refinery is a gasoline refinery, the cracking process will be directed toward producing light products, gasoline at the expense of diesel and heating oil. Conversely, if diesel is the desired end-product, gasoline product is sacrificed to produce more distillate streams. United States refineries are predominately gasoline-oriented. Conversely, Western European refineries are diesel-fuel-oriented. In Western Europe, the demand for gasoline is projected to decline over the next 10 years, and demand for middle distillates increase.[15] Therefore, Western European refiners must adapt operations not only to produce more diesel but also to minimize gasoline production.

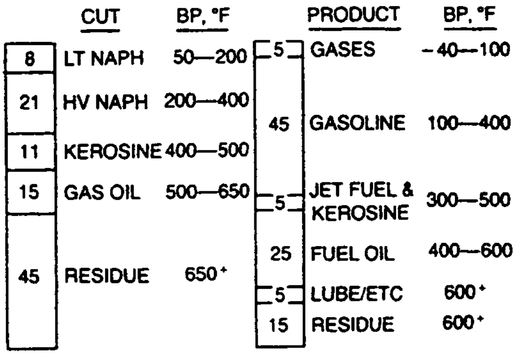


Fig. 18.11. Light Arabian crude oil compared to U.S. product deliveries.

For industrial areas, where the principal demand is for transportation fuels or high-quality heating oils, the simplified refining scheme is shown in Fig. 18.9. In the case of a United States refinery, the emphasis is directed into converting more of the crude oil into lighter products, namely gasoline. If this refinery processed a Light Arabian crude, nearly 80–85 vol.% of the products would be lighter than the boiling temperature of 650°F compared with the 55 vol.% existing in the feed crude oil (Fig. 18.11). More than half of all United States products are gasoline and lighter distillates (boiling temperatures below 400°F) compared with 29 vol.% in the crude oil. This comparison is unique for these circumstances. Refining technologies and catalysts have advanced from the earlier days. Notably, refiners can process a variety of crudes into valued end-products. Crudes that require more intense processing, that is, high-severity hydrocracking and hydrotreating, fetch a lower price on the market and are often referred to as *opportunity crudes*. Refiners processing lower-cost, sour, heavy crude must make more capital investment in processing capability. However, these refiners pay less for their feedstocks and risk attaining payback on capital investments through volume processing of lower-cost feedstocks. The design of an integrated refinery constantly balances the future price of oil against the return on investment for refining capacity. Thus, the decision on what types of crude to process will affect the design and operation of a refinery.

Cracking

As mentioned earlier, the refining process involves adding hydrogen to carbon molecules. Notably, the desired hydrocarbons are much lighter products; thus, the refining process strives to break the large, complex hydrocarbon molecules into smaller molecules and add hydrogen to the open bonds. Cracking processes typically break hydrocarbon molecules into two or more smaller molecules. Thermal cracking uses high-temperature (above 650°F) and a long residence time to sever hydrocarbon bonds. Higher pressure facilitates the cracking process; however, the capital investment for a high-pressure reactor is greater than the expense for low- or medium-pressure reactors.

In thermal cracking, the formation and deposition of coke on piping and equipment walls is an unwanted side reaction. Another option to crack crude oil into desired products at lower pressures and temperatures is *catalytic cracking*. Catalytic cracking splits the molecules quicker and at lower temperatures. Catalysts are used to promote the desired reaction rate for the process.

Catalytic cracking involves large reactors with large fluidized catalyst beds. As in the case of thermal cracking, coke is also formed during the catalytic process, which can deposit on the catalyst and hinder its activity. Thus, this process uses reactor–separators and regenerators to remove the catalyst and regenerate it and return the catalyst to the process. The fluidized bed mixes the feed with the catalyst to optimize contact time. The catalyst is separated from the hydrocarbon products. A portion is regenerated; the remainder is returned to the catalytic cracker reactor.

Catalytic cracking is very effective in upgrading heavy refining streams, such as gas oils, into motor gasoline stocks thereby increasing the octane number for product streams. This process produces less gas and coke as compared with thermal cracking operations. Catalytic cracking also yields more liquid products, which can be tailored toward gasoline or diesel fuel and home heating oil products. Different operating conditions and catalysts will define the product mix from a catalytic cracker.

Several factors determine the best feeds for catalytic crackers. Heavy feeds are preferred; thus, the lower boiling point is about 650°F. The feed should not be so heavy that it contains an undue amount of metal-bearing compounds or carbon-forming material. Deposition of metals and coke can quickly deactivate the catalyst.

Visbreaking is a mild, once-through thermal cracking process. It is used to crack resid products into fuel-oil specifications. Although some light products such as naphtha and gasoline are produced, this is not the purpose of the visbreaker.

Coking is another matter. It is a severe form of thermal cracking in which coke formation is tolerated to attain additional lighter liquids from the heavier, dirtier fractions of crude oil. In this process the metals that would foul catalysts are laid down with the coke. The coke settles out in large coke drums that are removed from service frequently (about once a day) to have the coke removed by hydraulic methods. Several coke drums are used to make the process continuous; thus, one drum is online while the other is being emptied and readied for the next cycle.[12]

Hydrocracking converts a wide variety of heavy refining product streams into light products; fuels and distillates. A robust catalyst system is used to desulfurize, denitrify, and hydrocrack the feed.[9,12,14] The process combines hydrotreating and catalytic cracking goals. However, hydrocracking is a more capital-intensive and operating-intensive step. The operating pressure is higher (up to 3000 psi); consequently, thick-wall vessels are used as reactors (up to 9 in. thick). Products from a hydrocracker are very clean (desulfurized, denitrified, and demetalized) and will contain isomerized hydrocarbons in greater quantity than from conventional catalytic cracking. This process consumes a large quantity of hydrogen, which adds considerably to its operating costs.

Vacuum Distillation

As mentioned earlier, most consumer products are light products: those with boiling points less than 400°F. However, in the refining of a crude oil, a significant portion of the products has a true boiling point above 650°F.

Atmospheric distillation is least effective in converting heavier products into lighter components. A second distillation column under vacuum is needed to further separate the heavier parts of crude oil into lighter fractions. Some fractions from the vacuum units have better quality than atmospheric distillation cuts because the metal-bearing compounds and carbon-forming materials are concentrated in the vacuum residue.

Reconstituting Gases

Cracking processes to convert heavy liquids into lighter products also create gases. Another option to make more liquid products is to combine the gaseous hydrocarbons. A gas separation unit may be added to a refinery to isolate individual types of gases. When catalytic cracking is part of the refining scheme, a large quantity of olefins (ethylene, propylene, and butylene) is co-produced. Two routes are available to reconstitute these gaseous olefins into gasoline blending stocks, as outlined below.

Polymerization uses a catalytic process to combine two or more olefins to make polymer gasoline. The double bond in only one olefin is changed to a single bond during each link between two olefins. Thus, the product will still have some double bonds. This process was developed in the 1940s to produce high-octane aviation fuel. However, the olefinic nature of polymer gasoline does have a drawback.[4] The gum-forming tendencies of the polymer gasoline are problematic especially during long storage in warm climates. The olefins continue to link up and form larger molecules—gum or sludge—which are undesirable. Some refiners still use catalytic polymerization of light ends. It is a lower-cost process, both in terms of operating and investment costs. However, due to new environmental specifications, hydrogenation of polymer gasoline may be necessary to meet emission standards for Bromine Number.[9] Hydrogenation can reduce the octane number of the polymer gasoline.

Alkylation catalytically combines light olefins—propylene and butylenes—with isobutane to produce a branched-chain paraffinic fuel.[14] Alkylate is a great blending component for the gasoline-blending pool. It has a high octane number (usually above 94), low vapor pressure, and is almost sulfur free.[16] Present-day alkylation processes are carried out in the presence of sulfuric or hydrofluoric acids. New health and safety issues are promoting research on solid-acid technologies. Some successes have been demonstrated in the laboratory and in pilot studies; however, no commercial units have been built.

The *ether* process combines an alcohol with an iso-olefin. In the United States, a weight percentage of oxygenate (2 wt.%) content is mandated for reformulated gasoline (RFG). The most common oxygenate currently used is methyl tertiary butyl ether (MTBE). Methanol and the iso-olefin form of isobutylene are reacted to form MTBE. Other alcohols, such as ethanol, may be reacted with iso-butylene to form ethyl tertiary butyl ether (ETBE). Methanol can be reacted with isoamylene, another iso-olefin, to form tertiary amyl-methyl ether (TAME). Of all the mentioned ethers, MTBE is the one most widely used as a gasoline-blending component.[16]

A MODERN REFINERY

A refining scheme incorporating the processes discussed above is shown in Fig. 18.9. The variations in this flow diagram are numerous. Types of crudes processed, product slate, and competitive quality goals of products are just a few factors that influence the processing needs for a refining complex. Many other processes play an important role in the final scheme. A partial list of these processes would be: dewaxing lubricating oils, deoiling waxes, deasphalting heavy fractions, manufacturing specific compounds for gasoline blending (alcohols, ethers, etc.), and isolating specific fractions for petrochemical applications. See Fig. 18.12.

Petrochemicals

Refining crude provides many products, depending on the types of products sought.

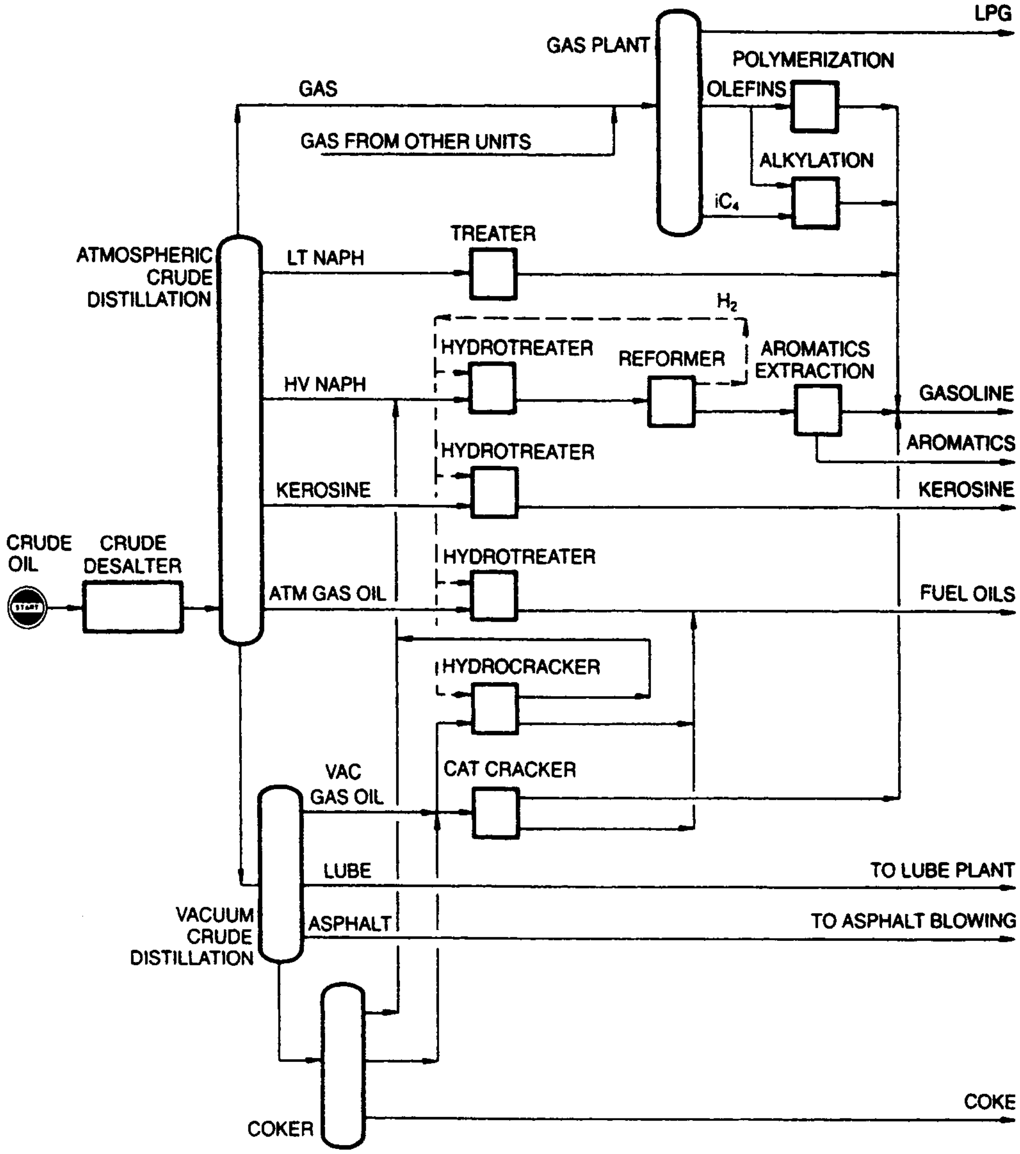


Fig. 18.12. High conversion refinery.

Lighter products from the refining of crude have higher value as petrochemical feeds than as gasoline-blending components. In particular, olefins and aromatic compounds possess higher values as petrochemicals than as gasoline components.

Ethylene is a key building block for the petrochemical industry. It is usually made by thermally cracking gases—ethane, propane, butane, or a mixture of these—as they exist in refinery off-gases. When gas feedstocks are scarce or expensive, naphthas and even whole crude oils have been used in specially designed ethylene crackers. The heavier feeds provide significant quantities of higher-molecular-weight olefins and aromatics.

Aromatics are typically concentrated in product streams from the catalytic reformer. When aromatics are sought for petrochemical applications, they typically are extracted from the reformer product stream by solvent extraction or distillation extraction. A common solvent used is sulfolane; new processes now use *n*-formylmorpholin as the extractive solvent.[12]

The mixture of aromatics is typically referred to as BTX and is an abbreviation for benzene, toluene, and xylene. The first two components, benzene and toluene, usually are separated by distillation, and the isomers of the third component, xylene, are separated by partial crystallization.[17] Benzene is the starting chemical for materials such as styrene, phenol, and many fibers and plastics. Toluene is used to make a number of chemicals, but most is blended into gasoline. Xylene usage is dependent on its isomer. *Para-xylene* (*p*-xylene) is a precursor compound for polyester. *Ortho-xylene* (*o*-xylene) is the building block for phthalic anhydride. Both compounds are widely used to manufacture consumer products.

PROCESS DETAILS

Thus far, the refining units have been described as they relate to other units and to the final product specifications. At this point, typical flow diagrams of some major processes will be presented to highlight individual features. In many cases the specific design shown is an arbitrary choice from the work of several qualified designers.

Crude Desalting

Salts such as sodium, calcium, and magnesium chloride are generally contained in water suspended in the oil phase of hydrocarbon feedstocks.[9] Other impurities are also present in crude oils as mechanical suspensions of silt (dirt), iron oxides, sand, and crystalline salt.[14] These contaminants must be removed before processing the crude oil feeds; thus, the best method is mixing the crude oil with water and creating an emulsion.[12]

A typical flow diagram is shown in Fig. 18.13 The desalter operation is incorporated into the preheat train of the crude distillation unit to conserve energy. Depending on the characteristics of the hydrocarbon feedstock,

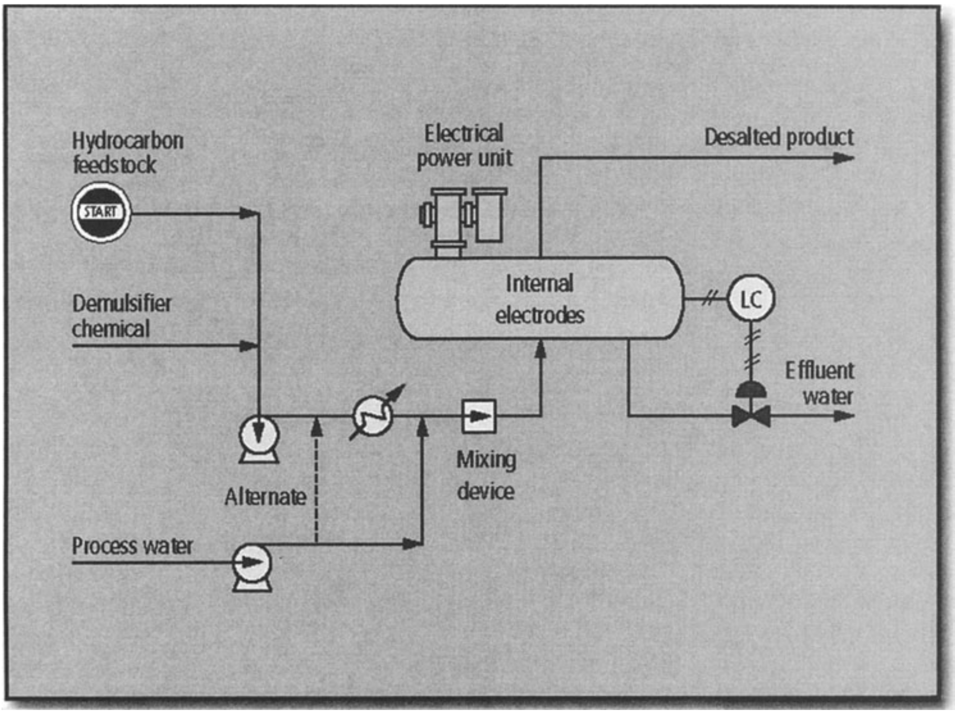


Fig. 18.13. Electric desalting—CB&I. Baker ProcessTechnology. Includes: heater, mixing device, and electrostatic settler. (Source: *Hydrocarbon Processing*, 2004 Refining Process Handbook, CD-ROM. Sept. 2004: Copyright 2002 by Gulf Publishing Co., all rights reserved.)

the crude oil is preheated to 150–300°F. The crude oil is preheated with crude unit products and pumparound reflux to the desired temperature. The operating pressure is 40 psig or more. The elevated temperature reduces oil viscosity to improve mixing, and the elevated pressure suppresses vaporization. The washwater, 3–6 vol.%, can be added upstream and/or downstream of the heat exchanger(s). The combined streams pass through a mixing device—a throttling valve or emulsion orifice—and create a stable water-in-oil emulsion. The properties of the emulsion are controlled by adjusting the pressure drop across the mixing device. Trace quantities of caustic, acid, polymers, other chemicals are sometimes added to promote treatment.[12]

The emulsion enters the desalter vessel where a high-voltage electrostatic field is applied. The electrostatic field causes the dispersed water droplets to coalesce, agglomerate, and settle to the lower portion of the vessel. The various contaminants from the crude oil concentrate in the water phase. The salts, minerals, and other water-soluble impurities are discharged from the settler to the effluent system. Clean, desalted hydrocarbon product flows from the top of the settler and is ready for the next processing step.

Additional stages can be used in series to gain additional reductions in the salt content of the crude oil. Two stages are typical, but some installations use three stages. About 90 percent of the emulsified water can be recovered in one step, whereas 99 percent recovery is possible with a two-step process.[9] The additional investment for multiple stages is offset by reduced corrosion, plugging, and catalyst poisoning of downstream equipment with the cleaner crude feed.

Crude Distillation

Single or multiple distillation columns are used to separate the crude oil into fractions determined by their boiling range. Common identification of these fractions was discussed using Fig. 18.12, but should only be considered as a guide. Many refining schemes can be used to alter the type of separation made at this point.

A typical flow diagram of a two-stage crude oil distillation system is shown in Fig. 18.14. The crude oil is preheated with hot products from the system and desalted before entering the fired heater. The typical feed to the crude-fired heater has an inlet temperature of 550°F, whereas the outlet temperature may reach 657–725°F. Heater effluent enters the crude distillation (CD) column, where light naphtha is drawn off the overhead tower. Heavy naphtha, kerosene, diesel, and cracking streams are sidestream drawoffs from the distillation column. External reflux for the tower is provided by several pumparound streams.[12]

The bottoms of the CD, also known as atmospheric residue, are charged to a second fired heater where the typical outlet temperature is about 750–775°F. From the second heater, the atmospheric residue is sent to a vacuum tower. Steam ejectors are used to create the vacuum so that the absolute pressure can be as low as 30–40 mm Hg (about 7.0 psia). The vacuum permits hydrocarbons to be vaporized at temperatures below their normal boiling point. Thus, the fractions with normal boiling points above 650°F can be separated by vacuum distillation without causing thermal cracking. In this example (Fig. 18.14), the distillate is condensed into two sections and withdrawn as two sidestreams. The two sidestreams are combined to form cracking feedstocks: vacuum gas oil (VGO) and asphalt base stock.

Atmospheric distillation is an energy-intensive process. With pressure to reduce operating costs, new design efforts are investigating energy conservation on the CD column. A new atmospheric distillation process by TECHNIP FINAELF uses a progressive distillation strategy to minimize total energy consumption, as shown in Fig. 18.15. In this processing scheme, two pre-flash towers separate the light products—LPG, naphtha (light, medium, and heavy), and kerosene—from the crude feed to the main atmospheric distillation column. The light products are fractionated as required in a gas plant and rectification towers.

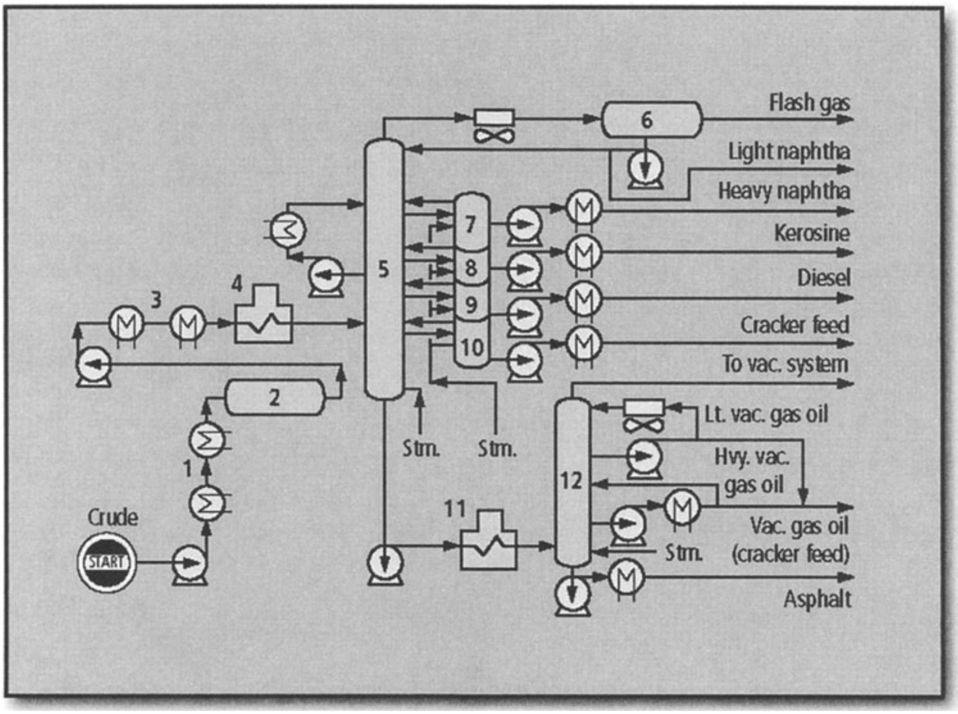


Fig. 18.14. Crude distillation—Foster Wheeler. Includes: exchanger heaters (1,3), desalter process (2), fired heater (4), main fractionator (5), overhead gas accumulator (6), sidestream strippers (7,8,9,10), second fired heater (11), and vacuum fractionator (12). (Source: *Hydrocarbon Processing*, 2004 Refining Process Handbook. CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

The topped crude is typically reduced by two-thirds of the total naphtha cut. The bottoms from the second pre-flash tower are sent to the charge heater and directed to the main distillation column and produce four product streams: heavy naphtha, several kerosene cuts, and bottoms residue. The residue is further processed in a vacuum column and produces VGO and several distillate streams.

Incidentally, the total refining capacity of a facility is reported in terms of its crude-oil handling capacity. Thus, the size of the first distillation column, whether a pre-flash or an atmospheric distillation column, sets the reported size of the entire refinery. Ratings in barrels per stream day (bpsd) will be greater than barrels per calendar day (bpcd). Processing units must be shut down on occasion for maintenance, repairs, and equipment replacement. The ratio of operating days to total days (or bpcd divided by bpsd) is called the "onstream" factor or "operating factor." The ratio can be expressed either as a percent or a decimal. For example, if a refinery unit undergoes one shutdown period for one month during a three-year duration, its operating factor is (36 − 1)/36, or 0.972, or 97.2%.

Outside the United States, refining capacity is cited in metric tons per year. Precise conversion from one unit of measure to the other depends upon the specific gravity of the crude oil, but an approximate relation is 1 barrel per day equals 50 tons per year (tpy).

Hydrotreating

Hydrotreating is one of the more mature refining processes still practiced today. Refiners began using catalytic hydrotreating in the 1950s to remove undesirable materials from refining product streams, as shown in Fig. 18.9. This process effectively removes contaminants such as sulfur, nitrogen, olefins, metals, and aromatics.[9,12,14] The chemistry of

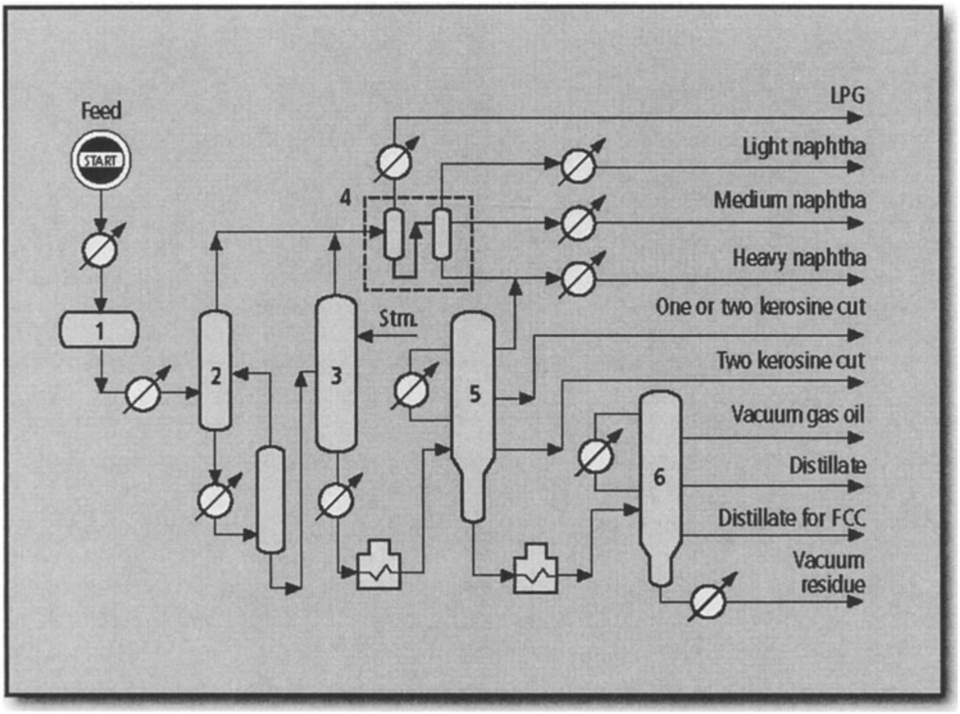


Fig. 18.15. Crude distillation—TOTALFINAELF andTechnip. Includes: desalter and preheater (1), preflash towers (wet and dry) (3,2), gas plant and rectifier tower (4), main fractionation tower (5), and vacuum fractionation tower (6). (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

hydrotreating can be further divided into three categories: hydrodesulfurization, hydrodenitrification, and hydrodearomatization (saturation of olefins and saturation of aromatics).[12,14]

The utility of most hydrotreating efforts is desulfurization. Sulfur-containing hydrocarbons are present in crude oil with many varying forms and boiling points. New product specifications limit the amount of sulfur present in finished fuels; thus, greater effort will be needed to remove more sulfur-containing compounds throughout the fuel-blending pool. Notably, more complex, high-boiling-point sulfur compounds must be extracted from the blending pool to meet lower fuel specifications, as shown in Table 18.5.[18]

Depending on the severity of the operation, hydrotreating is done at elevated temperatures and pressures. Higher temperatures and pressures are needed to open the complex ring compounds and remove the sulfur molecules. A typical flow diagram is shown in Fig. 18.16.[12] This process converts atmospheric and vacuum residue into lighter products. The oil feed is preheated with product streams and a charge heater, and mixed with a hydrogen-rich gas. This mixture is charged to the main reactor and passed over a fixed-bed catalyst system where exothermic hydrogenation reactions occur. Proper internals are needed in the reactor to evenly distribute the feed throughout the catalyst bed and prevent channeling. Product separation is done by a hot high-pressure separator, cold high-pressure separator, and fractionator. In the first high-pressure separator, unreacted hydrogen is taken as the overhead; it is scrubbed to remove hydrogen sulfide (H_2S). The cleaned hydrogen is recycled back to process. In the second high-pressure separator, the remaining gases and light products are removed from the liquid product. If the feed is a wide-boiling range material from which several blending stocks are to be made, the hot,

TABLE 18.5 Major Gasoline Sulfur Compounds Normal Boiling Point (NBP) and Hydrocarbon Boiling Range

Component	*NBP**	*Boiling Range °F*
Ethyl mercaptan	95	70–90
Dimethyl sulfide	99	75–80
Iso-propyl mercaptan	126	110–130
Tert-butyl mercaptan	147	120–150
Methyl ethyl sulfide	151	130–140
n-Propyl mercaptan	154	115–130
Thiophene	183	140–200
Iso-Butyl mercaptan	191	180–200
n-Butyl mercaptan	204	185–200
Dimethyl disulfide	230	190–200
2-Methyl thiophene	234	200–250
3-Methyl thiophene	239	210–270
Tetrahydrothiophene	250	220–260
1-Pentyl mercaptan	259	245–255
C_2 Thiophene	278	250–310
C_1 Tetrahydrothiophene	306	260–320
Hexyl mercaptan	307	290–340
C_3 Thiophene	317	300–340
C_2 Tetrahydrothiophene	318	300–340
C_3 Tetrahydrothiophene	329	320–340
C_4 Tetrahydrothiophene	340	320–360
C_4 Thiophene	361	340–380
C_5 Thiophene	411	390–420
Benzothiophenes and others	427+	400+

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high-pressure separator is followed by a fractionation column. The fractionator separates the treated feed into several liquid product streams; naphtha, middle distillate, VGO, and a very clean hydrotreated resid product.

The feed for hydrotreating can be a variety of different boiling-range materials from naphtha to vacuum residues. Generally, each fraction is treated separately to permit optimum operating conditions, the higher boiling-point materials require more severe treatment conditions. For example, naphtha hydrotreating can be done at 200–500 psia and at 500–650°F with a hydrogen consumption of 10–50 scf/bbl of feed. Conversely, a residue-hydrotreating process can operate at 1000–2000 psia and at 650–800°F, with a hydrogen consumption of 600–1200 scf/bbl.[19]

Hydrotreating is a versatile cleanup step; however, it is a large hydrogen-consuming process. Most refineries are able to meet their hydrogen-processing demands with hydrogen recovered from the catalytic reforming process. However, as refiners intensify hydrotreating efforts to meet tighter specifications for products, hydrogen demand will increase. Consequently, one option to balance hydrogen consumption is to construct onsite hydrogen plants to meet present and future hydrogen needs. Purchasing hydrogen from over-the-fence suppliers is another option.[20]

Catalyst formation constitutes a significant difference among hydrotreating processes. Refiners must address reducing sulfur concentrations to lower levels: 15 ppm for diesel and 30 ppm for gasoline. Consequently, the activity and efficiency of the hydrotreating catalysts become even more vital. Presently, cobalt–molybdenum (CoMo) and nickel–molybdenum (NiMo) catalysts are the preferred hydrotreating systems. CoMo catalysts are very effective at breaking carbon– sulfur (C–S) bonds, and NiMo catalysts are more effective at hydrogenation. Just using both systems—CoMo and NiMo—will not guarantee optimum results.[14,21] To obtain the very low ppm levels, desulfurization efforts become more specified at the compound that must be reacted to remove the sulfur from the product stream.

Catalytic Reforming

This process upgrades naphtha (light distillates) into aromatic-rich streams that can be used for octane enhancers for gasoline blending or as a petrochemical feedstock. Originally the process was developed in the 1950s to upgrade low-octane, straight-run gasoline to high-octane liquids, as shown in Table 18.6.[14] This process converts naphthenes into corresponding aromatics and isomerizes paraffinic structures to isomeric forms.[9] The naphtha charge is a varying mixture of C_6–C_{11} paraffins, naphthenes, and aromatics. In a catalytic reformer, aromatic compounds pass through the system unchanged, whereas naphthalenes react selectively to form aromatics.[14]

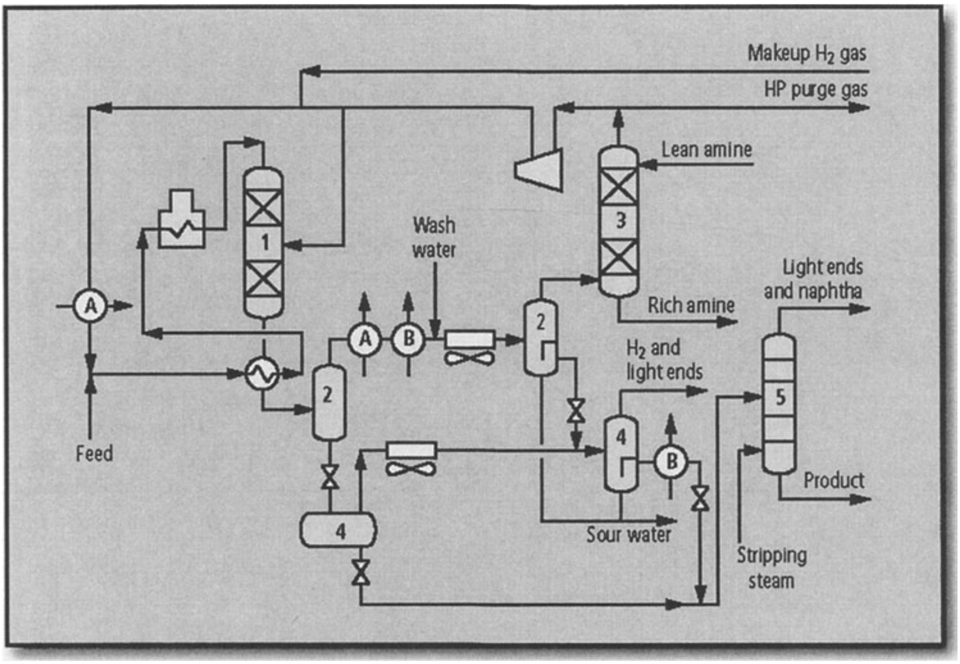

Fig. 18.16. Hydrotreating—Chevron Lummus Global LLC. Includes reactor (1), hot high pressure separator (2), hot low pressure separator (3), cold high pressure separator and product fractionator (4). (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

TABLE 18.6 Aromatics have Higher Octane Numbers[6]

		Octane Number, Clear	
Hydrocarbon Homologs		*Motor*	*Research*
C_7 hydrocarbons			
n-paraffin	C_7H_{16} (*n*-heptane)	0.0	0.0
naphthene	C_7H_{14} (cycloheptane)	40.2	38.8
	C_7H_{14} (methylcyclohexane)	71.1	74.8
Aromatic	C_7H_8 (toluene)	103.5	120.1
C_8 hydrocarbons			
n-paraffin	C_8H_{18} (*n*-octane)	−15[a]	−19[a]
naphthene	C_8H_{16} (cyclooctane)	58.2	71.0
	C_8H_{16} (ethylcyclohexane)	40.8	45.6
Aromatic	C_8H_{10} (ethylbenzene)	97.9	10.4
	C_8H_{10} (*o*-xylene)	100.0	120[a]
	C_8H_{10} (*m*-xylene)	115.0	117.5
	C_8H_{10} (*p*-xylene)	109.6	116.4

[a] Blending value at 20 vol.% in 60 octane number reference fuel.

In the reformer, multiple reactions occur simultaneously. This process is endothermic and is subject to carbon laydown; thus, refiners must regenerate reforming catalysts. Several catalyst-regenerating approaches are possible. Semi-regenerative processes use moving-bed catalyst reactors. The catalyst bed reactors are placed side-by-side, and hydrogen is used to lift and convey the catalyst to the next bed, except for the last bed where it is regenerated, as shown in Fig. 18.17.[12] Other reforming designs use a continuous moving

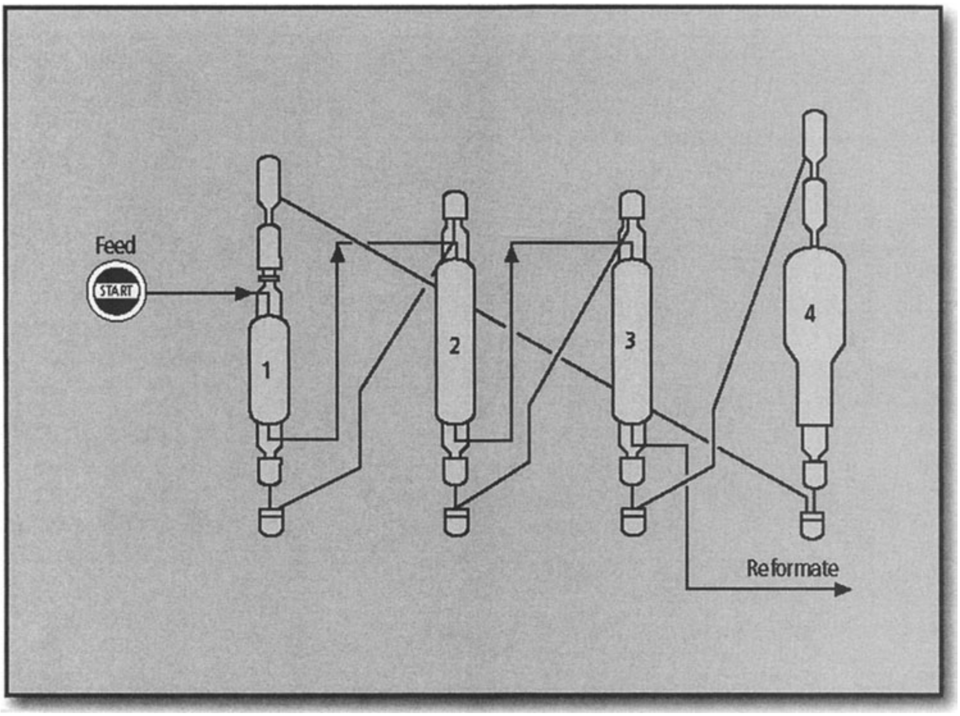

Fig. 18.17. Catalytic reforming—Axens. Includes moving-bed reactors (1,2,3) and regenerator (4). (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright Gulf Publishing Co., all rights reserved.)

bed to continuously regenerate a portion of the catalyst. The reactors are stacked on top of each other, and gravity moves the catalyst through the bed. From the last reactor, the catalyst is lifted by nitrogen or hydrogen to a catalyst collection vessel. The catalyst is regenerated in a regeneration tower and returned to process as shown in Fig. 18.18.[12]

In the catalytic reforming process, the feed is pumped to operating pressure and mixed with a hydrogen-rich gas before heating to reaction temperatures. The net hydrogen produced is a by-product of the dehydrogenation and cyclization reactions. Several reactions occur:

- Dehydrogenation of naphthene
- Isomerization of paraffins and naphthenes
- Dehydrocyclization of paraffins
- Hydrocracking and dealkylation of paraffins[14]

Reforming catalysts promote these reforming reactions. Isomerization is a desired reaction, especially to raise the octane value of the product. However, hydrocracking is an undesired side-reaction that produces light gases. Higher operating pressures are used to suppress hydrocracking. Unfortunately, higher operating pressures suppress reforming reactions also. Generally, a compromise is made between the desired reforming and undesired hydrocracking. The effects of operating conditions on competing reactions are shown in Table 18.7.[23]

In the late 1960s, it was discovered that adding certain promoters such as rhenium, germanium, or tin to the platinum-containing catalyst would reduce cracking and coke formation. The resulting bi-metallic and tri-metallic catalysts facilitate a lower operating pressure without fostering hydrocracking conditions. Earlier reforming pressures ranged around 500 psig; with improved catalyst systems, such operations now use operating pressures of 170–370 psig.[12] Advances in continuous catalyst design permit using operating pressures as low as 50 psig.[12]

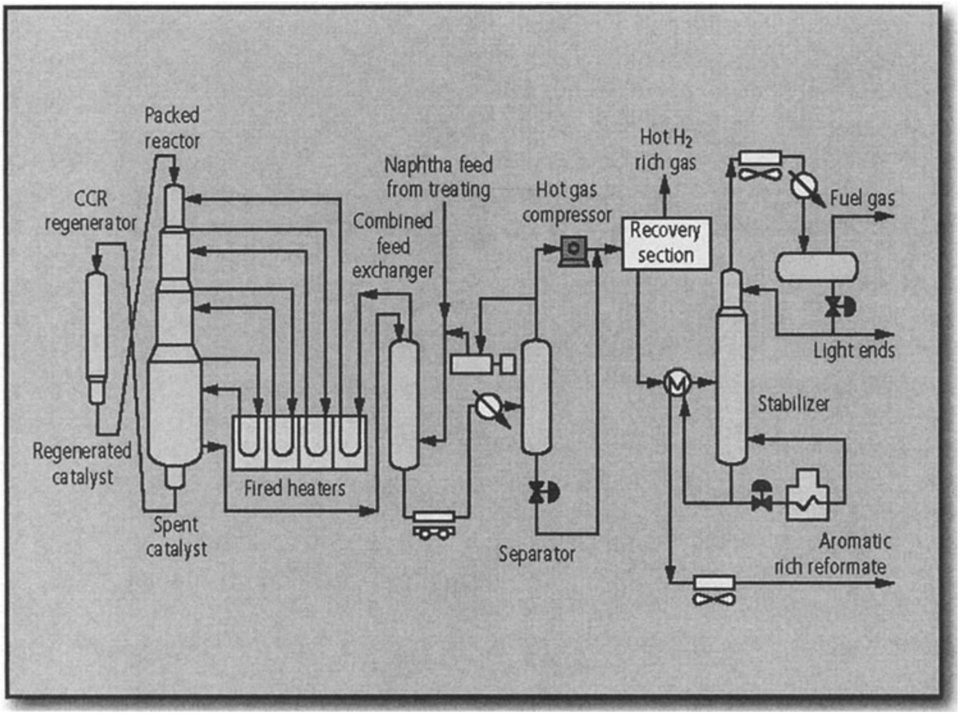

Fig. 18.18. Catalytic reforming—UOP LLC. Includes stacked reactor(s) and regenerator with product separation (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

TABLE 18.7 Favored Operating Conditions for Desired Reaction Rates[23]

Feed	*Reaction*	*Product*	*Desired rate*	*To Get Desired Rate* *Press.*	*Temp.*
Paraffins	Isomerization	Iso-paraffins	Inc.	Inc.	Inc.
	Dehydrocyclization	Naphthenes	Inc.	Dec.	Inc.
	Hydrocracking	Lower mol. wt.	Dec.	Dec.	Dec.
Naphthenes	Dehydrogenation	Aromatics	Inc.	Dec.	Inc.
	Isomerization	Iso-paraffins	Inc.	Inc.	Inc.
	Hydrocracking	Lower mol. wt.	Dec.	Dec.	Inc.
Aromatics	Hydrodealkylation	Lower mol. wt.	Dec.	Dec.	Dec.

Operating temperatures are also critical. The listed reactions are endothermic. The best yields occur along isothermal reaction zones, but are difficult to achieve. Instead, the reaction beds are separated into a number of adiabatic zones operating at 500–1000°F with heaters between stages to supply the necessary energy to promote reaction of heat and hold the overall train near or at a constant temperature. Three or four zones are commonly used to achieve high-octane products.

Catalytic Cracking

This process upgrades heavier products into lighter products, as shown in Fig. 18.19. Catalyst systems are used to catalytically crack the large, heavy hydrocarbons into

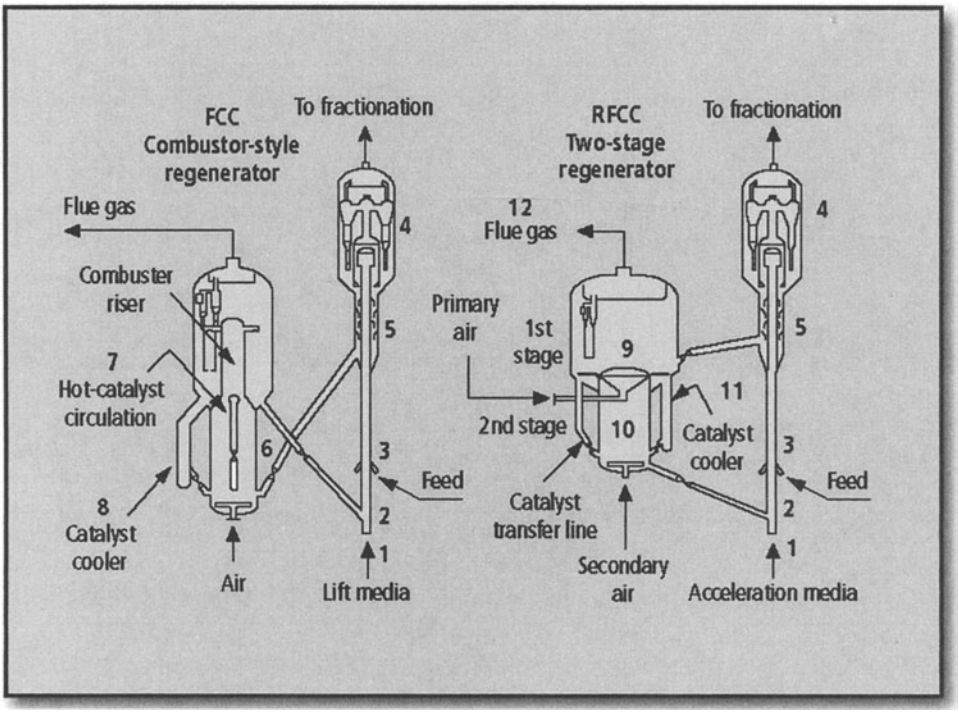

Fig. 18.19. Fluid catalytic cracking—UOP LLC. Combustor style is used to crack process gas oils and moderately contaminated resids, while the two-stage unit is used for more contaminated oils. (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

smaller compounds. The products contain a higher hydrogen-to-carbon ratio than the feed. Consequently, excess carbon is produced, which can deposit on the catalyst and piping and equipment walls; both effects are undesirable.[9]

A typical catalytic cracking unit is shown in Fig. 18.19. The unit comprises two large vessels: one to react feed with hot catalyst and the other to regenerate the catalyst by burning off the carbon deposits with air.[12] The key feature of the catalytic cracking operation is the short contact time between the catalyst and feed to produce the desired product. Extended contact between the feed and catalyst promotes overcracking and the creation of gases. The activity of newer catalysts selectively promotes primary cracking reactions. New catalysts use a distributed matrix structure; zeolites are applied to the surface and pores of the catalyst, thus increasing the number of active sites.[24] With more active sites, the activity of the catalysts increases and less contact time is necessary.

The short contact time is accomplished by using a transfer line between the regenerator and the reactor vessels. Most of the reaction occurs within the riser section.[9,12,14] A termination device can be used to separate the catalyst from the products that are taken quickly as overhead. The main reactor vessels contain cyclone separators to remove the catalyst from the products and provide additional space for cracking the heavier fraction of the feed.

In the fluidized catalytic cracking (FCC) process, the feed is injected into the reactor through a feed-nozzle system and mixed with the catalyst. The atomized oil mixes with the catalyst and ascends the riser. The cracking process—*riser cracking* or short-time contacting—has several advantages. This system can operate at high temperatures, thus promoting the conversion of feed into gasoline

TABLE 18.8 Typical Gasoline Pool Composition of a Refinery[25]

Gasoline Blendstocks	*Percent of Pool Volume*	*Percent of Pool Sulfur*
Alkylate	12	—
Coker naphtha	1	1
Hydrocracked naphtha	2	—
FCC naphtha	36	98
Isomerate	5	—
Light straight-run naphtha	3	1
Butanes	5	—
MTBE	2	—
Reformate	34	—
Total	100	100

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and olefins. It minimizes the destruction of any aromatics formed during cracking. The net effect is gasoline production with two to three higher octane.

The catalyst is regenerated at high temperatures (1300–1400°F). Coke that is deposited on the catalyst is quickly burned off with high-temperature air. Newer catalysts are rugged and can withstand the rigors of extreme heat and fluidizing.

The catalytic cracking unit is often referred to as the gasoline workhorse of a refining unit. As shown in Fig. 18.9, feeds to the catalytic cracking unit are gas oils from the atmospheric and vacuum distillation columns and delayed coker. These heavier fractions also carry metals such as nickel, vanadium, and iron. More important, sulfur compounds concentrate in the heavier product fractions. Table 18.8 lists a typical mass balance for sulfur.[25] FCC blendstocks comprise 36 percent of the volume of the gasoline pool. However, this stream also contributes 98 percent of the sulfur concentration to blended procucts.[25] As specifications on sulfur concentrations in diesel and gasoline tighten, more efforts are focused on how feeds and product streams from the FCC are pre- and posttreated for sulfur concentrations.

Coking

Coking is an extreme form of thermal cracking. This process converts residue materials—products that are pumpable but not easily changed into lighter products through catalytic cracking. Coking is a less expensive method to convert these residual fractions into lighter products. In the coking process, the coke is considered a by-product; its creation is tolerated in the interest of converting the bulk of the residuals into lighter products. The by-product coke can be sold as feedstock to power-generating utility companies. Electricity utility operations burn clean coke to generate high-pressure steam and power. Thus, refiners can sell coke to their over-the-fence power companies and, in return, purchase steam and electricity.[26]

A typical flow diagram for a delayed coker is shown in Fig. 18.20. Several processing configurations are possible. In this example, the feed is sent directly to the product fractionator to pick up heavier products to be recycled to the cracking operation. The term "delayed coker" indicates that the furnace adds the heat of cracking, and the cracking occurs during the long residence time in the coking drums. The feed and recycled products are heated by the coker heater to the desired operating temperature (900–950°F) and then sent to the coking drum, where partial vaporization occurs in addition to mild cracking at pressures ranging between 15 and 90 psig. Overhead vapors from the coke drum are sent to the fractionator and separated into lighter products such as refinery fuel gas, LPG, (coker) naphtha, and light and heavy gas oils.[12] The by-product coke accumulates in the coke drum.

The coking process uses several parallel coking drums. One drum is online while the other is being emptied. At the end of the coking cycle, the coke is steamed to remove any residual oil-liquid.[12,14] This mixture of steam and hydrocarbons is sent to the fractionator to recover hydrocarbons. The drum is cooled with water and then drained. After the coke drum is unloaded, high-pressure water jets are used to cut away the coke from the drum. Conveyors are used to move the coke to storage.

Fluid coking is a proprietary name given to a different type of coking process. In this process the coke is suspended as particles in

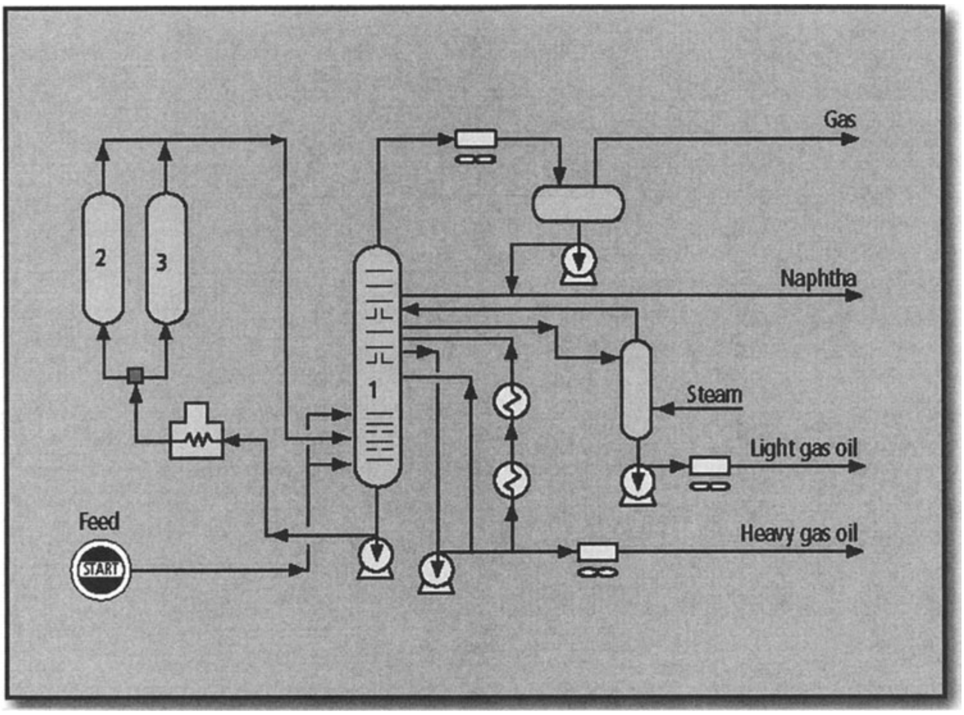

Fig. 18.20. Coking—Foster Wheeler and UOP LLC. Includes feed/product fractionator (1), coke drums (2,3), and vapor recovery. (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright by Gulf Publishing Co., all rights reserved.)

fluids that flow from a reactor to a heater and back again. When the coke is gasified, the process is called *flexicoking*. Both fluid coking and flexicoking are proprietary processes of ExxonMobil Research & Engineering Co.

A flow diagram for the flexicoking process is shown in Fig. 18.21. The first two vessels are typical of fluid coking, in which part of the coke is burned in the heater to provide hot coke nuclei to contact the feed in the reactor vessel. The cracked products are quenched in an overhead scrubber where entrained coke is returned to the reactor. Coke from the reactor circulates to the heater where it is devolatilized to yield light hydrocarbon gas and residual coke. A sidestream of coke is circulated to the gasifier, where, for most feedstocks, 95 percent or more of the gross coke is gasified at elevated temperature with steam and air. Sulfur entering the system is converted to hydrogen sulfide, exits the gasifier, and is recovered by a sulfur-removal step.

Hydrocracking

Before the late 1960s, most hydrogen used in processing crude oil was for pretreating catalytic reformer feed naphtha and for desulfurizing middle-distillate products. Later, sulfur requirements for fuels were lowered and became an important consideration. The heavier fractions of crude oil are the fractions with the highest sulfur concentrations and are more difficult to treat. With a constant decline in demand for heavy fuel oils, refiners needed to convert heavier fractions into lighter products. Thus, hydrocracking became a possible solution to the problem.

Figure 18.22 is a typical flow diagram of a hydrocracking process. The process is similar to hydrotreating. The feed is pumped to operating pressure, mixed with hydrogen-rich gas, heated, passed through a catalytic reactor, and distributed among various fractions. Yet this process significantly differs from hydrotreating. In the hydrocracking process, operating pressures are very high: 1500–3500 psia.

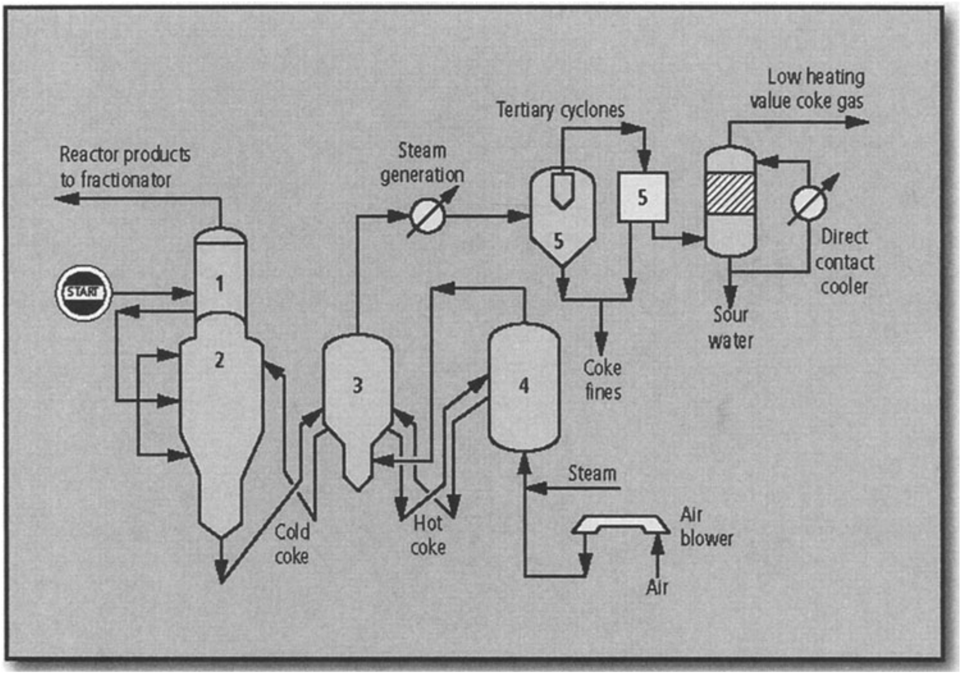

Fig. 18.21. Fluid coking (Flexicoking)—ExxonMobil Research and Engineering Co. Includes: reactor (1), scrubber (2), heater (3), gasifier (4), and coke fines (5). (Source: *Hydrocarbon Processing 2004 Refining Process Handbook*. CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

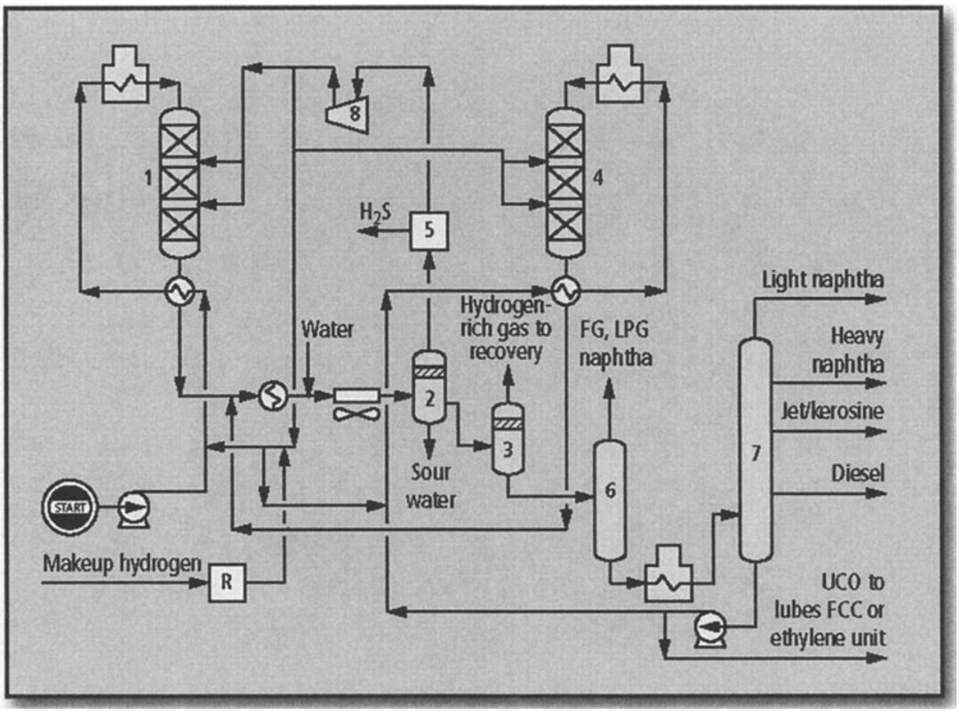

Fig. 18.22. Hydrocracking—Chevron Lummus Global LLC. Includes: staged reactors (1,4), HP separators (2,5), recycle scrubber (3), LP separator (6), and fractionation tower (7). (Source: *Hydrocarbon Processing 2004 Refining Process Handbook*. CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

Hydrogen consumption is also greater: 1200–1600 scf of hydrogen per barrel of feed, depending on the extent of cracking.[19] If the refinery has a high hydrogen demand due to hydrocracking needs, construction of an onsite hydrogen plant may be necessary.

Hydrocracking catalysts perform a dual function. They drive both hydrogenation and dehydrogenation reactions and have a highly acidic support to foster cracking reactions. The hydrogenation–dehydrogenation components of the catalyst are metals such as cobalt, nickel, tungsten, vanadium, molybdenum, platinum, palladium, or a combination of these metals. The acidic support can be silica–alumina, silica–zirconia, silica–magnesia, alumina–boria, silica–titania, acid-treated clays, acidic-metals phosphates, or alumina, to name a few.[27]

Greater flexibility is attributed to most hydrocracking processes. Under mild conditions, the process can function as a hydrotreater. Under severe conditions (high pressure and temperatures) this process can produce a variety of motor fuels and middle distillates, depending on the feedstock and operating variables. Even greater flexibility is possible if the process is tailored to convert naphthas into liquefied petroleum gases or convert heavy residues into lighter products.

Hydrocracking is a swing process; it is a treater and a cracker. Thus, this process function can be incorporated into a number of different places within a refining scheme. As a cracker, it can convert feeds that are too heavy or too contaminant-laden to go to catalytic cracking. As a treater, it can handle high boiling-point fractions such as heating oil and saturate this fraction to provide good burning quality.

With pending low-sulfur fuel specifications, hydrocracking efforts will be increased to break complex hydrocarbon compounds and expose embedded sulfur molecules. Notably hydrocracking significantly upgrades feeds to downstream processes and fuel products, especially diesel products.

Alkylation

Another method to convert light olefins into gasoline-blending stocks is alkylation. In this process, light olefins—propylene, butylenes, and amylenes with isobutane—are reacted in the presence of strong acids to form branched chain hydrocarbons. These branched hydrocarbons, often referred to as alkylate, have a high-octane value; thus, it is an excellent contributor to the octane pool.[9,12,14,16]

A flow diagram of an alkylation unit using sulfuric acid is shown in Fig. 18.23. Alkylation traditionally combines isobutane with propylene and butylene using an acid catalyst, either hydrofluoric (HF) acid or sulfuric acid. The reaction is favored by high temperatures, but competing reactions among the olefins to give polymers prevent high-quality yields. Thus, alkylation is usually done at low temperatures to deter polymerization reactions. Temperatures for HF acid-catalyzed reactions are approximately 100°F, and for sulfuric acid they are approximately 50°F.[14] Notably, some acid loss occurs with this process. Approximately 1–1.2 lb of HF acid/bbl of alkylate is consumed, and 25–30 lb of sulfuric acid/bbl of alkylate is consumed. The alkylation feed should be dried and desulfurized to minimize acid loss. Because the sulfuric-acid-catalyzed reactions are carried out below normal atmospheric temperatures, refrigeration facilities are needed.

As shown in Fig. 18.23, dry liquid feed containing olefins and isobutane is charged to a combined reactor–settler. In this example, the reactor uses the principle of a differential gravity head to circulate through a cooler before contacting a highly dispersed hydrocarbon feed in the reactor pipe. The hydrocarbon phase, generated in the settler, is sent to a fractionator, which separates LPG-quality propane, isobutane recycle, *n*-butane, and alkylate products. A small amount of dissolved catalyst is also removed from the propane product by a small stripper tower.

Environmental and safety concerns regarding acid-based processes are promoting research and development efforts on solid-acid alkylation processes. Liquid catalysts pose possible risks to the environment, employees, and the general public from accidental atmospheric releases. Also, these acid

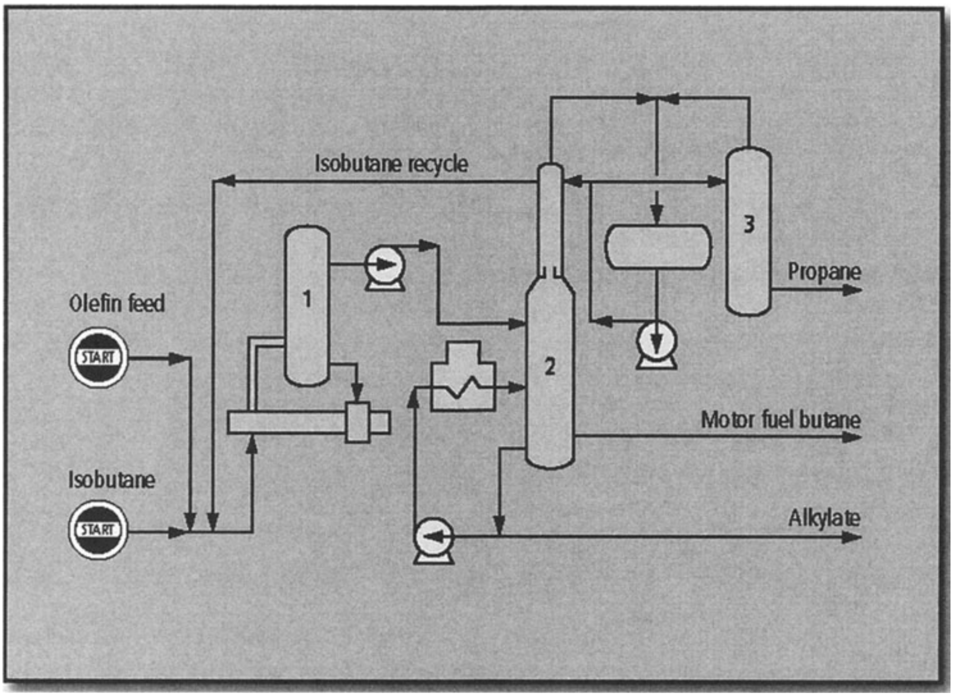

Fig. 18.23. Alkylation—Technology Solutions Division of ConocoPhillips. Include combination reactor/settler (1), main fractionator (2), and small propane stripper (3). (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook*. CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

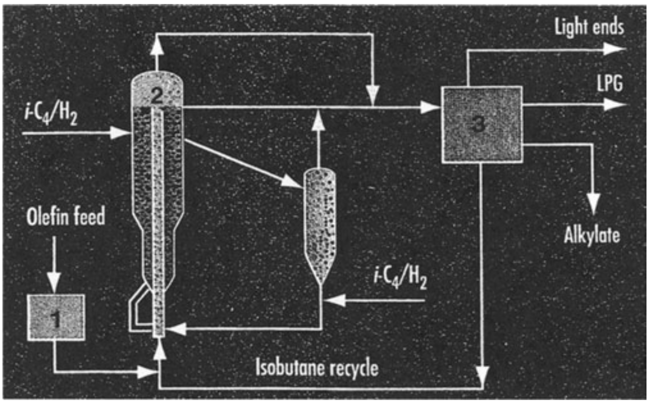

Fig. 18.24. Alkylation—UOP LLC. Solid Catalyst System removes impurities from the feed (1), clean feed, recycled isobutene, and catalyst and feed to main reactor (2), and final product are separated in fractionation section (3). (*Hydrocarbon Processing*, 79, No. 11. Nov. 2000: copyright 2000 by Gulf Publishing Co., all rights reserved.)

catalysts must be regenerated, another reliability and safety issue. Thus, research efforts are directed at investigating other methodologies to produce high-octane alkylation gasoline component streams.

UOP LLC has developed two alternate processes for liquid-acid alkylation. The direct alkylation method, Alkylene, uses a packed moving catalyst bed. The feed is pretreated to remove impurities such as diolefins, sulfur, oxygen, and nitrogen compounds. These components suppress catalyst activity and can also permanently deactivate the catalyst. As shown in Fig. 18.24, the olefinic feed

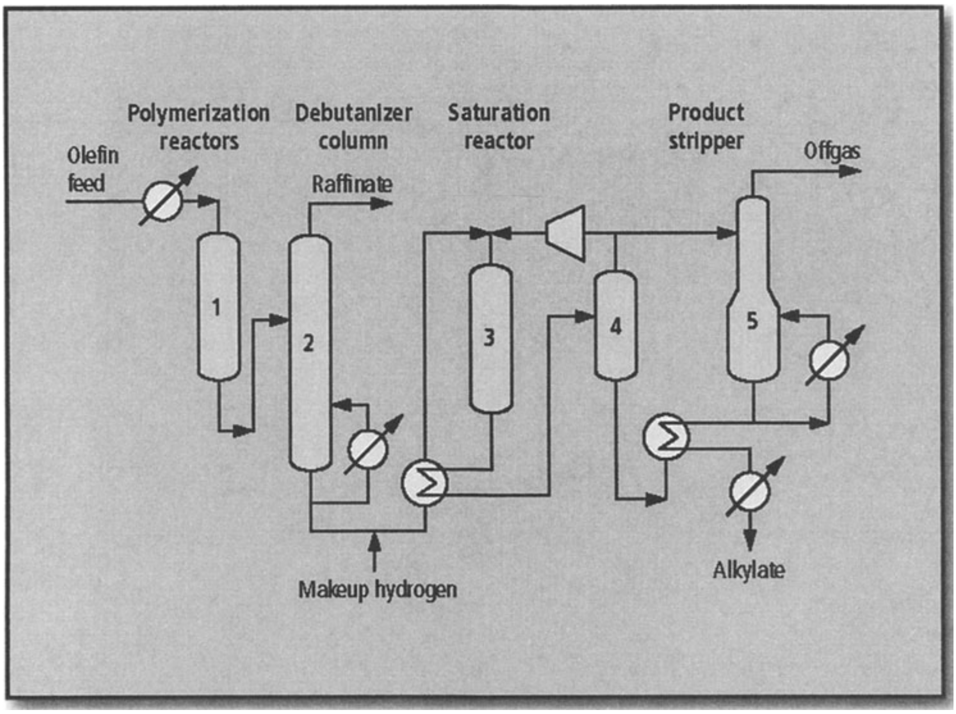

Fig. 18.25. Alkylation (indirect)—UOP LLC. Process uses solid catalyst; major processing steps include: polymerization (1), hydrogenation reactor (2), hydrogen recovery (3), and product stabilization (4). (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

and isobutane are combined and injected at the bottom of the riser, where the alkylation reaction occurs. At the exit of the riser the catalyst is separated from the hydrocarbons and flows by gravity to the reactivation zone.[12,28] The hydrocarbon stream is sent to the fractionation (distillation) section, where alkylate product is separated from the light paraffins and LPG product. Isobutane is recycled back to the main reactor. For this process, the feed is partially dehydrogenated to remove diolefins.

A second indirect alkylation process, InAlk, is also a solid catalyst process (Fig. 18.25).[12,29] InAlk combines two commercially proven technologies: polymerization and olefin saturation. Isobutylene is reacted with light olefins (C_3–C_5) in a polymerization reactor. The resulting mixture of iso-olefins is saturated in the hydrogenation reactor. Excess hydrogen is recycled and the product is stabilized to produce a paraffinic gasoline blending stream. Yet, new solid-acid alkylation processes face technical challenges. Solid-acid catalysts remain more difficult to regenerate and have a shorter service life. Research to overcome these operating problems is continuing.

Ether Processes

Refiners have always incorporated ethers into the gasoline pool when needing to increase octane. Ethers provide a high-octane stream with low vapor pressure. Beginning in 1995, United States reformulated gasoline (RFG) was required to have 2 wt.% oxygenate content. The choice of oxygenate was left to the refiners' discretion. Initially, the ethanol industry had hoped that ethanol would be selected as the primary oxygenate for RFG. However, refiners searched for other options. Methyl tertiary butyl ether (MTBE) became the oxygenate of choice for blending RFG. It is produced by reacting methanol with isobutylene, as shown in Fig. 18.26.[38] Other ether compounds can be made by a similar

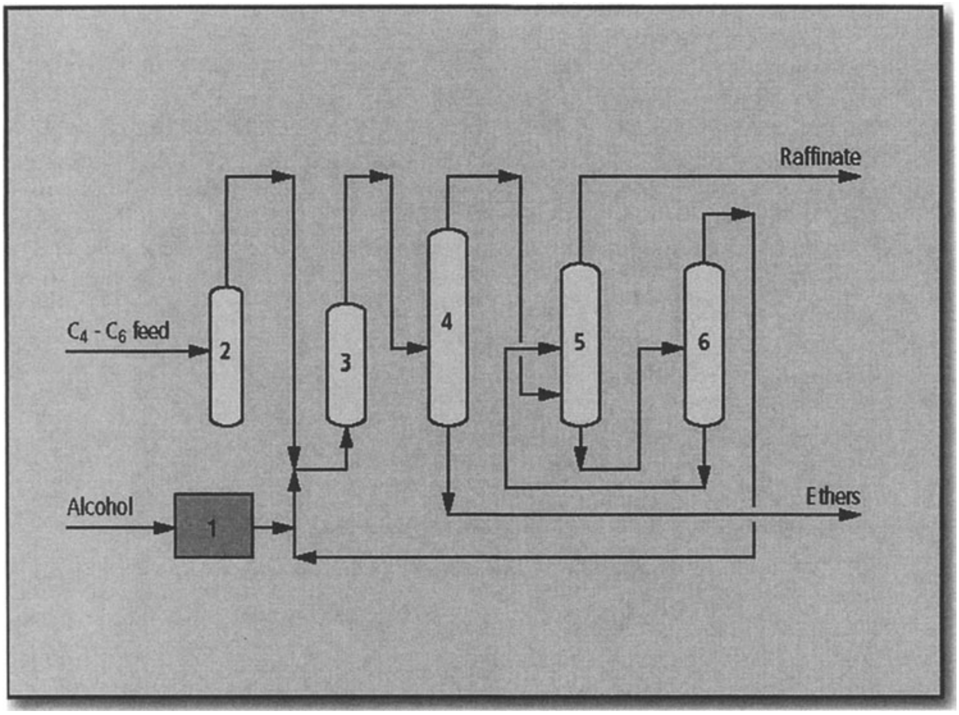

Fig. 18.26. Ethers—Axens. Includes: alcohol purification (1), hydrocarbon purification (2), main reactor (3), reactive distillation system (4), wastewater system to remove water from the raffinate (5), and product fractionation column (6). (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

process. Ethyl tertiary butyl ether (ETBE) is produced from ethanol and isobutylene; tertiary amyl methyl ether (TAME) is made from methanol and isoamylene. MTBE holds the lion's share of the oxygenate market.

Presently, MTBE's usage is at the center of a highly emotional, political struggle. As refiners began using MTBE at the 2 wt.% concentration, this ether was detected at trace levels in drinking water supplies in areas required to use RFG. Leaking underground storage tanks (USTs) were identified as the primary source for MTBE found in drinking water. The ether is found in water due its high affinity for water. Legislation was (and is) in place that required UST owners to install safeguards to prevent leakage; however, leakage did occur.

Because drinking water was affected by leakage from USTs, a political effort is underway to ban the use of MTBE in gasoline. At the time of this writing, much debate is ongoing. The State of California and several other states have banned using MTBE in RFG. However, the consequence of shortages in RFG supplies has raised some doubts and caused second thoughts on the MTBE ban.

Oxygenate usage is also required for gasolines supplied to nonattainment areas. The sister ethers—ETBE and TAME—are under the same disfavor as MTBE and are not logical replacements. Ethanol can be a substitute for MTBE; however, it also brings other problems. Ethanol usage raises the Reid vapor pressure of the fuel, which is also limited by fuel specifications. In the United States, ethanol receives an agricultural subsidy that elevates its price. In the United States market, ethanol capacity is located far from refining centers and fuel terminals; thus, transportation, distribution, and storage issues are challenges for ethanol.[30] Of course, the ultimate fate of MTBE capacity constructed in the mid-1990s to meet RFG blending demand is yet to be determined.

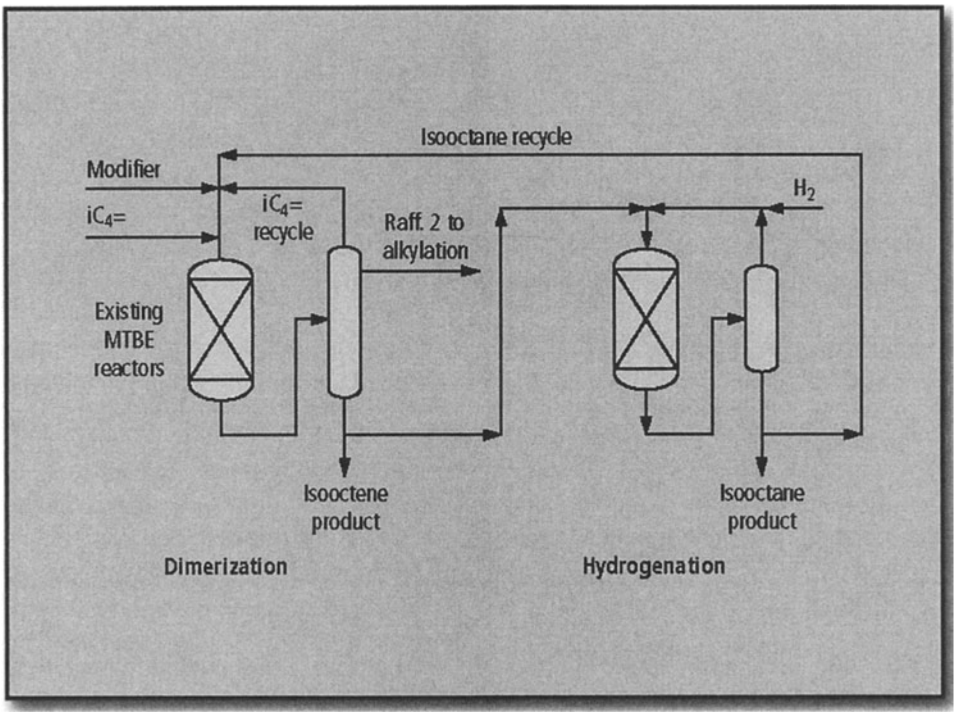

Fig. 18.27. Isooctane—Lyondell Chemical and Aker Kvaerner. Includes dimerization section and hydrogenation section. (Source: *Hydrocarbon Processing, 2004 Refining Process Handbook.* CD-ROM. September 2004: copyright 2004 by Gulf Publishing Co., all rights reserved.)

Should MTBE be banned, what would be the logical replacement(s)? There are several options available. Several refiners opted to build MTBE capacity and avoid purchasing the ether on the open market. MTBE units were an option to use the facility's isobutylenes. Several licensed processes can be used to convert existing MTBE units. Kvaerner and Lyondell Chemical Co. offer technologies to convert an MTBE unit to produce iso-octane, as shown in Fig. 18.27.[12] Snamprogetti SpA and CDTECH also have an iso-octene/iso-octane process. These processes can use various feedstocks such as "pure" iso-butane, steam-cracked C_4 raffinate, 50/50 iso-butane/iso-butene feeds, and FCC butane–butane streams. The process selectively dimerizes C_4 olefins to iso-octene and then hydrogenates the iso-octene (di-iso-butene) into iso-octane. The processes were developed to provide an alternative to MTBE. The dimerization reactor uses a catalyst similar to that for MTBE processes; thus, the MTBE reactor can easily be converted to iso-octane service. The product is low sulfur with 100 octane number, great for gasoline blending.[31]

FUTURE TRENDS

The refining industry is constantly required to meet cleaner fuel specifications. The only certainty is that, globally, fuels are becoming cleaner. Yet, clean fuels comprise a very broad spectrum that is totally dependent on the market served. In Asia and some parts of Europe, lead removal still remains a key issue. These refiners strive to maintain octane while phasing out lead. In other markets, more complex issues remain to be solved.

In developed markets, cleaner-fuel issues revolve around several product specifications. The fuels market is at various stages of removing sulfur and aromatics from gasoline and diesel. For global organizations, formulating a clean-fuels agenda is a very market-dependent issue, as shown in Table 18.4.

Costs and Drivers

So how much investment will be made to process low-sulfur fuels? A recent Energy Information Administration (EIA) report estimates that U.S. refiners will invest $6.3–9.3 billion to reach full compliance with the ultra-low sulfur diesel (ULSD) rule through 2011.[33] For Europe, refiners made investments of nearly $22.9 billion from 1997 to 2005 to meet gasoline and diesel specifications. From 2005 to 2015, an additional $9.7–14 billion may be spent on improving the quantity and quality of middle distillates in Europe.[15] Thus, considerable investment will be necessary to bring cleaner fuels to market.

A true unknown, beside how much a clean-fuels program will cost individual organizations, is how many refiners will make such an investment. Developed markets suffer from diminished demand growth for products. Mediocre returns from earlier environmental projects taint possible returns on future spending. With such a backdrop, hesitancy on expected spending is anticipated. Yet, the deadlines draw nearer, and plans must be formulated.

Drivers for investment are directly linked to market demand. In the European Union, gasoline demand is declining, whereas demand for diesel is increasing with modest increases for treating gas oil. Heavy fuel oil demand is also declining. Under such market forces, the E.U. product market is shifting and demand for middle distillates is increasing from 310 million tons (310 MMt) in 1997 to 390 MMt in 2015.[15] Production of LPG, naphtha, and other products is expected to increase.[15]

Under such conditions, the focus of retrofitting and revamping existing units will be optimizing middle-distillate production. Consequently, to meet higher quality requirements for middle distillates, E.U. refiners are projected to invest in hydrocracking capacity. Such investments may include standalone units and moderate conversion of units upstream of the FCC.[15] Refiners will also raise hydrotreating capability.

Technology Options

Due to the individuality of each refinery, multiple solutions are available. Selection will be directed toward final product slates for each facility. For gasoline-oriented facilities, several options are available. These are discussed below.

Sweetening. This application is most effective in treating straight-run (SR) gasoline streams. Amines are used to remove mercaptan species from the hydrocarbon stream. Caustic converts the mercaptans into disulfides, which are extracted by gravity separation or an extractive solvent.[12]

Hydrotreating. This treatment is used widely throughout the refinery. Hydrogen is reacted with the processing stream with a catalyst to remove sulfur compounds. Several licensed technologies are available at varying temperature and pressure ranges (Table 18.9).[34–36] Hydrotreating, depending on the severity of process conditions, effectively removes sulfur, nitrogen, metals, carbon residue, and asphaltene from the hydrocarbon stream. Mild hydrotreating—low pressure and temperature—removes sulfur and trapped metals and is done as a cleanup/upgrade step for downstream processes such as hydrocrackers, FCCs, resid catalytic crackers, and cokers. Processing streams typically treated include: naphthas, kerosenes, distillates, and gas oil (Fig. 18.9). This process consumes hydrogen.

For a conventional hydrotreating process, the process stream is heated and mixed with hydrogen. This stream is charged to a reactor filled with a high-activity catalyst. Single and multiple reactors can be used. Excess hydrogen is used. The reactor effluent is cooled and separated, and the hydrogen-enriched gas is recycled. Depending on sulfur levels of the feed, the hydrogen recycle may be amine scrubbed to remove hydrogen sulfide (H_2S). The liquid product is steam-stripped to remove lighter components and residual H_2S, and/or fractionated into multiple products.[12]

TABLE 18.9 Available Licensed Post-treating Technologies[34–36]

Approach	*Process Name*	*Technology Provider*
Conventional hydrotreating	Hydrotreating	Many
Selective hydrotreating	Scanfining	ExxonMobil
	Prime G	IFP
	Octgain 125	ExxonMobil
	Octgain 220	ExxonMobil
	ISAL	UOP LLC
Catalytic distillation	CDHydro/CD HDS	CD Tech
Adsorption	S Zorb SRT	Phillips Petroleum
Olefinic alkylation	Olefin alkylation of thiophenic sulfur	BP
Extractive mass	Exomer	ExxonMobil and Merrichem

As sulfur levels for products continue to decrease, refiners strive to systematically remove sulfur from the blending pool. Notably, back integration to strategically and systematically remove sulfur compounds throughout the processing scheme is needed. Lower sulfur specs now mandate removing complex sulfur species from various blending streams.

Hydrotreating is an effective method to desulfurize products. However, as desulfurization requirements continue to increase, newer, high-activity catalyst systems will be required to meet desulfurization targets. Existing capacity can be retrofitted with better catalyst systems. Improved reactor internals can more efficiently distribute feed throughout the reactor, optimize contact of reactants with the catalyst, and increase desulfurization efficiency. Refiners may elect to raise operating severity by increasing operating temperatures. However, higher operating temperatures can reduce the service life of the catalyst. Raising operating pressures is not viable and will depend on the pressure rating of the existing reactor. Yet, the new fuel specifications may warrant installing new reactor capacity.

As processing conditions increase, that is pressure and temperature, the hydrotreating process emerges more as a hydrocracking/hydrodesulfurization/hydrodearomatizing event. Deeper desulfurization of processing/product streams is inevitable.

Sulfur Segregation. Another option is to concentrate sulfur compounds into various streams and selectively treat them. Refiners can undercut* product; however, such tactics will reduce yields. For diesel, undercutting will lower diesel yield and increase gas-oil products, an undesirable consequence.

Desulfurization. As refiners strive to meet tighter restrictions on sulfur in product and blending streams, desulfurization technologies are attracting more interest. For gasoline, licensed posttreatment processes that are targeted at specific streams have high interest. Half the battle for clean fuels is identifying the highest sulfur contributors to the blending pool. For gasoline-oriented facilities, the FCC unit is the highest contributor. Nearly 95–98 percent of the sulfur present in blended gasoline is linked to FCC product cuts. Notably, FCC technology is instrumental in upgrading heavier refining streams into desired products. The school of thought for FCC is split between pretreating FCC feed and posttreating. Pretreating offers some great benefits. In particular, hydrotreating feed streams to the FCC upgrades the feed by removing sulfur and nitrogen compounds and saturates some

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*Undercutting is using distillation temperatures that are below the specification for the product. The refiner loses some light product to higher-temperature products as insurance to meet light-product specifications. It is product "give-away" and not a good practice.

aromatics. It can increase LPG and gasoline production, while reducing regenerator-SO_x emissions, light-cycle oil (LCO), and clarified-slurry oil (CSO) yields, and minimizing coke formation.[25,37] More important, it is reported that hydrotreating does not affect naphtha octane values.[25] However, hydrogen consumption becomes a limiting issue. The available hydrogen balance will affect how much hydrotreating can be done economically.

Another pretreat option is to replace hydrotreating the FCC feed with partial conversion hydrocracking operations. There are several variations to the process. However, partial conversion hydrocracking operation splits the FCC feed. Difficult-to-convert materials such as LCO and coker gas oils can be upgraded with hydrotreating and hydrocracking before being sent to the FCC unit. UOP LLC's Unicracking process uses two reactors and separates the hydrotreating and hydrocracking processes into distinct zones, as shown in Fig. 18.28. The sulfur content determines the severity of the hydrotreating reactor. This process is estimated to yield more naphtha and distillates than other desulfurization methods.[25] It also produces a higher quality diesel (cetane index of 50).

The Axen's mild hydrocracking process combines an ebullated-bed, mild hydrocracking process with an inline fixed-bed to pretreat FCC feed. The T-Star process can treat vacuum gas oil (VGO) and deasphalted oils, and offers high selectivity toward diesel products. The efficient catalyst system enables more flexibility for processing various FCC feeds. The feed streams are cracked first and then hydrotreated.

Post-treating processes hold keen interest also. Table 18.9 lists several post-treating methods. Many of the newer processes recently have been commercially demonstrated and several commercial units have been completed and are now in operation. How effective these new processes will prove to be remains to be seen.

Tomorrow's fuels will contain less sulfur to be compatible with the more sophisticated engine designs of new automobiles. Fuels specifications will further reduce the concentrations of gasoline compounds that are listed and/or considered to be toxic. Refiners will continue to upgrade heavier components to lighter products and refineries will continue to use innovative catalysts and processing equipment to cost-effectively manufacture fuels and petrochemical feedstocks. We have barely touched on the sophisticated engineering needed to transform a barrel of crude oil into consumable products.

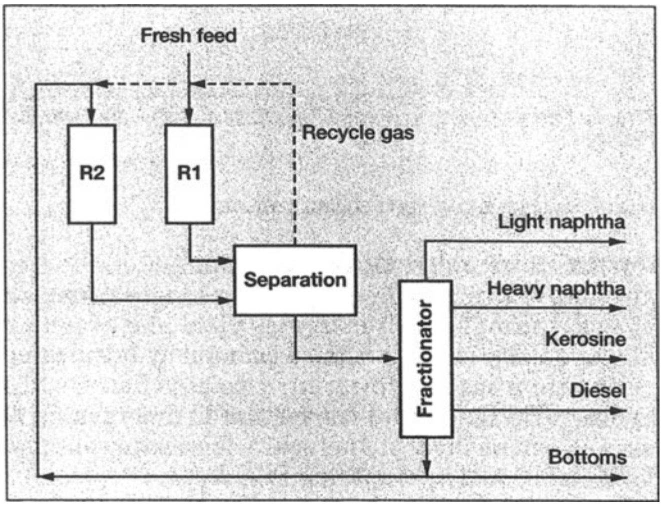

Fig. 18.28. Two-staged, partial-conversion hydro cracking process.[25] (Copyright 1999 by Gulf Publishing Co. and reprinted by permission of the copyright owner. All rights reserved.)

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