# PETROLEUM REFINERY PROCESSES

## 1. Introduction

Petroleum (also called *crude oil*), in the unrefined or crude form, like many industrial feedstocks has little or no direct use and its value as an industrial commodity is only realized after the production of salable products. Even then, the market demand dictates the type of products that are needed. Therefore, the value of petroleum is directly related to the yield of products and is subject to the call of the market.

Petroleum refining, also called petroleum processing, is the recovery and/or generation of usable or salable fractions and products from crude oil, either by distillation or by chemical reaction of the crude oil constituents under the effects of heat and pressure. Synthetic crude oil, produced from tar sand (oil sand) bitumen, is also used as feedstocks in some refineries. Heavy oil conversion (1), as practiced in many refineries, does not fall into the category of synthetic fuels (syncrude) production. In terms of liquid fuels from coal and other carbonaceous feedstocks, such as oil shale, the concept of a synthetic fuels industry has diminished over the past several years as being uneconomical in light of current petroleum prices.

As the basic elements of crude oil, hydrogen and carbon form the main input into a refinery, combining into thousands of individual constituents and the economic recovery of these constituents varies with the individual petroleum according to its particular individual qualities, and the processing facilities of a particular refinery. In general, crude oil, once refined, yields three basic groupings of products that are produced when it is separated into a variety of different generic, but often overlapping fractions (Table 1). The amounts of these fractions produced by distillation depend on the origin and properties of crude petroleum (2).

The gas and gasoline cuts form the lower boiling products and are usually more valuable than the higher boiling fractions and provide gas (liquefied petroleum gas), naphtha, aviation fuel, motor fuel, and feedstocks, for the petrochemical industry. Naphtha, a precursor to gasoline and solvents, is extracted from both the light and middle range of distillate cuts and is also used as a feedstock for the petrochemical industry. The middle distillates refer to products from the middle boiling range of petroleum and include kerosene, diesel fuel, distillate fuel oil, and light gas oil; waxy distillate and lower boiling lubricating oils are sometimes include in the middle distillates. The remainder of the crude oil includes the higher boiling lubricating oils, gas oil, and residuum (the nonvolatile fraction of the crude oil). The residuum can also produce heavy lubricating oils and waxes, but is more often used for asphalt production. The complexity of petroleum is emphasized insofar as the actual proportions of light, medium, and heavy fractions vary significantly from one crude oil to another.

When petroleum occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark-to-light colored liquid, it is often referred to as conventional petroleum. In some oil fields, the downhole pressure is sufficient for recovery without the need for pumping. Heavy oil differs from conventional petroleum in that its flow properties are reduced and it is much more difficult to recover from the subsurface reservoir. These materials have a much higher viscosity and lower API (American Petroleum Institute) gravity than conventional petroleum, and primary recovery of these petroleum types usually requires thermal stimulation of the reservoir.

Heavy oil generally has an API gravity of $<20^\circ$ and usually, but not always, a sulfur content of $>2\%$ by weight. Extra heavy oil occurs in the near-solid state and is virtually incapable of free flow under ambient conditions. Tar sand bitumen, often referred to as native asphalt, is a subclass of extra heavy oil and is frequently found as the organic filling in pores and crevices of sandstones, limestones, or argillaceous sediments, in which case the organic and associated mineral matrix is known as rock asphalt.

A residuum, often shortened to resid, is the residue obtained from petroleum after nondestructive distillation has removed all the volatile materials. The temperature of the distillation is usually $<345^\circ$C because the rate of thermal decomposition of petroleum constituents is substantial $>350^\circ$C. Temperatures as high as 425°C can be employed in vacuum distillation. When such temperatures are employed and thermal decomposition occurs, the residuum is usually referred to as pitch. By inference, the name is used in the same manner as when it refers to the nonvolatile residue from the thermal decomposition of coal tar (3).

Asphalt, prepared from petroleum, often resembles native asphalt. When asphalt is produced by distillation, the product is called residual, or straight-run, asphalt. However, if the asphalt is prepared by solvent extraction of residua or by light hydrocarbon (propane) precipitation, or if it is blown or otherwise treated, the name should be modified accordingly to qualify the product, eg, propane asphalt.

Sour and sweet are terms referring to a crude oil's approximate sulfur content, which relates to odor. A crude oil that has a high sulfur content usually contains hydrogen sulfide, $H_2S$, and/or mercaptans, RSH; it is called sour. Without this disagreeable odor, the crude oil is judged sweet.

## 2. History

The use of petroleum or derived materials, such as asphalt, and the heavier nonvolatile crude oils is an old art (2). In fact, petroleum utilization has been documented for $>5000$ years. The earliest documented uses occurred in Mesopotamia (ancient Iraq) when it was recognized that the nonvolatile derivatives (bitumen or natural asphalt and manufactured asphalt) could be used for caulking and as an adhesive for jewelry or as a mastic for construction purposes. There is also documented use of bitumen for medicinal use.

Approximately 2000 years ago, Arabian scientists developed methods for the distillation of petroleum, which were introduced into Europe by way of the Arabian incursions into Spain. Petroleum, used in China since it was encountered when drilling for salt, appears in documents of the third century. The Baku region of northern Persia was also reported by Marco Polo in 1271–1273 as having a commercial petroleum industry.

Interest in naphtha (nafta) began with the discovery that petroleum could be used as an illuminant and as a supplement to bituminous incendiaries, which were becoming increasingly common in warfare. Greek fire was a naphtha–bitumen (or naphtha–asphalt) mix; the naphtha provided the flame and the bitumen (or asphalt) provided the adhesive properties that prolonged the incendiary effect.

Modern refining began in 1859 with the discovery of petroleum in Pennsylvania. After completion of the first well, the surrounding areas were immediately leased and extensive drilling took place. In the post-1945 era, Middle Eastern countries continued to rise in importance because of new discoveries of vast reserves. The United States, though continuing to be the biggest producer, was also the principal consumer and thus was not an exporter of oil. At this time, oil companies began to roam much farther in the search for oil, which has resulted in significant discoveries in Europe, Africa, and Canada.

The impetus to develop the petroleum refining industry came from several changes in life-styles. The increased needs for illuminants, for fuel to drive the factories of the industrial revolution, for gasoline to power the automobiles, as well as the demand for aviation fuel, all contributed to the increased use of petroleum.

The product slate has also changed. The increased demand for gasoline and lubricants brought about an emphasis on refining crude oil. This, in turn, brought about changes in the way crude oil was refined and led to innovations and developments in the refining industry, thereby giving birth to the integrated petroleum refinery (Fig. 1).

## 3. Feedstock Evaluation

The evaluation of petroleum feedstocks is determined by using a series of staandard test methods that are set by organizations varying from country to country. For example, in the United States, the American Society for Testing and Materials (ASTM) and the American Petroleum Institute (API) are recognized for establishing specifications on both products and methods for testing. In the United Kingdom, it is the Institute of Petroleum (IP); in Germany, it is Deutsche Institut für Normung (DIN); and in Japan, it is the Ministry of International Trade and Industry (MITI).Three frequently specified properties are density–specific gravity–API gravity, characterization factor, and sulfur content (2,4,5).

Many petroleum companies use these standards but many also have their own individual standards that are proprietary and very rarely published.

The API gravity is a measure of density or specific gravity:

$$^{\circ}\text{API} = (141.5/\text{specific gravity}) - 131.5$$

Specific gravity is 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 (15.6°C). This method of measuring density and gravity first arose as a result of the need to define the character of products in more detail; it was natural to extend the measure to crude oils in general.

The Watson characterization factor ($K$) has also been used as a measure of the chemical character of a crude oil or its fractions:

$$K = (T_{\mathrm{B}})^{1/3}/\text{specific gravity}$$

where $T_{\mathrm{B}}$ is the absolute boiling point in degrees Rankine ($^{\circ}\mathrm{R} = 9/5\,\mathrm{K}$) and specific gravity is specific gravity compared to water at 60°F (15.6°C).

For a wide boiling range material such as crude oil, the boiling point is taken as an average of the five temperatures at which 10, 30, 50, 70, and 90% of the material is vaporized. A highly paraffinic crude oil can have a characterization factor as high as 13, whereas a highly naphthenic crude oil can be as low as 10.5, and the breakpoint between the two types of crude oil is ~12.

## 4. Refinery Processes

A refinery is a group of manufacturing plants that vary in number according to the variety of products produced (1,2). Refinery processes must be selected to convert crude oil into products according to demand. A refinery must also be flexible and be able to change operations as needed, especially if heavier oils are the primary feedstocks. This is accomplished through two basic process concepts: carbon rejection (eg, coking processes) and hydrogen addition (eg, hydroprocesses). However, certain downstream processes, such as catalytic reforming, applied to the product streams do not fit into either of these categories.

The conversion of conventional petroleum to products is well established but the conversion of high boiling feedstocks (such as heavy oils and residua) is now in a significant transition period as the demand for transportation fuels increases. In order to satisfy the changing pattern of product demand, significant investments in heavy feedstock conversion processes will be necessary and technologies are needed that will take conversion of these feedstocks beyond current limits and, at the same time, reduce the amount of coke and other nonessential products.

Such a conversion schemes may require the use of two or more technologies in series rather than an attempt to develop a whole new one-stop conversion technology. New processes for the heavy feedstock conversion probably are used perhaps not in place of but in conjunction with of visbreaking and coking options with some degree of hydroprocessing as a primary conversion step. In addition, other processes may replace or, more likely, augment the deasphalting units in many refineries.

There remains room for improving coking and hydroconversion processes by reducing hydrocarbon gas formation, by inhibiting the formation of polynuclear aromatic compounds not originally present in the resid, and by separating an intermediate quality fraction, which produces low amounts of coke, before or during conversion. In addition, the challenge for hydroconversion is to take advantage of the nickel and vanadium in the heavy feedstocks to generate an in situ dispersed catalyst and to eliminate catalyst cost.

**4.1. Desalting and Dewatering.** Crude oil is recovered from the reservoir mixed with a variety of substances: gases, water, and dirt (minerals) (6). Thus, refining actually commences with the production of fluids from the well or reservoir and is followed by pretreatment operations that are applied to the crude oil either at the refinery or prior to transportation. Pipeline operators, eg, are insistent upon the quality of the fluids put into the pipelines; therefore, any crude oil to be shipped by pipeline or, for that matter, by any other form of transportation must meet rigid specifications in regard to water and salt content. In some instances, sulfur content, nitrogen content, and viscosity may also be specified.

Field separation, which occurs at a field site near the recovery operation, is the first attempt to remove the gases, water, and dirt that accompany crude oil coming from the ground. The separator may be no more than a large vessel that gives a quieting zone for gravity separation into three phases: gases, crude oil, and water containing entrained dirt.

Desalting operations are necessary to remove salt from the brines that are present with the crude oil after recovery. The salt or brine suspensions may be removed from crude oil by heating (90–150°C, 200–300°F) under pressure (50–250 psi) that is sufficient to prevent vapor loss and then allowing the material to settle in a large vessel. Alternatively, coalescence is aided by passage through a tower packed with sand, gravel, and the like.

Desalting is a water-washing or electrostatic operation performed at the production field and at the refinery site for additional crude oil cleanup. If the petroleum from the separators contains water and dirt, water washing can remove much of the water-soluble minerals and entrained solids. If these crude oil contaminants are not removed, they can cause operating problems during refinery processing, such as equipment plugging and corrosion as well as catalyst deactivation.

The usual practice is to blend crude oils of similar characteristics, although fluctuations in the properties of the individual crude oils may cause significant variations in the properties of the blend over a period of time. Blending several crude oils prior to refining can eliminate the frequent need to change the processing conditions that may be required to process each of the crude oils individually. However, incompatibility of different crude oils, which can occur if, eg, a paraffinic crude oil is blended with a heavy asphaltic oil, can cause sediment formation in the unrefined feedstock or in the products, thereby complicating the refinery process (7).

Emulsions may also be broken by addition of treating agents, such as soaps, fatty acids, sulfonates, and long-chain alcohols. When a chemical is used for emulsion breaking during desalting, it may be added at one or more of three points in the system. First, it may be added to the crude oil before it is mixed with fresh water. Second, it may be added to the fresh water before mixing with the crude oil. Third, it may be added to the mixture of crude oil and water. A high potential field across the settling vessel also aids coalescence and breaks emulsions, in which case dissolved salts and impurities are removed with the water.

**4.2. Distillation.** The first and most fundamental step in the refining process (after the crude oil has been cleaned and any remnants of brine removed) is distillation and which is often referred to as the primary refining process. Distillation involves the separation of the different hydrocarbon compounds that occur naturally in a crude oil, into a number of different fractions (a fraction is often referred to as a *cut*).

Originally, distillation was a batch operation in which the still was a cast-iron vessel mounted on brickwork over a fire and the volatile materials were passed through a pipe or gooseneck that led from the top of the still to a condenser. The latter was a coil of pipe, or a *worm* (hence the expression *worm end products*), immersed in a tank of running water.

Fractions from the atmospheric and vacuum towers are often used as feedstocks to these second stage refinery processes that break down the fractions, or bring about a basic chemical change in the nature of a particular hydrocarbon compound to produce specific products.

*Atmospheric Distillation.* The petroleum distillation unit in the 1990s brings about a fairly efficient degree of fractionation (separation). The feed to a distillation tower is heated by flow through pipes arranged within a large furnace. The heating unit is known as an atmospheric pipe still heater or pipe still furnace, and the heating unit and fractional distillation tower make up the essential parts of a distillation unit or pipe still.

The pipe still furnace heats the feed to a predetermined temperature, usually a temperature at which a predetermined portion of the feed changes into vapor. The vapor is held under pressure in the pipe in the furnace until it discharges as a foaming stream into the fractional distillation tower. Here the nonvolatile or liquid portion of the feed descends to the bottom of the tower to be pumped away as a bottom nonvolatile product, while the vapors pass up the tower to be fractionated into gas oil, kerosene, and naphtha.

Pipe still furnaces vary greatly and, in contrast to the early units where capacity was usually 31.8–79.5 $m^3$/day (200–500 bbl/day), can now accommodate 3975 $m^3$ (25,000 bbl) or more of crude oil per day. The walls and ceiling are insulated with firebrick and the interior of the furnace is partially divided into two sections: a smaller convection section where the oil first enters the furnace and a larger section fitted with heaters where the oil reaches its highest temperature.

The primary fractions from a distillation unit are equilibrium mixtures and contain some proportion of the lighter constituents characteristic of a lower boiling fraction. The primary fractions are stripped of these constituents (stabilized) before storage or further processing.

*Vacuum Distillation.* Vacuum distillation evolved as the need arose to separate the less volatile products, such as lubricating oils, from petroleum without subjecting these higher boiling materials to cracking conditions. The boiling point of the heaviest cut obtainable at atmospheric pressure (101.3 kPa = 760 mmHg) is limited by the temperature (~350°C, 662°F) at which the residue starts to decompose or crack. It is at this point that distillation in a vacuum pipe still is initiated.

Operating conditions for vacuum distillation are usually in the range of 7–13 kPa (50–100 mmHg). In order to minimize large fluctuations in pressure in the vacuum tower, the units are usually shorter in height and larger in diameter than the respective atmospheric units. By this means, a heavy gas oil can be obtained as an overhead product at temperatures of ~150°C (302°F) and lubricating oil cuts can be obtained at 250–350°C (482–662°F). In some designs, the partial pressure of the hydrocarbons is reduced still further by the injection of steam that is added to the column for stripping the nonvolatile constituents in the base of the column.

Fractions from the atmospheric and vacuum towers are often used as feedstocks to these second stage refinery processes that break down the fractions, or bring about a basic chemical change in the nature of a particular hydrocarbon compound to produce specific products.

Alternatively, the atmospheric residuum or the vacuum residuum may be sent to a deasphalting unit to remove the very high molecular weight constituents (collectively called asphalt) and the deasphalted oil is used as feedstock to a catalytic cracking unit. Solvent deasphalting is a unique separation process in which the residue is separated by molecular weight (density), instead of by boiling point as in the distillation process. The purpose of a deasphalting unit is to produce asphalt as final product and to produce a soluble stream (deasphalted oil that can be used in a catalytic cracking unit and have reduced coke deposition on the catalyst. The solvents used in a deasphalting unit vary from propane to pentane and the yields of asphalt and deasphalted oil vary with the hydrocarbon used in the unit.

*Azeotropic Distillation and Extractive Distillations.* Effective as they are for producing various liquid fractions, distillation units generally do not produce specific fractions. In order to accommodate the demand for such products, refineries have incorporated azeotropic distillation and extractive distillation in their operations.

The principle of azeotropic distillation depends on the ability of a chemically dissimilar compound to cause one or both components of a mixture to boil at a temperature other than the one expected. Thus, the addition of a nonindigenous component forms an azeotropic mixture with one of the components of the mixture, thereby lowering the boiling point and facilitating separation by distillation. The separation of components of similar volatility may become economical if an entrainer can be found that effectively changes the relative volatility. It is also desirable that the entrainer be reasonably cheap, stable, nontoxic, and readily recoverable from the components. In practice, it is probably the ready recoverability that limits the application of extractive and azeotropic distillation.

The majority of successful processes are those in which the entrainer and one of the components separate into two liquid phases on cooling if direct recovery by distillation is not feasible. A further restriction in the selection of an azeotropic entrainer is that the boiling point of the entrainer is 10–40°C (50–104°F) below that of the components.

### 4.3. Thermal Cracking.

When kerosene (lamp oil) was the principal desired product, gasoline was the portion of crude petroleum too volatile to be included in kerosene. The refiners of the 1890s and early 1900s had no use for gasoline and often discarded an accumulation of it. However, as the demand for gasoline and aviation fuel increased with the onset of World War I and the increased production of automobiles during the 1920s, more fuels had to be produced to meet the demand.

The problem of how to produce more of the lower boiling fractions from crude oil was solved in 1913 when cracking units were incorporated into refinery operations and fractions heavier than gasoline were converted into gasoline by thermal decomposition. The use of residua as feedstocks for thermal processes has become economically advantageous because, on the one hand, the end result is the production of lower boiling salable materials, and, on the other, the asphaltic materials in the residua are regarded as the unwanted coke-forming constituents.

The basic processes introduced to bring about thermal decomposition of the higher boiling streams are known as *cracking*. In these processes, the higher boiling fractions are converted to lower boiling products. *Catalytic cracking* is the most common cracking process, in which heavy feedstock or cuts are broken down or changed by being heated, and reacted with catalysts.

The concept behind *thermal cracking* is the thermal decomposition of higher molecular weight constituents of petroleum to produce lower molecular weight, normally more valuable, products. The first commercial process was in 1913 and is known as the Burton process. Even though catalyst cracking generally replaced thermal cracking in 1940s, noncatalytic cracking processes using high temperature to achieve the decomposition are still in operation. Catalytic processes usually produce more gasoline having a higher octane number, but with lesser yields of gases and heavy fuel oil. The gases produced by catalytic cracking contain more olefins than those produced by thermal cracking.

*Thermal Cracking.* In the thermal cracking process, a feedstock (eg, gas oil) is fed to the fractionator with their thermal reactivity to separate gasoline, light, and heavy oil. The light oil is then fed to the heater at 540–595°C (1000–1100°F) and a pressure of 350–700 psi, the light oil transforms to the vapor phase and is sent to the soaker. If the feedstock is heavy oil, temperatures on the order of 400–480°C (750–900°F) are used and higher pressures (350–700 psi) are used to maintain the feedstock in the liquid phase, then it is fed to the soaker. The liquid- and vapor-phase mix in the soaker and sent to the separator, with the products coming out on the bottom as fuel oil and the light recycle back to the fractionator. Coking in the reactor is the main problem when heavy oil is heated at high temperatures.

*Visbreaking.* Viscosity breaking (reduction) is a mild cracking operation used to reduce the viscosity of residual fuel oils and residua (8). The process, evolved from the older and now obsolete thermal cracking processes, is classed as mild because the thermal reactions are not allowed to proceed to completion.

Residua are sometimes blended with lighter heating oils to produce fuel oils of acceptable viscosity. By reducing the viscosity of the nonvolatile fraction, visbreaking reduces the amount of the more valuable light heating oil that is required for blending to meet the fuel oil specifications. The process is also used to reduce the pour point of a waxy residue. Visbreaking conditions range from 455 to 510°C (851–950°F) and 345 to 2070 kPa (50 to 300 psi) at the heating coil outlet. Liquid-phase cracking takes place under these low severity conditions. In addition to the primary product, fuel oil, material in the gas oil and gasoline boiling range is produced. Gas oil can be used as additional feed for catalytic cracking units or as heating oil.

In the process (Fig. 2), a crude oil residuum is passed through a furnace where it is heated to ~480°C (896 °F) under an outlet pressure of ~690 kPa (100 psi). The heating coils in the furnace are arranged to provide a soaking section of low heat density, where the charge remains until the visbreaking reactions are completed; subsequently, the cracked products are passed into a flash-distillation chamber. The overhead material from this chamber is then fractionated to produce a low quality gasoline as an overhead product and a light gas oil as bottom. The liquid products from the flash chamber are cooled with a gas oil flux and then sent to a vacuum fractionator. This yields a heavy gas oil distillate and a residual tar of reduced viscosity. Quench oil may also be used to terminate the reactions (2,9).

The main limitation to thermal conversion is that the products can be unstable. Thermal cracking at low pressure gives olefins, particularly in the naphtha fraction; such olefins yield an unstable product that tends to form gum as well as heavier products that form sediments (7).

*Coking Processes.* Coking is a generic term for a series of thermal processes used for the conversion of nonvolatile heavy feedstocks into lighter, distillable products (10). The feedstock is typically a residuum and the products are gas, naphtha, fuel oil, gas oil, and coke. Gas oil can be the primary product of a coking operation and serves primarily as a feedstock for catalytic cracking units. The coke obtained is usually used as fuel, but specialty uses, such as electrode manufacture and the production of chemicals and metallurgical coke, are also possible, thus increasing the value of the coke.

*Delayed coking* (Fig. 3) is a semicontinuous process in which the heated charge is transferred to large soaking, or coking, drums, which provide the residence time needed for the cracking reactions to proceed to completion (11,12). The feed to these units is normally a vacuum residuum, although residua from other thermal processes are also used. The feedstock is introduced into the product fractionator. The fractionator bottoms, including a recycle stream of heavy product, are heated in a furnace whose outlet temperature varies from 480 to 515°C (896–959°F). The heated feedstock then enters one of a pair of coking drums where the cracking reactions continue.

The cracked products leave as overhead materials, and coke deposits form on the inner surface of the drum. To provide continuous operation, two drums are used; while one drum is on-stream, the one off-stream is being cleaned, steamed, water-cooled, and decoked in the same time interval. The temperature in the coke drum is in the range of 415–450°C (779–842°F) with pressures in the range of 103–621 kPa (15–90 psi). Overhead products go to the fractionator, where naphtha and heating oil fractions are recovered. The nonvolatile material is combined with preheated fresh feed and returned to the furnace. The coke drum is usually on stream for ~24 h before becoming filled with porous coke, after which the coke is removed hydraulically.

*Fluid coking* (Fig. 4) is a continuous process that uses the fluidized solids technique to convert atmospheric and vacuum residua to more valuable products (12,13). The residuum is converted to coke and overhead products by being sprayed into a fluidized bed of hot, fine coke particles, which permits the coking reactions to be conducted at higher temperatures and shorter contact times than they can be in delayed coking. Moreover, these conditions result in decreased yields of coke; greater quantities of more valuable liquid product are recovered in the fluid coking process.

Fluid coking uses two vessels: a reactor and a burner; coke particles are circulated between the two to transfer heat generated by burning a portion of the coke to the reactor. The reactor holds a bed of fluidized coke particles, and steam is introduced at the bottom of the reactor to fluidize the bed.

*Flexicoking* (Fig. 5), also a continuous process, uses the same configuration as the fluid coker, but has a gasification section in which excess coke can be gasified to produce refinery fuel gas. Flexicoking is a process by which excess cokemake is reduced in view of the gradual incursion of the heavier feedstocks into refinery operations. Such feedstocks are notorious for producing high yields of coke (>15% by weight) in thermal and catalytic operations.

**4.4. Catalytic Cracking.** Fluid catalytic cracking (FCC) (Fig. 6) was first introduced in 1942 and uses a fluidized bed of catalyst with continuous feedstock flow. In the process, which has progressively supplanted thermal cracking, the thermal decomposition of petroleum constituents occurs in the presence of a catalyst (14,15). The acid catalysts first used in catalytic cracking were designated low alumina catalysts; amorphous solids composed of ~87% silica, $SiO_2$, and 13% alumina, $Al_2O_3$. Later, high alumina catalysts containing 25% alumina and 75% silica were used. However, this type of catalyst has largely been replaced by catalysts containing crystalline aluminosilicates (zeolites) or molecular sieves (16–18).

The catalyst is employed in bead, pellet, or microspherical form and can be used as a fixed, moving, or fluid bed. The fixed-bed process was the first process used commercially and employs a static bed of catalyst in several reactors, which allows a continuous flow of feedstock to be maintained. The cycle of operations consists of (*1*) the flow of feedstock through the catalyst bed; (*2*) the discontinuance of feedstock flow and removal of coke from the catalyst by burning; and (*3*) the insertion of the reactor back on-stream. The moving-bed process uses a reaction vessel, in which cracking takes place, and a kiln, in which the spent catalyst is regenerated and catalyst movement between the vessels is provided by various means. The fluid-bed process differs from the fixed-bed and moving-bed processes, insofar as the powdered catalyst is circulated essentially as a fluid with the feedstock. The several fluid catalytic cracking processes in use differ primarily in mechanical design. Side-by-side reactor-regenerator construction and unitary vessel construction (the reactor either above or below the regenerator) are the two main mechanical variations.

Catalytic cracking has progressively supplanted thermal cracking as the most advantageous means of converting distillate oils into gasoline and a better yield of higher octane gasoline can be obtained than by any known thermal operation. At the same time the gas produced consists mostly of propane and butane with less methane and ethane. The production of heavy oils and tars, higher in molecular weight than the charge material, is also minimized, and both the gasoline and the uncracked *cycle oil* are more saturated than the products of thermal cracking.

**4.5. Hydroprocessing.** *Hydroprocesses* use the principle that the presence of hydrogen during a thermal reaction of a petroleum feedstock will terminate many of the coke-forming reactions and enhance the yields of the lower boiling components such as gasoline, kerosene, and jet fuel. Thus, in this group of refining processes, which includes hydrotreating and hydrocracking, the feedstock is heated with hydrogen at high temperature and under pressure. The outcome is the conversion of a variety of feedstocks to a range of products (Table 2) (1,2,4,9,19).

The purpose of hydroprocessing is (*1*) to improve existing petroleum products or develop new products or uses; (*2*) to convert inferior or low grade materials into valuable products; and (*3*) to transform near-solid residua to liquid fuels. Products are as follows: from naphtha, reformed feedstock and liquefied petroleum gas (LPG); from atmospheric gas oil, diesel and jet fuel, petrochemical feedstock, and naphtha; from vacuum gas oil, catalytic cracker feedstock, kerosene, diesel and jet fuel, naphtha, LPG, and lubricating oil; and from residuum, catalytic cracker and coker feedstock, diesel fuel, etc.

Hydroprocesses for the conversion of petroleum and petroleum products can be classified as *destructive* or *nondestructive*. The former (*hydrogenolysis* and *hydrocracking*) is characterized by the rupture of carbon–carbon bonds and is accompanied by hydrogen saturation of the fragments to produce lower boiling products. Such treatment requires rather high temperatures and high hydrogen pressures, the latter to minimize coke formation.

Hydrogenolysis is analogous to hydrolysis and ammonolysis, which involve the cleavage of a bond induced by the action of water and ammonia, respectively. Chemical bonds that are broken by hydrogenolysis reactions include carbon–carbon, carbon–oxygen, carbon–sulfur, and carbon–nitrogen bonds. An example of hydrogenolysis is the hydrodealkylation of toluene to form benzene and methane:

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$$

On the other hand, nondestructive, or simple hydrogenation is generally used for the purpose of improving product quality without appreciable alteration of the boiling range. Examples are the removal of various sulfur compounds (Table 3), which would otherwise have an adverse effect on product quality. Treatment under such mild conditions is often referred to as hydrotreating or hydrofining and is essentially a means of eliminating, in addition to sulfur, nitrogen and oxygen as ammonia and water, respectively.

*Hydrocracking.* Hydrocracking is a catalytic process (>350°C, 662°F) in which hydrogenation accompanies cracking (20). Relatively high pressures, 6900–21,000 kPa (1000–3000 psi), are employed and the overall result is the conversion of the feedstock to lower boiling products. Another attractive feature of hydrocracking is the low yield of gaseous components, such as methane, ethane, and propane, which are less desirable than the gasoline components. Essentially all the initial reactions of catalytic cracking occur, but some of the secondary reactions are inhibited or stopped by the presence of hydrogen.

In the first, pretreating stage of a hydrocracking process, the main purpose is to convert organic nitrogen compounds and organic sulfur in the feedstock to hydrocarbons and to ammonia and hydrogen sulfide by hydrogenation and mild hydrocracking. The purpose is to reduce the organic nitrogen and sulfur compounds to low levels (<50 ppm). Typical conditions are 340–390°C (644–734°F), 10,350–17,250 kPa (1500–2500 psi), and a catalyst contact time of 0.5–1.5 h, up to 1.5 wt% hydrogen is absorbed, partly by conversion of the nitrogen compounds, but chiefly by aromatic compounds that are hydrogenated.

This first stage is usually carried out with a bifunctional catalyst containing hydrogenation promoters, eg, nickel and tungsten or molybdenum sulfides, on an acidic support. The metal sulfides hydrogenate aromatics and nitrogen compounds, and retard deposition of carbonaceous deposits; the acidic support accelerates nitrogen removal as ammonia by breaking carbon–nitrogen bonds. The catalyst is generally used as 0.32 × 0.32-cm or 0.16 × 0.32-cm pellets, as well as spheres or other shapes.

Most of the hydrocracking is accomplished in the second stage. Hydrogen sulfide, ammonia, and low boiling products are usually removed from the first-stage product; the remaining oil, which is low in nitrogen–sulfur compounds, is passed over the second-stage catalyst. Some catalyst systems do not require the removal of adsorbed compounds between stages. In the second stage, typical conditions are 300–370°C (572–698°F), 7000–17,250 kPa (1000–2500 psi) hydrogen pressure, and 0.5–1.5 h contact time; 1–1.5 wt% hydrogen may be absorbed. Conversion to gasoline or jet fuel is seldom complete in one contact with the catalyst, so the lighter oils are removed by distillation of the products, and the heavier, high boiling product is combined with fresh feed and recycled over the catalyst until it is completely converted.

The catalyst for the second stage is also a bifunctional catalyst containing hydrogenating and acidic components. Metals such as nickel, molybdenum, tungsten, or palladium are used in various combinations and dispersed on solid acidic supports, such as synthetic amorphous or crystalline silica–alumina, eg, zeolites. These supports contain strongly acidic sites and sometimes are enhanced by the incorporation of a small amount of fluorine.

A long period of operation (eg, >3 years) between catalyst regeneration is desirable; this is achieved by keeping a low nitrogen content in the feed and avoiding high temperatures and high end-point feedstock, which leads to excess cracking and consequent deposition of coke on the catalyst. Feedstock conversion is the key insofar as the conversion dictates the temperature employed. When activity of the catalyst has decreased, it can often be restored by controlled burning of the coke.

*Hydrotreating.* On the other hand, *hydrotreating* is a catalytic process converts sulfur- and/or nitrogen-containing hydrocarbons into low sulfur low nitrogen liquids, hydrogen sulfide, and ammonia (21). A wide variety of metals are active hydrogenation catalysts; those of most interest are nickel, palladium, platinum, cobalt, and iron. Special preparations of the first three are active at room temperature and atmospheric pressure. The metallic catalysts are easily poisoned by sulfur- or arsenic-containing compounds, and even by other metals. To avoid such poisoning, less effective, but more resistant metal oxides or sulfides are frequently employed, generally those of tungsten, cobalt, or molybdenum. Alternatively, catalyst poisoning can be minimized by mild hydrogenation to remove nitrogen, oxygen, and sulfur from feedstocks in the presence of more resistant catalysts, such as cobalt–molybdenum–alumina, Co–Mo–$Al_2O_3$.

The process temperature affects the rate and the extent of hydrogenation as it does any chemical reaction. Practically every hydrogenation reaction can be reversed by increasing temperature. If a second functional group is present, high temperatures often lead to the loss of selectivity and, therefore, loss of desired product yield. As a practical measure, hydrogenation is carried out at as low a temperature as possible which is still compatible with a satisfactory reaction rate.

Hydrotreating is carried out by charging the feed to the reactor together with hydrogen at 300–345°C (572–653°F); the hydrogen pressures are ~3450–6900 kPa (500–1000 psi). The reaction generally takes place in the vapor phase but, depending on the application, can also be a mixed-phase reaction.

After passing through the reactor, the treated oil is cooled and separated from the excess hydrogen recycled through the reactor. The treated oil is pumped to a stripper tower where hydrogen sulfide, formed by the hydrogenation reaction, is removed by steam or by hydrocarbon vapor via reboiling, and the finished product leaves the bottom of the stripper tower. The catalyst can be regenerated *in situ* and ultimately be replaced after several regenerations.

**4.6. Reforming.** *Reforming processes* are used to change the inherent chemical structures of the hydrocarbons that exist in distillation fractions crude oil into different compounds. Catalytic reforming is one of the most important processes in a modern refinery, altering straight run fraction or fractions from a catalytic cracker into new compounds through a combination of heat and pressure in the presence of a catalyst. Reforming processes are particularly important in producing high quality gasoline fuels. Reforming processes are classified as continuous, cyclic, or semiregenerative, depending upon the frequency of catalyst regeneration.

When the demand for higher octane gasolines increased during the early 1930s, attention was directed to ways and means of improving the octane number of fractions within the boiling range of gasoline. Straight-run (distilled) gasolines frequently had low octane numbers, and any process that could improve the octane numbers would aid in meeting the demand for higher octane number gasoline. Such a process, called thermal reforming, was developed and used widely, but to a much lesser extent than thermal cracking. Thermal reforming was a natural development from older thermal cracking processes; cracking converts heavier oils into gasoline whereas reforming converts (reforms) gasolines into higher octane gasolines. The equipment for thermal reforming is essentially the same as for thermal cracking, but higher temperatures are used in the former.

In carrying out thermal reforming, a feedstock such as 205°C (400°F) end-point naphtha or a straight-run gasoline is heated to 510–595°C (950–1100°F) in a furnace, much the same as a cracking furnace, with pressures from 400 to 1000 psi (27 to 68 atm). As the heated naphtha leaves the furnace, it is cooled or quenched by the addition of cold naphtha. The material then enters a fractional distillation tower where any heavy products are separated. The remainder of the reformed material leaves the top of the tower to be separated into gases and reformate. The higher octane of the reformate is due primarily to the cracking of longer-chain paraffins into higher octane olefins. The products of thermal reforming are gases, gasoline, and residual oil or tar, the latter being formed in very small amounts (~1%). The amount and quality of the gasoline, known as reformate, is very dependent on the temperature. A general rule is:

The higher the reforming temperature, the higher the octane number, but the lower the yield of reformate.

Catalytic reforming usually is carried out by feeding a naphtha (after pretreating with hydrogen if necessary to remove nitrogen and sulfur compounds) and hydrogen mixture to a furnace where the mixture is heated to the desired temperature (450–520°C; 842–968°F) and then passed through fixed-bed catalytic reactors at hydrogen pressures of 350–2700 kPa (50–400 psi). Normally, several reactors are used in series and heaters are located between adjoining reactors in order to compensate for the endothermic reactions taking place.

Thermal reforming, less effective and less economical than catalytic processes, has been largely supplanted. Like thermal reforming, catalytic reforming converts low octane gasolines into high octane gasolines, ie, reformate. Whereas thermal reforming produces reformate having research octane numbers in the 65–80 range, depending on the yield, catalytic reforming produces reformate having octane numbers on the order of 90–105. Catalytic reforming is conducted in the presence of hydrogen over hydrogenation–dehydrogenation catalysts, eg, in the platforming process (22). Catalytic reformer feeds are saturated, ie, not olefinic, materials. Catalytic cracker naphtha and hydrocracker naphtha that contains substantial quantities of naphthenes are also suitable reformer feedstocks.

Dehydrogenation is a main chemical reaction in catalytic reforming, and hydrogen gas is consequently produced in large quantities. Hydrogen is recycled through the reactors where the reforming takes place to provide the atmosphere necessary for the chemical reactions, and also prevents carbon from being deposited on the catalyst, thus extending its operating life. Because of an excess of hydrogen above, whatever is consumed in the process is produced, catalytic reforming processes are unique in that they are the only petroleum refinery processes to produce hydrogen as a by-product.

The composition of a reforming catalyst is dictated by the composition of the feedstock and the desired reformate. The catalysts used are principally platinum or platinum–rhenium on an alumina base. The purpose of platinum on the catalyst is to promote dehydrogenation and hydrogenation reactions. Nonplatinum catalysts are used in regenerative processes for feedstocks containing sulfur, although pretreatment (hydrodesulfurization) may permit platinum catalysts to be employed.

### 4.7. Isomerization.

Isomerization is used with the objective of providing additional feedstock for alkylation units (isobutane) or high octane fractions for gasoline blending (pentane and hexane) (23). The latter application is useful in the production of reformulated gasoline by increasing the octane number while converting or removing benzene (24,25).

Initially, aluminum chloride was the catalyst used to isomerize butane, pentane, and hexane. Since then, supported metal catalysts have been developed for use in high temperature processes that operate at 370–480°C (698–896°F) and 2070–5170 kPa (300–750 psi), whereas aluminum chloride and hydrogen chloride are universally used for the low temperature processes.

Nonregenerable aluminum chloride catalyst is employed with various carriers in a fixed-bed or liquid contactor. Platinum or other metal catalyst processes that utilize fixed-bed operation can be either regenerable or nonregenerable.

The reaction conditions vary widely, between 40 and 480°C (104–896°F) and 1035–6900 kPa (150–1000 psi), depending on the particular process and feedstock.

### 4.8. Alkylation.

The combination of olefins with paraffins to form higher isoparaffins is termed *alkylation*. Alkylate is a desirable blendstock because it has a relatively high octane number and serves to dilute the total aromatics content. Reduction of the olefins in gasoline blendstocks by alkylation also reduces tail pipe emissions. In refinery practice, butylenes are routinely alkylated by reaction with isobutane to produce isobutane–octane (26). In some plants, propylene and/or pentylenes (amylenes) are also alkylated (27).

Alkylate is composed of a mixture of isoparaffins whose octane numbers vary with the olefins from which they were made. Butylenes produce the highest octane numbers, propylene the lowest, and amylenes (pentylenes) the intermediate values. All alkylates, however, have high (>87) octane numbers that make them particularly valuable.

Propylene, butylenes, or amylenes are combined with isobutane in the presence of an acid catalyst, eg, sulfuric acid or hydrofluoric acid, at low temperatures (1–40°C; 33.8–104) and pressures, 102–1035 kPa (1 to 10 atm). Sulfuric acid or hydrogen fluoride are the catalysts used commercially in refineries. The acid is pumped through the reactor and forms an emulsion with reactants, and the emulsion is maintained at 50% acid. The rate of deactivation varies with the feed and isobutane charge rate. Butene feeds cause less acid consumption than the propylene feeds.

### 4.9. Polymerization.

In the petroleum industry, polymerization is the process by which olefin gases are converted to higher molecular weight liquid products that may be suitable for gasoline (polymer gasoline) or other liquid fuels.

The feedstock, usually consisting of propylene and butylenes (various isomers of $C_4H_8$) from cracking processes, may even consist of selective olefins for dimer, trimer, or tetramer production:

| | |
|---|---|
| $RCH{=}CH_2$ | monomer |
| $—[CH(R)—CH_2)_2—$ | dimer |
| $—[CH(R)—CH_2)_3—$ | trimer |
| $—[CH(R)—CH_2)_4—$ | tetramer |

The molecular size of the product is limited insofar as the reaction is terminated at the dimer or trimer stage. Thus the process is more properly termed oligomerization. The 4- to 12-carbon compounds required as the constituents of liquid fuels are the prime products.

Thermal polymerization is not as effective as catalytic polymerization, but has the advantage that it can be used to polymerize saturated materials that cannot be induced to react by catalysts. The process consists of the vapor-phase cracking of, eg, propane and butane, followed by prolonged periods at high temperature (510–595°C; 950–1103°F) for the reactions to proceed to near completion. Olefins can also be conveniently polymerized by means of an acid catalyst. Thus, the treated olefin-rich feed stream is contacted with a catalyst, such as sulfuric acid, copper pyrophosphate, or phosphoric acid, at 150–220°C (302–428°F) and 1035–8275 kPa (150–1200 psi), depending on feedstock and product requirement.

Phosphates are the principal catalysts used in polymerization units; the commercially used catalysts are liquid phosphoric acid, phosphoric acid on kieselguhr, copper pyrophosphate pellets, and phosphoric acid film on quartz. The last is the least active and has the disadvantage that carbonaceous deposits must occasionally be burned off the support. Compared to other processes, the one using liquid phosphoric acid catalyst is far more responsive to attempts to raise production by increasing temperature.

## 5. Treating

Since the original crude oils contain some sulfur compounds, the resulting products and gasolines also contain sulfur compounds, including hydrogen sulfide, mercaptans, sulfides, disulfides, and thiophenes. The processes used to sweeten, ie, desulfurize, the products depend on the type and amount of the sulfur compounds present and the specifications of the finished gasoline or other stocks.

Hydrotreating is the most widely practiced treating process for all types of petroleum products. However, there are other treating processes suitable for the removal of mercaptans and hydrogen sulfide; such processes are necessary and are performed as part of the product improvement and finishing procedures. For example, mercaptan, RSH, removal is achieved by using regenerative solution processes, in which the treatment solutions are regenerated rather than discarded. Mercaptan conversion is essentially a process of oxidation to disulfides, RSSR, by lead sulfide treatment, copper chloride–oxygen treatment, sodium hypochlorite treatment, or oxygen treatment with a chelated cobalt catalyst in either a caustic solution or fixed bed.

Hydrogen sulfide, $H_2S$, is removed by a variety of processes, of which one is a regenerative solution process using aqueous solutions of sodium hydroxide, NaOH; calcium hydroxide, $Ca(OH)_2$; sodium phosphate, $Na_3PO_4$; and sodium carbonate, $Na_2CO_3$.

**5.1. Alkali Treatment.** Caustic washing is the treatment of materials, usually products from petroleum refining, with solutions of caustic soda. The process consists of mixing a water solution of lye (sodium hydroxide or caustic soda) with a petroleum fraction. The treatment is carried out as soon as possible after the petroleum fraction is distilled, since contact with air forms free sulfur, which is corrosive and difficult to remove. The lye reacts either with any hydrogen sulfide present to form sodium sulfide, which is soluble in water, or with mercaptans, followed by oxidation, to form the less nocuous disulfides.

$$H_2S + 2\ NaOH \rightarrow Na_2S + 2\ H_2O$$

$$RSH + NaOH \rightarrow NaSR + H_2O$$

$$4\,NaSR + O_2 + 2\ H_2O \rightarrow 2\,RSSR + 4\ NaOH$$

Nonregenerative caustic treatment is generally economically applied when the contaminating materials are low in concentration and waste disposal is not a problem. However, the use of nonregenerative systems is on the decline because of the frequently occurring waste disposal problems that arise from environmental considerations and because of the availability of numerous other processes that can effect more complete removal of contaminating materials.

Steam-regenerative caustic treatment is directed toward the removal of mercaptans from such products as gasoline and low boiling solvents (naphtha). The caustic is regenerated by steam blowing in a stripping tower. The nature and concentration of the mercaptans to be removed dictate the quantity and temperature of the process. However, the caustic gradually deteriorates because of the accumulation of material that cannot be removed by stripping; the caustic quality must be maintained by either continuous or intermittent discard and/or replacement of a minimum amount of the operating solution.

**5.2. Acid Treatment.** The treatment of petroleum products with acids has been in use for a considerable time in the petroleum industry. Various acids, such as hydrofluoric acid, hydrochloric acid, nitric acid, and phosphoric acid, have been used in addition to the most commonly used sulfuric acid, but in most instances there is little advantage in using any acid other than sulfuric.

Sulfuric acid also has been employed for refining kerosene distillates and lubricating oil stocks. Although a greater part of the acid-treating processes has been superseded by other processes, acid treating has continued to some extent; it is used for desulfurizing high boiling fractions of cracked gasoline distillates, for refining paraffinic kerosene, for manufacturing low cost lubricating oils, and for making specialty products such as insecticides, pharmaceutical oils, and insulating oils.

**5.3. Clay Treatment.** The original method of clay treating was to percolate a petroleum fraction through a tower containing coarse clay pellets. As the clay adsorbed impurities from the petroleum fraction, the clay became less effective. The activity of the clay was periodically restored by removing it from the tower and burning the adsorbed material under carefully controlled conditions so as not to sinter the clay. The percolation method of clay treating was widely used for lubricating oils, but has been largely replaced by clay contacting.

However, this use of clay treating has been superseded by other processes; in particular, by the use of inhibitors, which, when added in small amounts to gasoline, can prevent gums from forming. Nevertheless, clay treating is still used as a finishing step in the manufacture of lubricating oils and waxes. The clay removes traces of asphaltic materials and other compounds that give oils and waxes unwanted odors and colors.

**5.4. Solvent Treatment.** Solvent processes can be divided into two main categories: solvent extraction and solvent dewaxing. The solvent used in the extraction processes include propane and cresylic acid, 2,2′-dichlorodiethyl ether, phenol, furfural, sulfur dioxide, benzene, and nitrobenzene. In the dewaxing process (28), the principal solvents are benzene, methyl ethyl ketone, methyl isobutyl ketone, propane, petroleum naphtha, ethylene dichloride, methylene chloride, sulfur dioxide, and *N*-methylpyrrolidinone.

The early developments of solvent processing were concerned with the lubricating oil end of the crude. Solvent extraction processes are applied to many useful separations in the purification of gasoline, kerosene, diesel fuel, and other oils.

In solvent dewaxing, the oil is diluted with a solvent that has a high affinity for oil, chilled to precipitate the wax, filtered to remove the wax, stripped of solvent, and dried. The solvents [principally propane, naphtha, methyl ethyl ketone (MEK)] act as diluents for the high molecular weight oil fractions to reduce the viscosity of the mixture and provide sufficient liquid volume to permit pumping and filtering. Wax, produced by the solvent dewaxing process, is used to make (*1*) paraffins for candle wax, (*2*) microwax for cosmetics, and (*3*) wax for petroleum jelly.

Catalytic dewaxing is a process in which the chemical composition of the feed is changed. The process involved catalytic cracking of long paraffin chains into shorter chains to remove the wax and produced lower molecular weigh products suitable for other uses. As an example, the feedstock is contacted with hydrogen at elevated temperature and pressure over a catalyst (such as a zeolite) that selectively cracks the normal paraffins to methane, ethane, and propane. This process also knows as hydrodewaxing. There are two types of catalytic dewaxing: (*1*) single-catalyst process that is used for pour point reduction and to improve the oxygen stability of the product, and (*2*) a two-catalyst process that uses a fixed-bed reactor and essentially no methane or ethane is formed in the reaction.

In addition, solvent extraction can replace fractionation in many separation processes in the refinery. For example, propane deasphalting (Fig. 7) has replaced, to some extent, vacuum distillation as a means of removing asphalt from reduced crude oils.

## 6. Gas Processing

The gas streams produced during petroleum refining usually contain many noxious constituents that have an adverse effect on the use of the gas for other purposes, eg, as a fuel or as a petrochemical feedstock, and some degree of cleaning is required (29).

Gas purification processes fall into three categories: the removal of gaseous impurities, the removal of particulate impurities, and ultrafine cleaning. The extra expense of the last process is only justified by the nature of the subsequent operations or the need to produce a pure gas stream. Because there are many variables in gas treating, several factors must be considered (*1*) the types and concentrations of contaminants in the gas; (*2*) the degree of contaminant removal desired; (*3*) the selectivity of acid gas removal required; (*4*) the temperature, pressure, volume, and composition of the gas to be processed; (*5*) the carbon dioxide/hydrogen sulfide ratio in the gas; and (*6*) the desirability of sulfur recovery on account of process economics or environmental issues.

Process selectivity indicates the preference with which the process removes one acid gas component relative to or in preference to another. For example, some processes remove both hydrogen sulfide and carbon dioxide, whereas other processes are designed to remove hydrogen sulfide only. Thus it is important to consider the process selectivity for hydrogen sulfide removal compared to carbon dioxide removal, ie, the carbon dioxide/hydrogen sulfide ratio in the natural gas, in order to ensure minimal concentrations of these components in the product.

One of the principal aspects of refinery gas cleanup is the removal of acid gas constituents, ie, carbon dioxide, $CO_2$, and hydrogen sulfide, $H_2S$. Treatment of natural gas to remove the acid gas constituents is most often accomplished by contacting the natural gas with an alkaline solution. The most commonly used treating solutions are aqueous solutions of the ethanolamines or alkali carbonates. There are several hydrogen sulfide removal processes, most of which are followed by a Claus plant that produces elemental sulfur from the hydrogen sulfide (29).

## 7. Petroleum Products

The constant demand for products, such as liquid fuels, is the main driving force behind the petroleum industry (5,30). In fact, it is the changes in product demand that have been largely responsible for the evolution of the industry.

In general, when the product is a fraction that has been produced from covnentioal petroleum or from heavy oil or resid and includes a large number of individual hydrocarbons, the fraction is classified as a refined product. Examples of refined products are gasoline, diesel fuel, heating oils, lubricants, waxes, asphalt, and coke. In contrast, when the product is limited to, perhaps, one or two specific hydrocarbons of high purity, the fraction is classified as a petrochemical product. Examples of petrochemicals are ethylene ($CH{=}CH_2$), propylene ($CH_3CH{=}CH_2$), benzene ($C_6H_6$), toluene ($C_6H_5CH_3$), and xylene ($CH_3C_6H_4CH_3$).

**7.1. Liquefied Petroleum Gas.** Certain specific hydrocarbons, such as propane, butane, pentane, and their mixtures, exist in the gaseous state under atmospheric ambient conditions, but can be converted to the liquid state under conditions of moderate pressure at ambient temperature. This is termed LPG. Liquefied petroleum gas is a refinery product and the individual constituents, or light ends (Table 4), are produced during a variety of refining operations.

The presence of ethane in LPG must be avoided because of the inability of this lighter hydrocarbon to liquefy under pressure at ambient temperature and its tendency to register abnormally high pressures in the LPG containers. On the other hand, the presence of pentane in liquefied petroleum gas must also be avoided because this particular hydrocarbon, a liquid at ambient temperatures and pressures, can condense and separate in the liquid state in the gas lines.

Liquefied petroleum gases precipitate asphaltic and resinous materials from crude residues while the lubricating oil constituents remain in solution. Although all liquefied gases possess this property to some extent, propane and butane are used to deasphalt residual lubricating oils because of their relative low cost and their ease of separation from lubricating oils.

Fuel gas or refinery gas (that also contains low boiling hydrocarbons) is produced in considerable quantities during the different refining processes and is used as fuel for the refinery itself and as an important feedstock for the petrochemical industry.

**7.2. Gasoline.** Gasoline (also known as *petrol* in many parts of the world) is one of the more important refinery products. The final gasoline product as a transport fuel is a carefully blended mixture having a predetermined composition that is adequate to power requirements (octane number) and climatic conditions.

Octane number is a measure of a fuel's ability to avoid knocking. The octane number of a gasoline is determined in a special single-cylinder engine where various combustion conditions can be controlled. The test engine is adjusted to give trace knock from the fuel to be rated. Various mixtures of isooctane (2,2,4-trimethyl pentane) and normal heptane are then used to find the ratio of the two reference fuels that produce the same intensity of knock as that by the unknown fuel.

By defining isooctane as having an octane number of 100 and *n*-heptane as having an octane number of 0, the volumetric percentage of isooctane in heptane that matches the knock from the unknown fuel can be calculated as the octane number of the fuel. For example, 90 vol% isooctane and 10 vol% normal heptane produce a 90-octane-number reference fuel.

Two kinds of octane number ratings are specified, although other methods are often used for engine and fuel development. Both methods use the same reference fuels and essentially the same test engine, but engine operating conditions are different. In one test, called the research method (hence the Research Octane Number, RON), the spark advance is fixed, the air inlet temperature is 125°F (52°C), and engine speed is 600 rpm. The other, called the motor method (hence the Motor Octane Number, MON), uses variable spark timing, a higher mixture temperature of 300°F (149°C), and a faster engine speed of 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, the motor octane number of a commercial blend tends to be lower than the research octane number. Common practice is to label gasoline with an arithmetic average of both ratings, abbreviated as (R+M)/2, and often referred to as road octane number.

The naphtha fraction from crude oil distillation is ultimately used to make gasoline. The two streams are isolated early in the refining scheme so that each can be refined separately for optimum blending in order to achieve the required specifications, including the octane number.

Gasoline is a complex mixture of hydrocarbons that boils <200°C (392°F). The hydrocarbon constituents in this boiling range are those that have 4–12 carbon atoms in their molecular structure. Gasolines can vary widely in composition, even those having the same octane number can be quite different (30). Because of the differences in composition of the various gasolines, gasoline blending is necessary. The physical process of blending the components is simple, but determination of how much of each component to include in a blend is much more difficult. The operation is carried out by simultaneously pumping all the components of a gasoline blend into a pipeline that leads to the gasoline storage, and the pumps must be set to deliver automatically the proper proportion of each component. Sophisticated instrumentation is employed to achieve the desired blends.

The objective of gasoline (in fact, product) *blending* is to allocate the available blending components in such a way as to meet product demands and specifications. In the blending process, product streams from other units are collected and blended to produce the desired product. For example, in gasoline blending, product streams from hydrotreating units, reforming units, polymerization units and alkylation units are blended to produce specification gasoline.

Aviation gasoline, usually used in light aircraft and older civil aircraft, have narrower boiling ranges (38–170°C; 100.4–338°F) than automobile gasoline (0–200°C; 32–392°F). In winter, the extreme temperatures in the northern climates allow a certain amount of butane to be dissolved in the gasoline to facilitate vaporization. The narrower boiling range ensures better distribution of the vaporized fuel through the more complicated induction systems of aircraft engines. Aircraft operates at altitudes where the prevailing pressure is less than the pressure at the surface of the earth, eg, at 5334 m, 52 kPa (7.5 psi) compared to 101.3 kPa (14.7 psi). As a result, the vapor pressure of aviation gasolines, which is a function of the fuel's boiling range, must be limited to reduce boiling in the tanks, fuel lines, and carburetors.

Another condition to keep gasoline engines running smoothly is to allow the fuel–air mixture to start burning at a precise time in the combustion cycle. An electrical spark starts the ignition. The remainder of the fuel–air mixture should be consumed by a flame front moving out from the initial spark. Under certain conditions, a portion of the fuel–air mixture ignites spontaneously instead of waiting for the flame front from the carefully timed spark. The extra pressure pulses resulting from spontaneous combustion are usually audible above the normal sounds of a running engine and give rise to the phenomenon called knock, of which pinging and rumbling are special attributes. However, knocks are undesirable because they waste some of the available power of an otherwise smooth-running engine.

Reformulated gasoline is believed to be the answer to many environmental issues that arise from the use of automobiles and there has been a serious effort to produce reformulated gasoline components (Table 5) from a variety of processes (25).

However, reformulation may increase gasoline consumption, when in fact the converse is preferable (24).

The production of low sulfur gasoline (and diesel fuel) is a necessary step to assure clean air and to reduce air pollution from the transportation sector. Sulfur is a pollutant and prevents the adoption of all major pollution control technologies. No significant air pollution reduction strategy can work without reducing sulfur to near-zero levels. When sulfur-containing fuels are burned, sulfur is emitted as sulfur dioxide, $SO_2$, or sulfate particulate matter. Any reduction in fuel sulfur immediately reduces these sulfur compounds and, as sulfur levels decline past a certain point, the benefits increase to include total pollutant emissions. Reduced sulfur fuel (~150 ppm sulfur) makes existing vehicles cleaner and decreases emissions. These benefits increase as vehicles are designed to meet higher emissions standards and sulfur levels are reduced further. Low sulfur fuel (~50 ppm sulfur) allows for the further benefit of advanced control technologies for diesel vehicles. Diesel particulate filters can be used with low sulfur fuel, but only achieves ~50% control efficiency. Selective catalytic reduction can be used for >80% control of $NO_x$ emissions.

Near-zero sulfur fuel (<10 ppm sulfur) allows for the use of $NO_x$ adsorbers, increasing $NO_x$ control to >90% in both diesel and gasoline vehicles. This enables more fuel-efficient engine designs, designs that are incompatible with current emissions control systems. Particulate filters achieve the maximum efficiency with near-zero sulfur fuels, approaching 100% control of particulate matter emissions.

The technologies required to reduce sulfur to near-zero levels are in use in many refineries and the refining industry continues to make progress in developing more active catalysts and novel processes for removal of sulfur. Refiners are using hydrotreating technologies in which the feedstock (be it a distillate fraction or even the residuum) is treated with hydrogen to reduce sulfur levels, and hence to make processing easier. The result has been reduced sulfur levels and lower permitted emissions standards for all types of vehicles. Long-term environmental challenges and the prospect of still stricter requirements in the future are spurring further research and technology development.

**7.3. Solvents.** Petroleum naphtha is a generic term applied to refined, partly refined, or unrefined petroleum products. Naphthas are prepared by any of several methods, including fractionation of distillates or even crude petroleum, solvent extraction, hydrocracking of distillates, polymerization of unsaturated (olefinic) compounds, and alkylation processes. Naphtha can also be a combination of product streams from more than one of these processes.

The main uses of petroleum naphtha fall into the general areas of solvents (diluents) for paints, etc, dry-cleaning solvents, solvents for cutback asphalt, solvents in rubber industry, and solvents for industrial extraction processes. Turpentine, the older, more conventional solvent for paints, has been almost completely replaced by the cheaper and more abundant petroleum naphtha.

**7.4. Kerosene.** Kerosene, also called kerosine, originated as a straight-run (distilled) petroleum fraction that boiled over the temperature range of 205–260°C (401–500°F). Kerosene was the major refinery product before the onset of the *automobile age*, but now kerosene might be termed as one of several other petroleum products after gasoline. In the early days of petroleum refining, some crude oils contained kerosene fractions of high quality, but other crude oils, such as those having a high proportion of asphaltic materials, had to be thoroughly refined to remove aromatics and sulfur compounds before a satisfactory kerosene fraction could be obtained.

Kerosene is believed to be composed chiefly of hydrocarbons containing 12–15 carbon atoms per molecule. Low proportions of aromatic and unsaturated hydrocarbons are desirable to maintain the lowest possible level of smoke during burning. Although some aromatics may occur within the boiling range assigned to kerosene, excessive amounts can be removed by extraction.

The significance of the total sulfur content of kerosene varies greatly with the type of oil and the use to which it is put. Sulfur content is of great importance when the kerosene to be burned produces sulfur oxides, which are of environmental concern. The color of kerosene is of little significance, but a product darker than usual may have resulted from contamination or aging; in fact, a color darker than specified may be considered by some users as unsatisfactory. Kerosene, because of its use as a burning oil, must be free of aromatic and unsaturated hydrocarbons; the desirable constituents of kerosene are saturated hydrocarbons.

Diesel fuel, jet fuel, kerosene (range oil), No. 1 fuel oil, No. 2 fuel oil, and diesel fuel are all popular distillate products coming from the kerosene fraction of petroleum. One grade of jet fuel uses the heavy naphtha fraction, but the kerosene fraction supplies the more popular and heavier grade of jet fuel, as well as smaller amounts that are sold as burner fuel (range oil) or No. 1 heating oil. Some heating oils (generally No. 2 heating oil) and diesel fuel are similar and can sometimes substitute for each other. The home heating oil is intended to be burned with a furnace for space heating. The diesel fuel is intended for compression–ignition engines.

The cetane number of a diesel fuel is a number that indicates the ability of a diesel engine fuel to ignite quickly, and burn smoothly, after being injected into the cylinder. In high speed diesel engines, a fuel with a long ignition delay tends to produce rough operation. The cetane number should not be confused with the cetene number, an obsolete designation for the starting and running quality of diesel fuel that uses cetene, $C_{16}H_{30}$, as the reference fuel. The cetene number has been replaced by the cetane number, a scale based on the ignition characteristics of two well-defined hydrocarbons, cetane, (*n*-hexadecane), and 2,3,4,5,6,7,8-heptamethylnonane.

Cetane has a short delay period during ignition and is assigned a cetane number of 100; heptamethylnonane has a long delay period and has a cetane number of 15. Just as the octane number is meaningful for automobile fuels, the cetane number is a means of determining the ignition quality of diesel fuels and is equivalent to the percentage by volume of cetane, in the blend with heptamethylnonane, that matches the ignition quality of the test fuel. The cetane number of diesel fuel usually falls into the 30–60 range; a high cetane number is an indication of the potential for easy starting and smooth operation of the engine.

Other methods are also available for the estimation of diesel fuel quality. For example, the diesel index (DI) is defined by the relation:

$$\mathrm{DI} = (\mathrm{A}^{\circ}\mathrm{F} \times {}^{\circ}\mathrm{API})/100$$

where A°F is the aniline point in degrees Fahrenheit and °API is the American Petroleum Institute gravity. A high aniline point corresponds to a high proportion of paraffins in the diesel fuel; such a fuel has a high diesel index and, therefore, a high cetane number.

**7.5. Fuel Oil.** Fuel oil is classified in several ways, but generally into two main types: distillate fuel oil and residual fuel oil. Distillate fuel oil is vaporized and condensed during a distillation process; it has a definite boiling range and does not contain high boiling oils or asphaltic components. A fuel oil that contains any amount of the residue from crude distillation hydrocracking is a residual fuel oil. However, the terms distillate fuel oil and residual fuel oil are losing their significance because fuel oils are made for specific uses and can be either distillates, residuals, or mixtures of the two. The terms domestic fuel oil, diesel fuel oil, and heavy fuel oil are more indicative of the uses of fuel oil.

Domestic fuel oils are those fuel oils used primarily in the home and include kerosene, stove oil, and furnace fuel oil. Diesel fuel oils are also distillate fuel oils, but residual oils have been successfully used to power marine diesel engines, and mixtures of distillates and residuals have been used on locomotive diesels. Heavy fuel oils include a variety of oils, ranging from distillates to residual oils, that must be heated to 260°C or higher before they can be used. In general, heavy fuel oil consists of residual oil blended with distillate to suit specific needs. Heavy fuel oil includes various industrial oils and, when used to fuel ships, is called bunker oil.

Stove oil is a straight-run (distilled) fraction from crude oil, whereas other fuel oils are usually blends of two or more fractions. The straight-run fractions available for blending into fuel oils are heavy naphtha, light and heavy gas oils, and residua. Cracked fractions such as light and heavy gas oils from catalytic cracking, cracking coal tar, and fractionator bottoms from catalytic cracking may also be used as blends to meet the specifications of different fuel oils.

Heavy fuel oil usually contains residuum that is mixed (cut back) to a specified viscosity with gas oils and fractionator bottoms. For some industrial purposes in which flames or flue gases contact the product (eg, ceramics, glass, heat treating, and open hearth furnaces), fuel oils must be blended to low sulfur specifications; low sulfur residues are preferable for these fuels.

The manufacture of fuel oils at one time largely involved using what was left after removing desired products from crude petroleum. Now fuel oil manufacture is a complex matter of selecting and blending various petroleum fractions to meet definite specifications.

Fuel oil that is used for heating is graded from No. 1 Fuel Oil, to No. 6 Fuel Oil, and cover light distillate oils, medium distillate, heavy distillate, a blend of distillate and residue, and residue oil. For example No. 2 and No. 3 Fuel oils refer to medium to light distillate grades used in domestic central heating fuel oil refers to a medium heavy residual oil used for heating large commercial premises.

### 7.6. Lubricating Oil.

Lubricating oil is distinguished from other petroleum fractions by the high (>400°C) boiling point as well as their high viscosity. Lubricating oil may be divided into many categories according to the types of service; however, there are two main groups: oils used in intermittent service, such as motor and aviation oils, and oils designed for continuous service, such as turbine oils.

Lubricating oil used in intermittent service must show the least possible variation in viscosity with respect to temperature and must be changed at frequent intervals to remove the foreign matter collected during service. The stability of such oil is therefore of less importance than the stability of oil used in continuous service for prolonged periods without renewal. Lubricating oil for continuous service must be extremely stable because the engines in which it is used operate at fairly constant temperature without frequent shutdown.

Lubricating oil may be divided into many categories according to the types of service it is intended to perform. However, there are two main groups: (*1*) oils used in intermittent service, such as motor and aviation oils and (*2*) oils designed for continuous service such as turbine oils.

**7.7. Wax.** Petroleum waxes are of two general types: paraffin wax in distillates and microcrystalline wax in residua. The melting point of wax is not directly related to its boiling point because waxes contain hydrocarbons of different chemical structure. Nevertheless, waxes are graded according to their melting point and oil content. Paraffin wax is a solid crystalline mixture of straight-chain (normal) hydrocarbons ranging from mostly $C_{20}$–$C_{30}$ and higher. Wax constituents are solid at ordinary temperatures (25°C; 77°F) whereas petrolatum (petroleum jelly) contains both solid and liquid hydrocarbons.

Wax production by *wax sweating* was originally used in Scotland to separate wax fractions by employing various melting points from the wax obtained from shale oils. Wax sweating is still used to some extent, but is being replaced by the more convenient wax recrystallization process. In wax sweating, a cake of slack wax, also known as crude or raw wax, is slowly warmed to a temperature at which the oil in the wax and the lower melting waxes become fluid and drip (or sweat) from the bottom of the cake, leaving a residue of higher melting wax.

Insofar as they are used to purify other products, several processes used in the refinery fall under the classification of dewaxing processes; however, such processes must also be classified as wax production processes (1,2). Most commercial dewaxing processes utilize solvent dilution, chilling to crystallize the wax, and filtration (28). The MEK process (MEK–toluene solvent) is widely used. Wax crystals are formed by chilling through the walls of scraped surface chillers, and wax is separated from the resultant wax–oil–solvent slurry by using fully enclosed rotary vacuum filters.

Solvents used for dewaxing are naphtha, propane, sulfur dioxide, acetone–benzene, trichloroethylene, ethylenedichloride-benzene (Barisol), MEK–benzene (benzol), methyl *n*-butyl ketone, and methyl *n*-propyl ketone. Other solvents in commercial use for dewaxing include *N*-methylpyrrolidinone, MEK–MIBK (methyl isobutyl ketone), dichloroethane-methylene dichloride, and propylene–acetone.

Solvent dewaxing can be applied to light, intermediate, and heavy lubricating oil distillates, but each distillate produces a different kind of wax, and each of these waxes is actually a mixture of a number of waxes. For example, the wax obtained from light paraffin distillate consists of a series of paraffin waxes that have melting points in the range of 30–70°C (86–158°F) and are characterized by a tendency to harden into large crystals. However, heavy paraffin distillate yields a wax composed of a series of waxes that have melting points in the range of 60–90°C (140–194°F) and that harden into small crystals from which they derive the name microcrystalline waxes or microwaxes.

On the other hand, intermediate paraffin distillates contain paraffin waxes and waxes intermediate in properties between paraffin and microwaxes. Thus, the solvent dewaxing process produces three different slack waxes depending on whether light, intermediate, or heavy paraffin distillate is processed. The slack wax from heavy paraffin distillate may be sold as dark raw wax, the wax from intermediate paraffin distillate as pale raw wax. The latter is treated with lye and clay to remove odor and improve color.

In the propane process, part of the propane diluent is allowed to evaporate by reducing pressure so as to chill the slurry to the desired filtration temperature, and rotary pressure filters are employed. Complex dewaxing requires no refrigeration, but depends on the formation of a solid urea–$n$-paraffin complex that is separated by filtration and then decomposed. This process is used to make low viscosity lubricants that must remain fluid at low temperatures (refrigeration, transformer, and hydraulic oils) (28).

Another method of separating petrolatum from residua is by centrifuge dewaxing. In this process, the reduced crude oil is dissolved in naphtha and chilled to $-18^{\circ}$C or lower, which causes the wax to separate. The mixture is then fed to a battery of centrifuges where the wax is separated from the liquid. However, the centrifuge method has been largely displaced by solvent dewaxing methods, as well as more modern methods of wax removal. Similar use is anticipated for catalytic dewaxing processes based on selective hydrocracking of the normal paraffins; such processes use a molecular sieve-based catalyst in which the active hydrocracking sites are accessible only to the paraffin molecules.

Catalytic dewaxing (31) is a hydrocracking process operated at elevated temperatures (280–400°C; 536–752°F) and pressures, 2070–10,350 kPa (300–1500 psi). However, the conditions for a specific dewaxing operation depend on the nature of the feedstock and the product pour point required. The catalyst employed for the process is a mordenite-type catalyst that has the correct pore structure to be selective for normal paraffin cracking. Platinum on the catalyst serves to hydrogenate the reactive intermediates so that further paraffin degradation is limited to the initial thermal reactions.

Another catalytic dewaxing process also involves selective cracking of normal paraffins and those paraffins that may have minor branching in the chain. In the process (Fig. 8), the catalyst can be reactivated to fresh activity by relatively mild nonoxidative treatment. The time allowed between reactivations is a function of the feedstock; after numerous reactivations it is possible that there will be coke buildup on the catalyst.

A catalytic dewaxing process can be used to dewax a variety of lubricating base stocks; as such, it has the potential to replace solvent dewaxing, or even be used in combination with solvent dewaxing (Fig. 9), as a means of relieving the bottlenecks which can, and often do, occur in solvent dewaxing facilities.

**7.8. Asphalt.** Asphalt manufacture is, in essence, a matter of distilling everything possible from crude petroleum until a residue with the desired properties is obtained (32). This is usually done by stages; crude distillation at atmospheric pressure removes the lower boiling fractions and yields a reduced crude that may contain higher boiling (lubricating) oils, asphalt, and even wax. Distillation of the reduced crude under vacuum removes the oils (and wax) as volatile overhead products and the asphalt remains as a bottom (or residual) product. At this stage the asphalt is frequently (and incorrectly) referred to as pitch. In terms of meeting specifications, asphalt can be made softer by blending hard asphalt with the extract obtained in the solvent treatment of lubricating oils. On the other hand, soft asphalts can be converted into harder asphalts by oxidation (air blowing).

Road oils are liquid asphalt materials intended for easy application to earth roads. They provide a strong base or a hard surface and maintain a satisfactory passage for light traffic. Liquid road oils, cutbacks, and emulsions are of recent date, but the use of asphaltic solids for paving goes back to the European practices of the early 1800s.

Cutback asphalts are mixtures in which hard asphalt has been diluted with a lighter oil to permit application as a liquid without drastic heating. They are classified as rapid, medium, and slow curing, depending on the volatility of the diluent, which governs the rates of evaporation and consequent hardening.

Asphalt can be emulsified with water to permit application without heating. Such emulsions are normally of the oil-in-water type. They reverse or break on application to a stone or earth surface, so that the oil clings to the stone and the water disappears. In addition to their usefulness in road and soil stabilizations, they are useful for paper impregnation and waterproofing. The emulsions are chiefly either the soap or alkaline type, or the neutral or clay type. The former breaks readily on contact, but the latter is more stable and probably loses water mainly by evaporation. Good emulsions must be stable during storage or freezing, suitably fluid, and amenable to control for the speed of breaking.

Recently, asphalt has grown to be a valuable refinery product. In the post-1980 period, a shortage of good quality asphalt has developed. This is due in no short measure to the tendency of refineries to produce as much liquid fuels (eg, gasoline) as possible. Thus, residua that would have once been used for asphalt manufacture are now being used to produce liquid fuels (and coke).

**7.9. Coke.** Coke is the residue left by the destructive distillation (coking) of residua. The composition of coke varies with the source of the crude oil, but in general, large amounts of high molecular weight complex hydrocarbons (rich in carbon, but correspondingly poor in hydrogen) make up a high proportion. The solubility of coke in carbon disulfide has been reported to be as high as 50–80%, but this is, in fact, a misnomer, since the coke is an insoluble, honeycomb-type material that is the end product of thermal processes.

Petroleum coke is employed for a number of purposes; its principal use is in the manufacture of carbon electrodes for aluminum refining, which requires a high purity carbon that is low in ash and free of sulfur. In addition, coke is employed in the manufacture of carbon brushes, silicon carbide abrasives, structural carbon (eg, pipes and Rashig rings), as well as calcium carbide manufacture from which acetylene is produced. Coke produced from low quality crude oil is mixed with coal and burned as a fuel. Flue gas scrubbing is required. Coke is used in fluidized-bed combustors or gasifiers for power generation.

## 8. Petrochemicals

The petrochemical industry began in the 1920s as suitable by-products became available through improvements in the refining processes. It developed parallel with the oil industry and has rapidly expanded since the 1940s, with the oil refining industry providing plentiful cheap raw materials.

A *petrochemical* is any chemical (as distinct from fuels and petroleum products) manufactured from petroleum (and natural gas) and used for a variety of commercial purposes. The definition, however, has been broadened to include the whole range of aliphatic, aromatic, and naphthenic organic chemicals, as well as carbon black and such inorganic materials as sulfur and ammonia. Petroleum and natural gas are made up of hydrocarbon molecules, which are comprised of one or more carbon atoms, to which hydrogen atoms are attached. Currently, oil and gas are the main sources of the raw materials because they are the least expensive, most readily available, and can be processed most easily into the primary petrochemicals. Primary petrochemicals include olefins (ethylene, propylene and butadiene) aromatics (benzene, toluene, and the isomers of xylene); and methanol. Thus, petrochemical feedstocks can be classified into three general groups: olefins, aromatics, and methanol; a fourth group includes inorganic compounds and synthesis gas (mixtures of carbon monoxide and hydrogen). In many instances, a specific chemical included among the petrochemicals may also be obtained from other sources, such as coal, coke, or vegetable products. For example, materials such as benzene and naphthalene can be made from either petroleum or coal, while ethyl alcohol may be of petrochemical or vegetable origin.

Petrochemicals are generally divided into three groups: (*1*) aliphatics, such as butane and butene; (*2*) cycloaliphatics, such as cyclohexane, cyclohexane derivatives, and aromatics (eg, benzene, toluene, xylene, and naphthalene); and (*3*) inorganics, such as sulfur, ammonia, ammonium sulfate, ammonium nitrate, and nitric acid.

**8.1. Aliphatics.** Methane, obtained from crude oil or natural gas, or as a product from various conversion (cracking) processes, is an important source of raw materials for aliphatic petrochemicals (Fig. 10). Ethane, also available from natural gas and cracking processes, is an important source of ethylene, which, in turn, provides more valuable routes to petrochemical products (Fig. 11).

Ethylene ($CH_2{=}CH_2$), an important olefin, is usually made by cracking gases such as ethane, propane, butane, or a mixture of these as might exist in a refinery's off-gases. When gas feedstock is scarce or expensive, naphthas and even whole crude oil have been used in specially designed ethylene crackers. The heavier feeds also give significant quantities of higher molecular weight olefins and aromatics. Ethylene is consumed in larger amounts than any other hydrocarbon for the production of aliphatic petrochemicals, but it is by no means the only source of aliphatic petrochemicals. Propane and butane are also important aliphatic hydrocarbons (Fig. 12). Propane is usually converted to propylene by thermal cracking, although some propylene is also available from refinery gas streams. The various butylenes are more commonly obtained from refinery gas streams. Butane dehydrogenation to butylene is known, but is more complex than ethane or propane cracking, and its product distributions are not always favorable. The production of gasoline and other liquid fuels consumes large amounts of butane.

The gaseous constituents produced in a refinery give rise to a host of chemical intermediates that can be used for the manufacture of a wide variety of products (1,2). Synthesis gas (carbon monoxide, CO, and hydrogen, $H_2$) mixtures are also used to produce valuable industrial chemicals (Fig. 13).

**8.2. Cycloaliphatics and Aromatics.** Cyclic compounds (cyclohexane and benzene) are also important sources of petrochemical products (Fig. 14). Aromatics are in high concentration in the product streams from a catalytic reformer. When aromatics are needed for petrochemical manufacture, they are extracted from the reformer's product using solvents, such as glycols (eg, the Udex process) and sulfolane.

The mixed monocyclic aromatics are called BTX as an abbreviation for benzene, toluene, and xylene. The benzene and toluene are isolated by distillation, and the isomers of the xylene are separated by superfractionation, fractional crystallization, or adsorption. Benzene is the starting material for styrene, phenol, and a number of fibers and plastics. Benzene and cyclohexane are responsible for products such as nylon and polyester fibers, polystyrene, epoxy resins, phenolic resins, and polyurethanes.

Toluene is used to make a number of chemicals, but most of it is blended into gasoline. Xylene use depends on the isomer: *p*-xylene goes into polyester and *o*-xylene into phthalic anhydride. Both are involved in a wide variety of consumer products.

Benzene, toluene, and xylene are made mostly from catalytic reforming of naphthas with units similar to those already discussed. As a gross mixture, these aromatics are the backbone of gasoline blending for high octane numbers. However, there are many chemicals derived from these same aromatics; thus many aromatic petrochemicals have their beginning by selective extraction from naphtha or gas-oil reformate.

**8.3. Inorganics.** Of the inorganic chemicals, ammonia is by far the most common. Ammonia is produced by the direct reaction of hydrogen with nitrogen; air is the source of nitrogen: $N_2 + 3\,H_2 \rightarrow 2\,NH_3$. Refinery gases, steam reforming of natural gas (methane) and naphtha streams, and partial oxidation of hydrocarbons or higher molecular weight refinery residual materials (residua, asphalts) are the sources of hydrogen. Ammonia is used predominantly for the production of ammonium nitrate, $NH_4NO_3$, as well as other ammonium salts and urea, $H_2NCONH_2$, which are primary constituents of fertilizers.

Carbon black, also classed as an inorganic petrochemical, is made predominantly by the partial combustion of carbonaceous (organic) material in a limited supply of air. Carbonaceous sources vary from methane to aromatic petroleum oils to coal tar by-products. Carbon black is used primarily for the production of synthetic rubber.

Sulfur, another inorganic petrochemical, is obtained by the oxidation of hydrogen sulfide:

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S$$

Hydrogen sulfide is a constituent of natural gas and also of the majority of refinery gas streams, especially those off-gases from hydrodesulfurization processes. A majority of the sulfur is converted to sulfuric acid for the manufacture of fertilizers and other chemicals. Other uses for sulfur include the production of carbon disulfide, refined sulfur, and pulp and paper industry chemicals.

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Table 1. **Distillation Fractions of Petroleum**

| Fraction | Boiling, °C |
|---|---|
| light naphtha | −1 to 150 |
| gasoline | −1 to 180 |
| heavy naphtha | 150 to 205 |
| kerosene | 205 to 260 |
| stove oil | 205 to 290 |
| light gas oil | 260 to 315 |
| heavy gas oil | 315 to 425 |
| lubricating oil | >400 |
| vacuum gas oil | 425 to 600 |
| residuum | >600 |

Table 2. **General Process Characteristics for Hydroprocessing Various Feedstocks**

| Process | Naphtha | Atmospheric gas oil | Vacuum gas oil | Residuum |
|---|---|---|---|---|
| hydrocracking | + | + | + | + |
| aromatics removal |  | + | + |  |
| sulfur removal | + |  | + | + |
| nitrogen removal | + |  | + | + |
| metals removal |  |  | + | + |
| coke mitigation |  |  |  | + |
| *n*-paraffins removal |  | + |  |  |
| olefins removal | + |  |  |  |

Table 3. **Sulfur Removal from Organic Compounds by Hydrotreating**

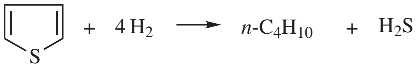
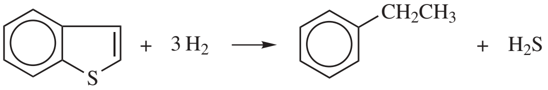
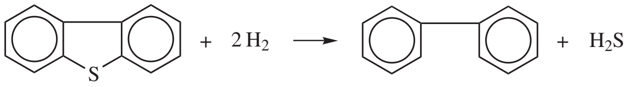
| Name | Typical reaction |
|---|---|
| thiols (mercaptans) | $R—SH + H_2 \longrightarrow RH + H_2S$ |
| disulfides | $R—S—S—R' + 3\,H_2 \longrightarrow RH + R'H + 2\,H_2S$ |
| sulfides | $R—S—R' + 2\,H_2 \longrightarrow RH + R'H + H_2S$ |
| thiophenes |  |
| benzothiophenes |  |
| dibenzothiophenes |  |

Table 4. **Constituents of Light Ends**

| Hydrocarbon | Carbon atoms | Molecular weight | Boiling point, °C | Uses |
|---|---|---|---|---|
| methane | 1 | 16 | −182 | fuel gas |
| ethane | 2 | 30 | −89 | fuel gas |
| ethylene | 2 | 28 | −104 | fuel gas, petrochemicals |
| propane | 3 | 44 | −42 | fuel gas, LPG |
| propylene | 3 | 42 | −48 | fuel gas, petrochemicals, polymer gasoline |
| isobutane | 4 | 58 | −12 | alkylate, motor gasoline |
| *n*-butane | 4 | 58 | −1 | motor gasoline |
| isobutylene | 4 | 56 | −7 | synthetic rubber and chemicals, polymer gasoline, alkylate, motor gasoline |
| butylene-1[a] | 4 | 56 | −6 | synthetic rubber and chemicals, |
| butylene-2[a] | 4 | 56 | 1 | alkylate, polymer gasoline, motor gasoline |
| isopentane | 5 | 72 | 28 | motor and aviation gasolines |
| *n*-pentane | 5 | 72 | 36 | motor and aviation gasolines |
| pentylenes | 5 | 70 | 30 | motor gasolines |
| isohexane | 6 | 86 | 61 | motor and aviation gasolines |
| *n*-hexane | 6 | 86 | 69 | motor and aviation gasolines |

[a] Numbers refer to the positions of the double bond; eg, butylene-1 (or butene-1 or but-1-ene) is $CH_3CH_2CH{=}CH_2$ and butylene-2 (or butene-2 or but-2-ene) is $CH_3CH{=}CHCH_3$.

Table 5. **Refining Technologies for Producing Reformulated Gasoline Constituents**

| Technology | Objective |
|---|---|
| catalytic reformer prefractionation | reduce benzene |
| reformate fractionation | reduce benzene |
| isomerization | increase octane |
| aromatics saturation | reduce total aromatics |
| catalytic reforming | oxygenates for octane enhancement |
| MTBE synthesis | provide oxygenates |
| isobutane dehydrogenation | feedstock for oxygenate synthesis |
| catalytic cracker naphtha fractionation | increase alkylate; increase oxygenates; reduce olefins and sulfur |
| feedstock hydrotreating | reduce sulfur |

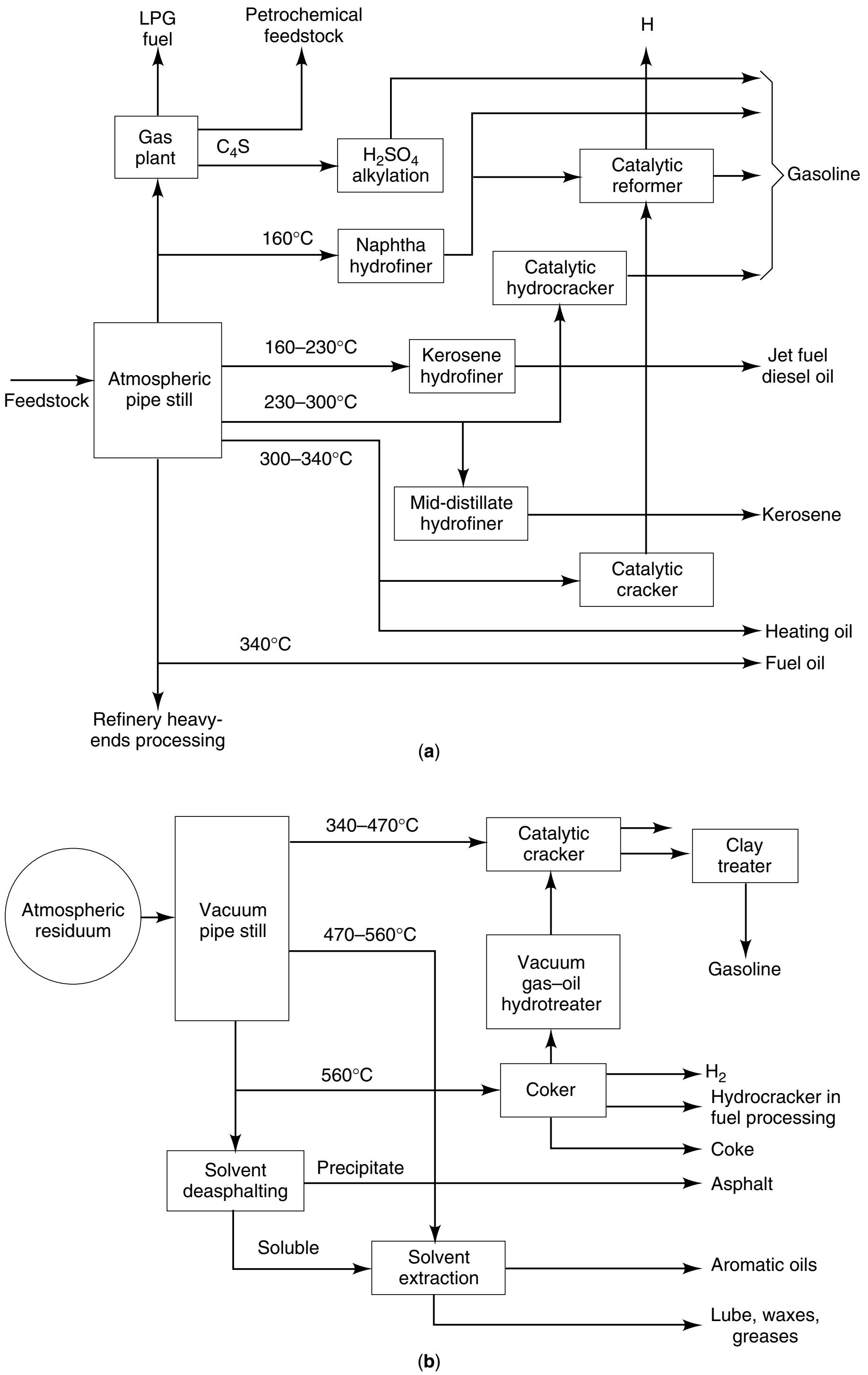


**Fig. 1.** General refinery operations: (**a**) light petroleum refining section; (**b**) heavy feedstock refining section.

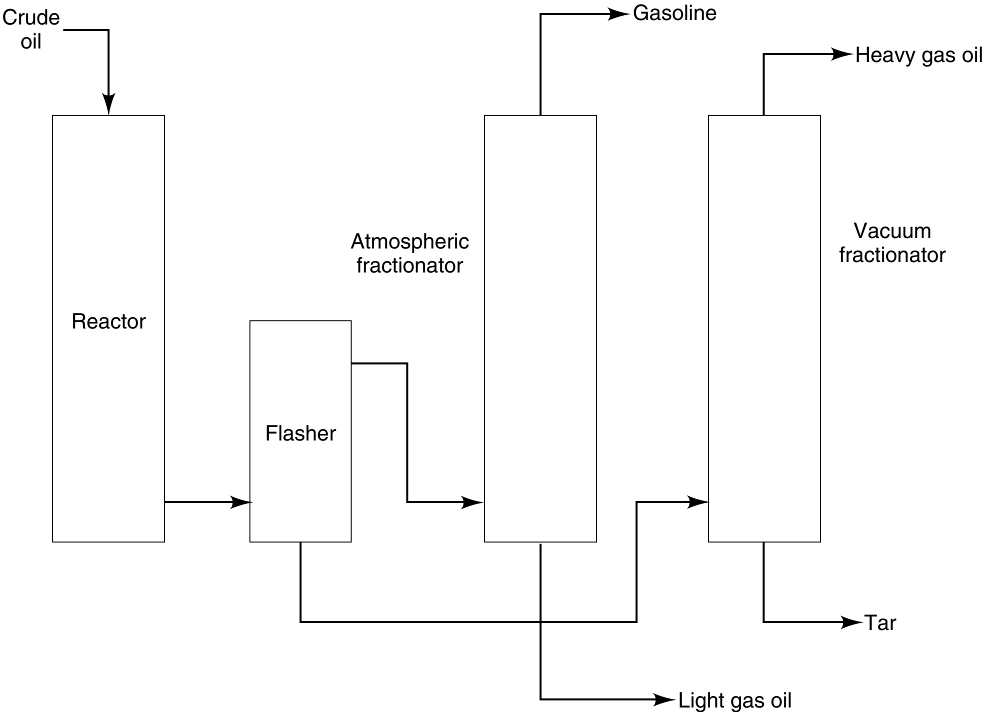


**Fig. 2.** The visbreaking process.

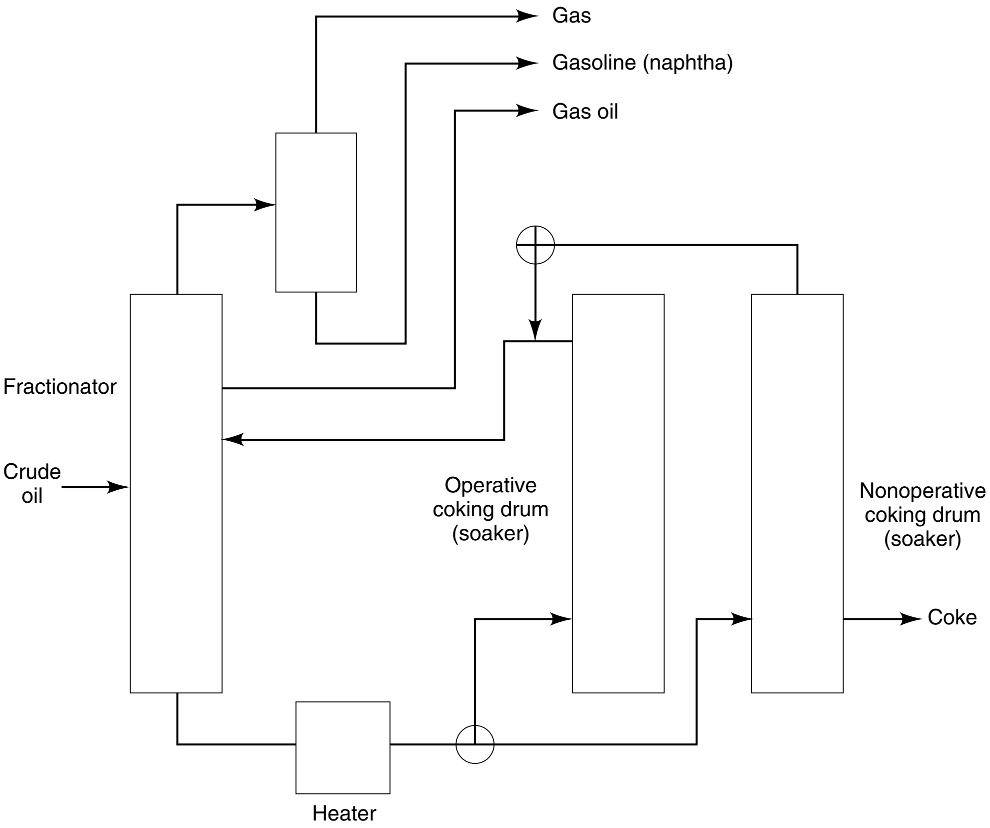


**Fig. 3.** The delayed coking process.

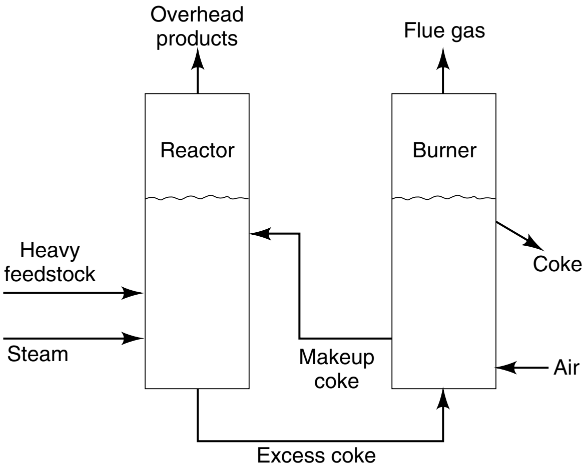


**Fig. 4.** Fluid coking.

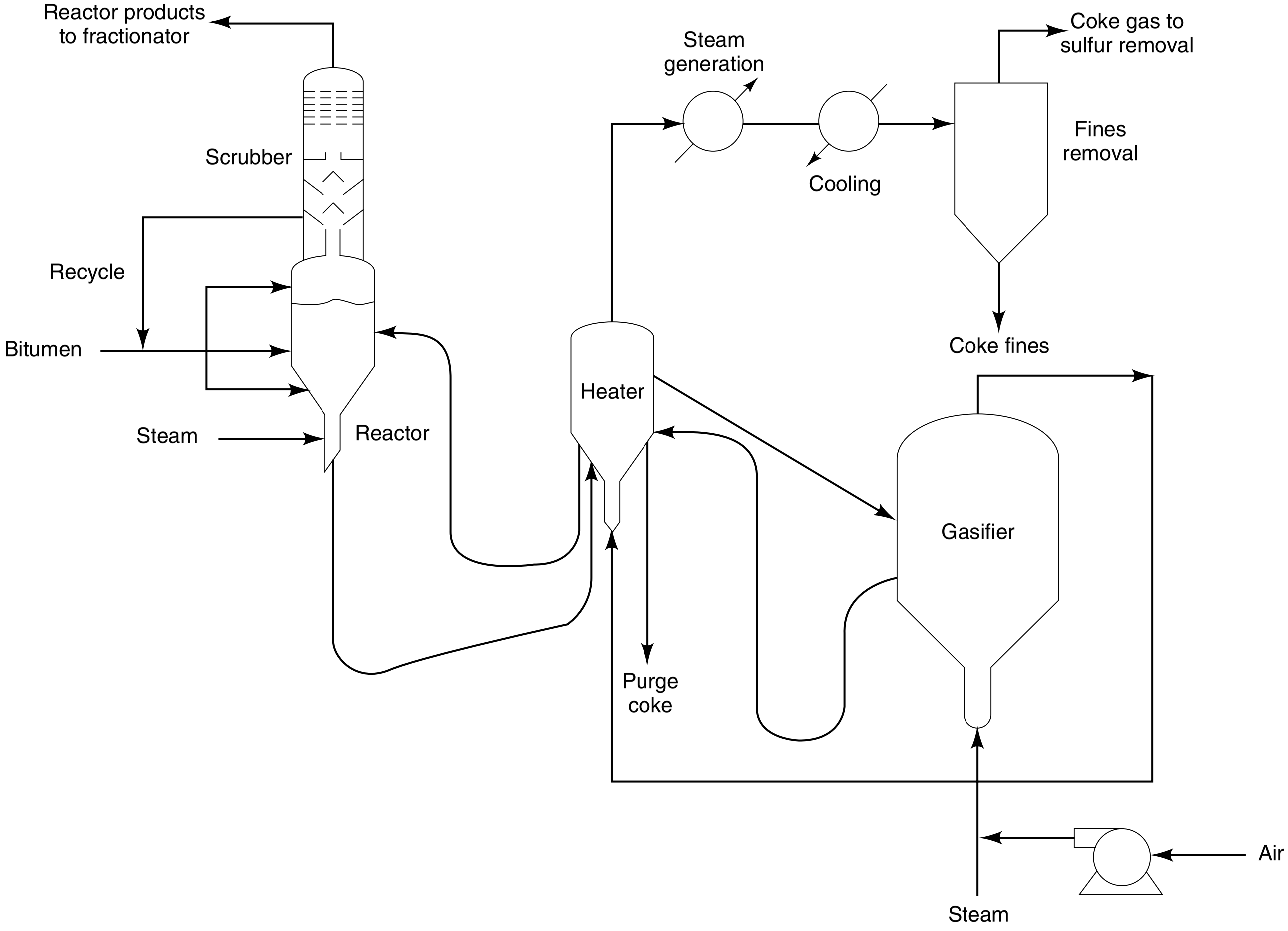


**Fig. 5.** The flexicoking process.

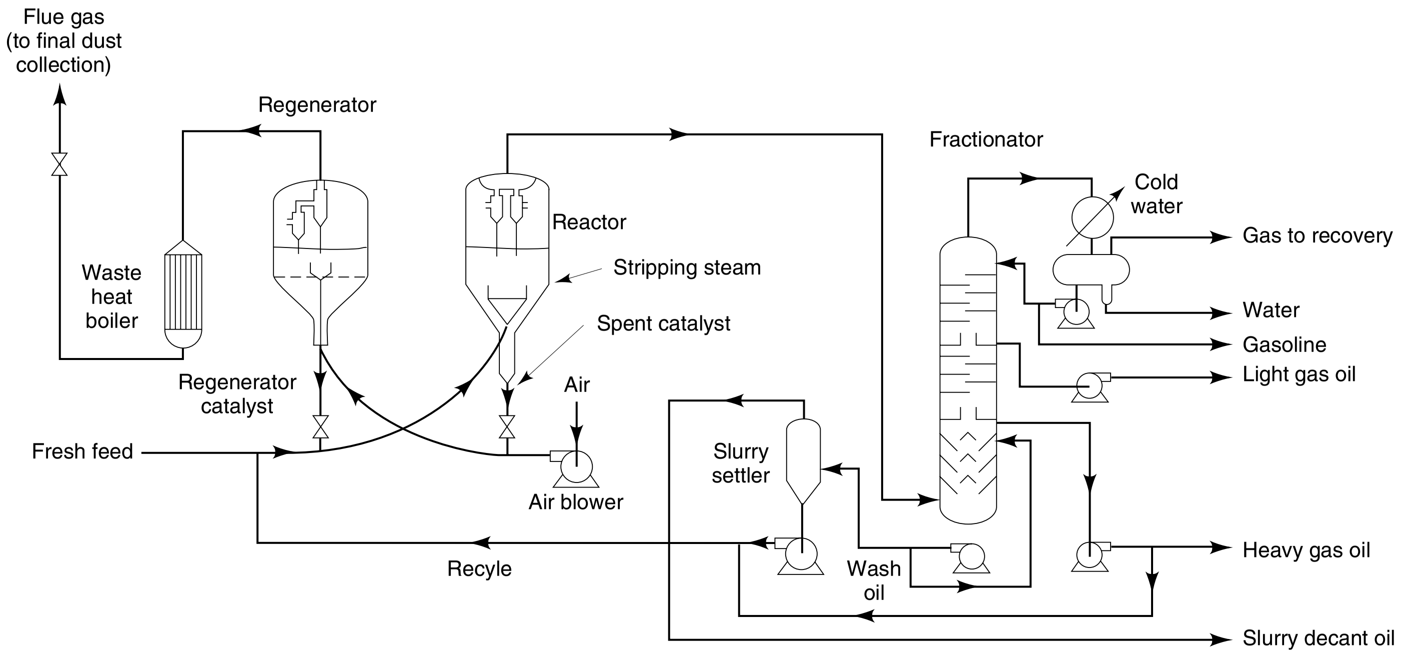


**Fig. 6.** Fluid-bed catalytic cracking with product separation.

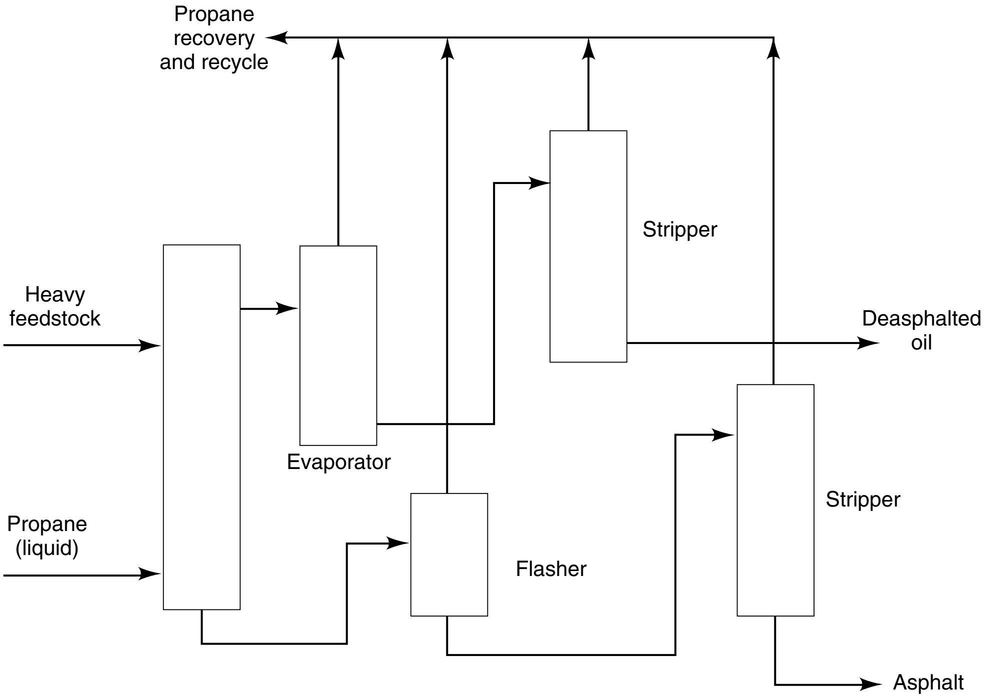


**Fig. 7.** Propane deasphalting.

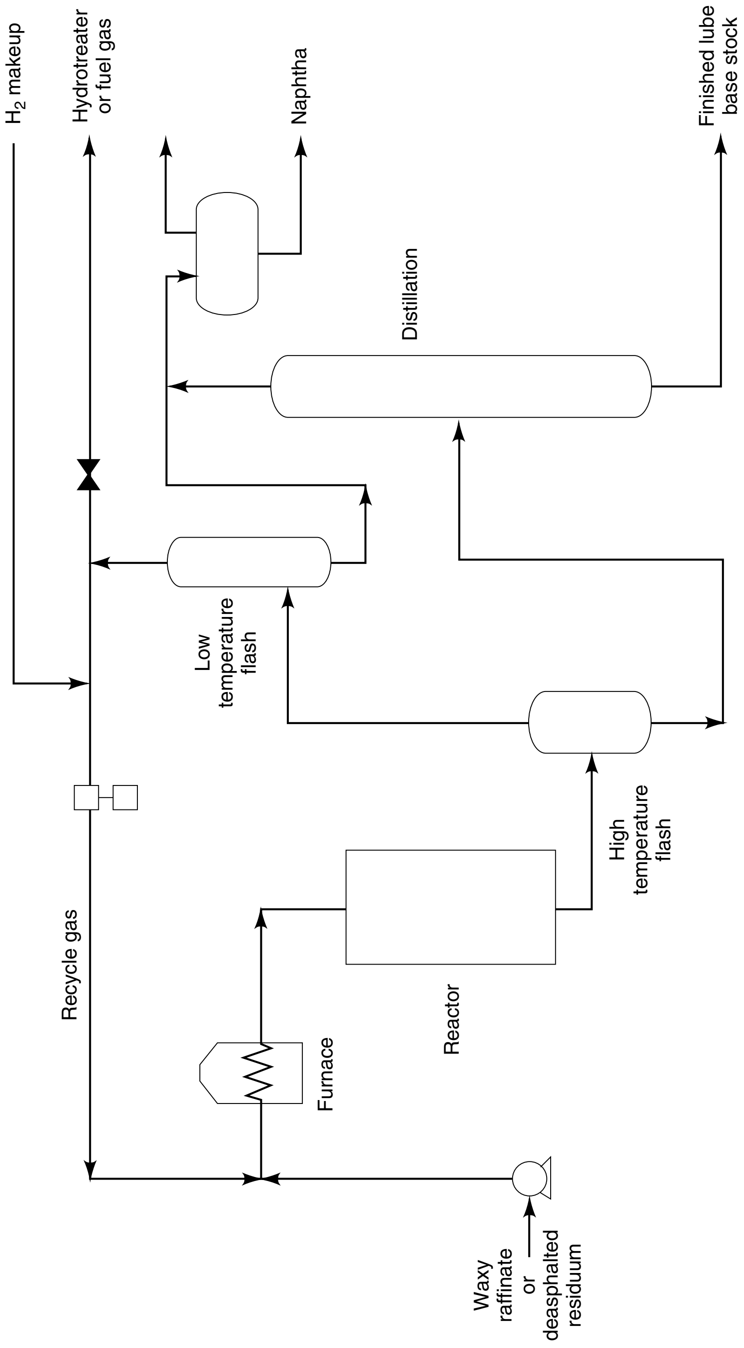


**Fig. 8.** Catalytic dewaxing.

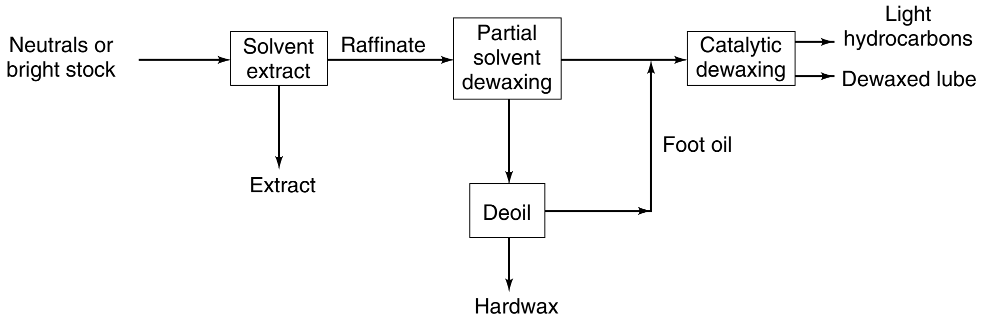


**Fig. 9.** Catalytic dewaxing used in conjunction with solvent dewaxing.

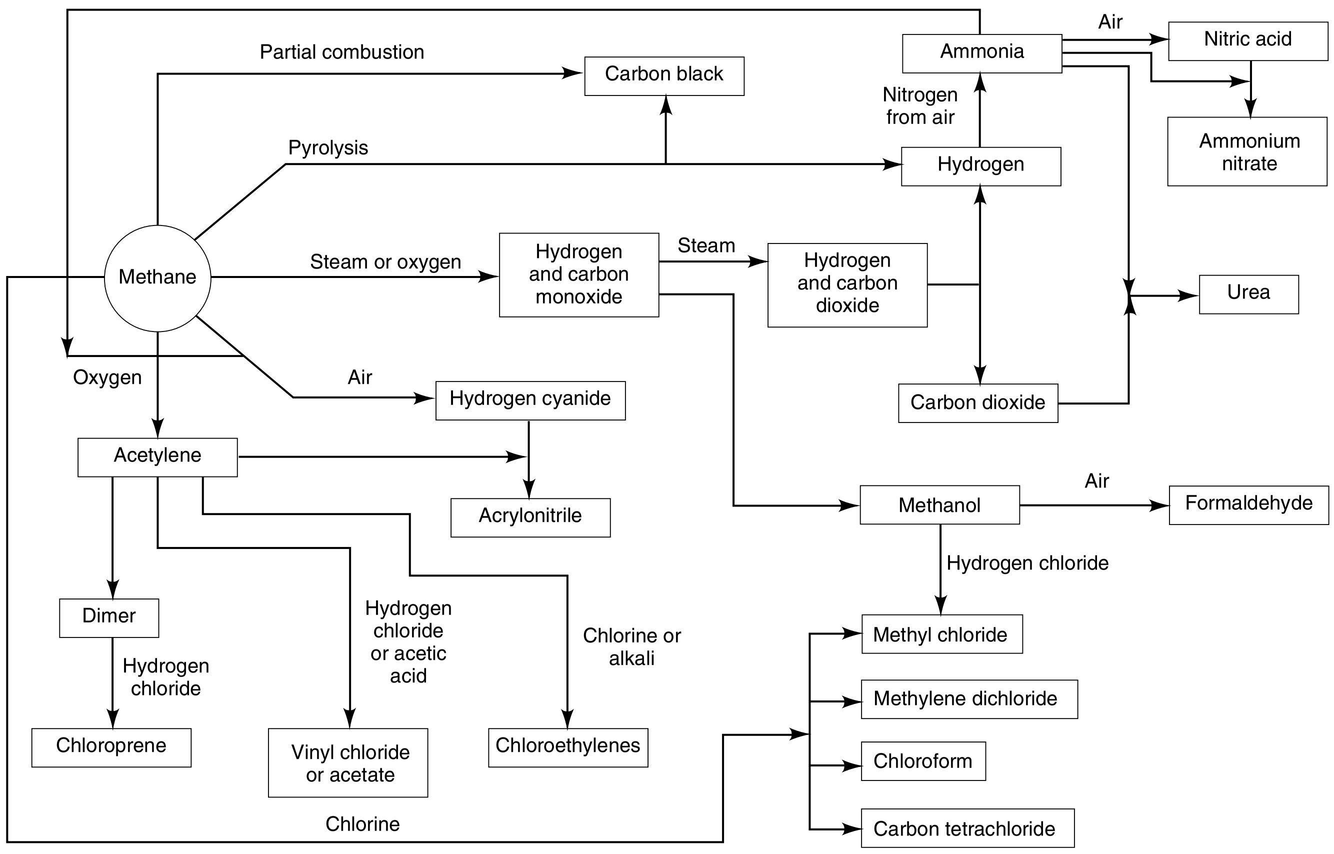


**Fig. 10.** Methane as a source of petrochemicals.

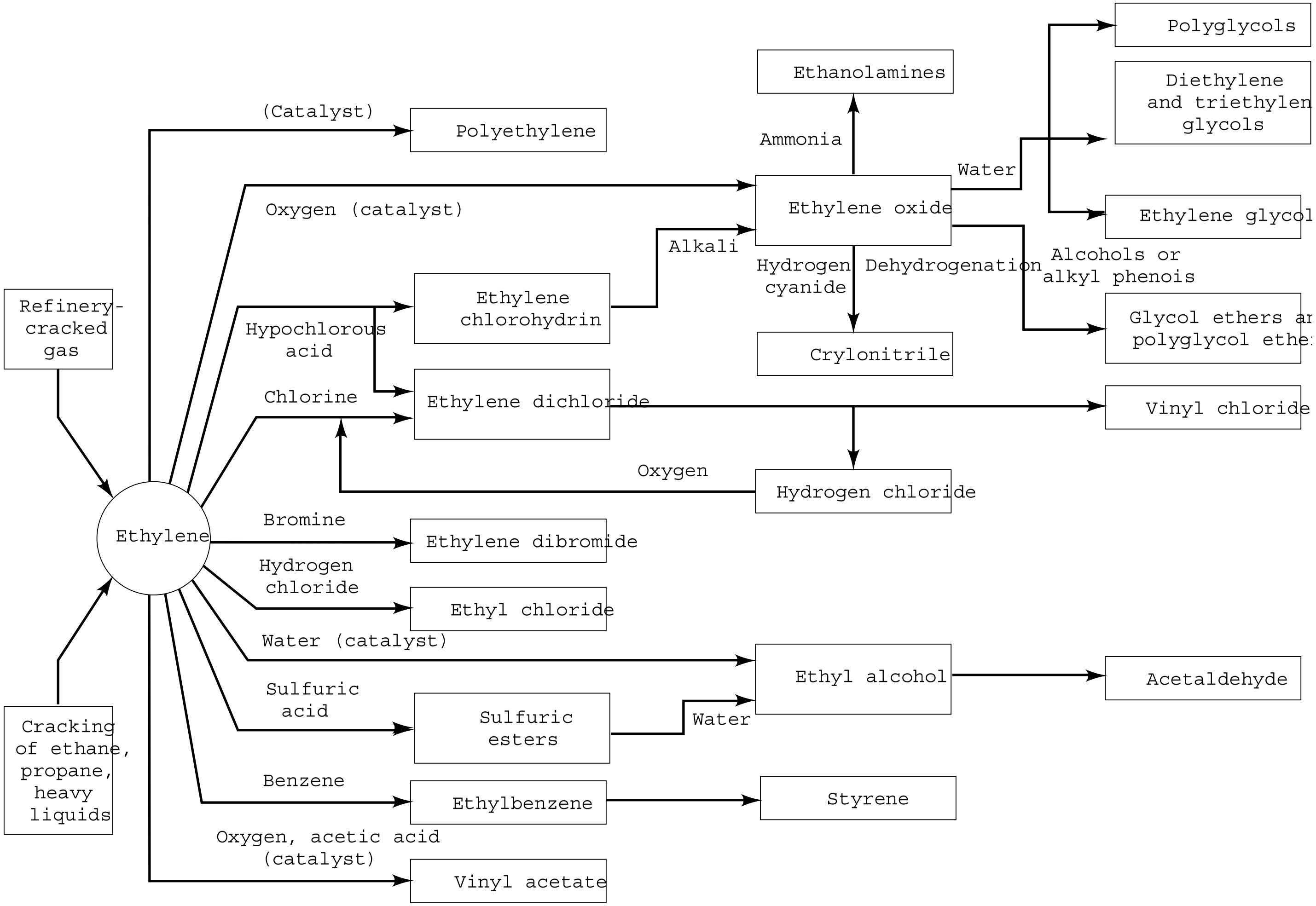


Fig. 11. Ethylene as a source of petrochemicals.

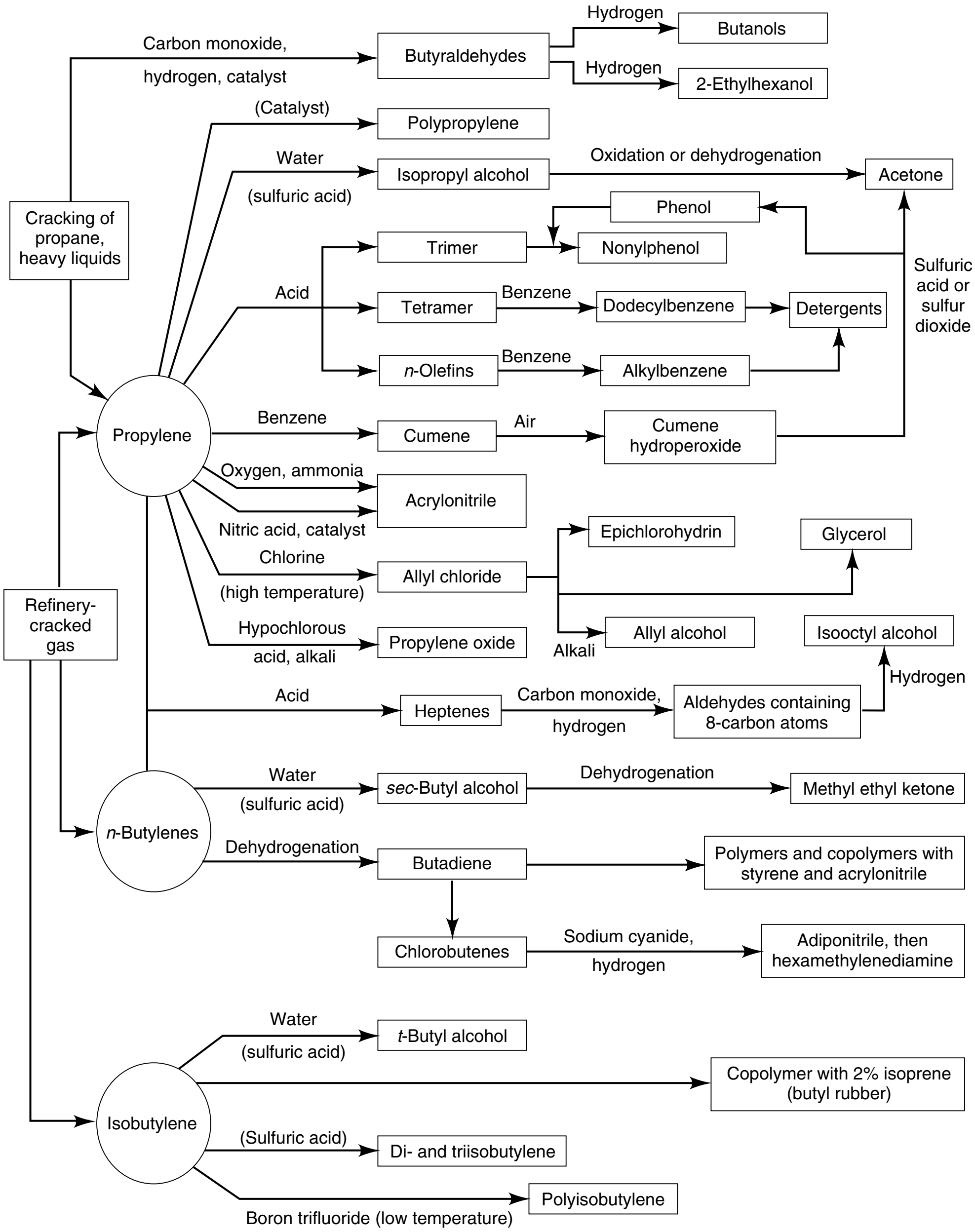


**Fig. 12.** Use of propylene and butylene(s) as sources of petrochemicals.

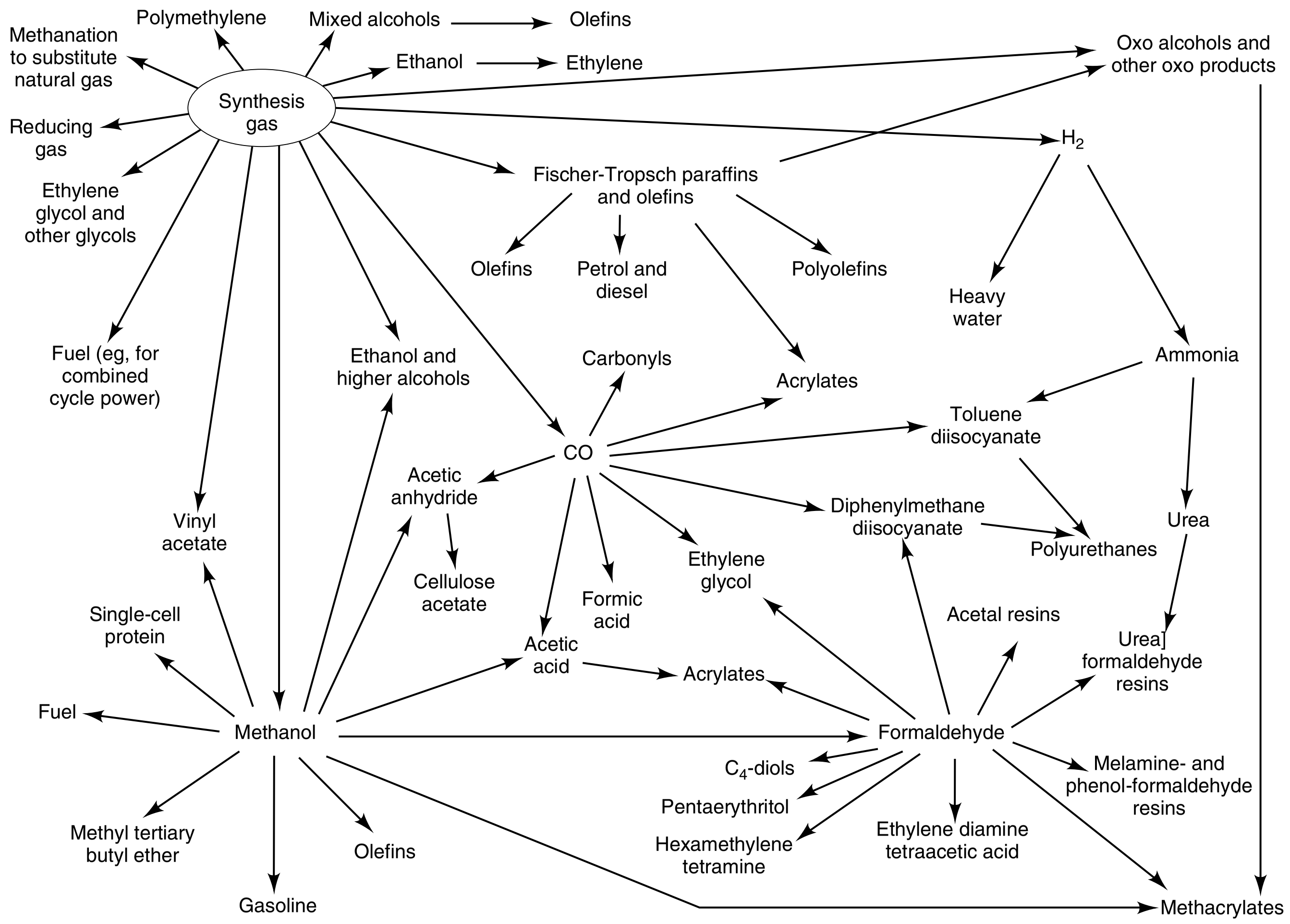


**Fig. 13.** Chemicals from synthesis gas.

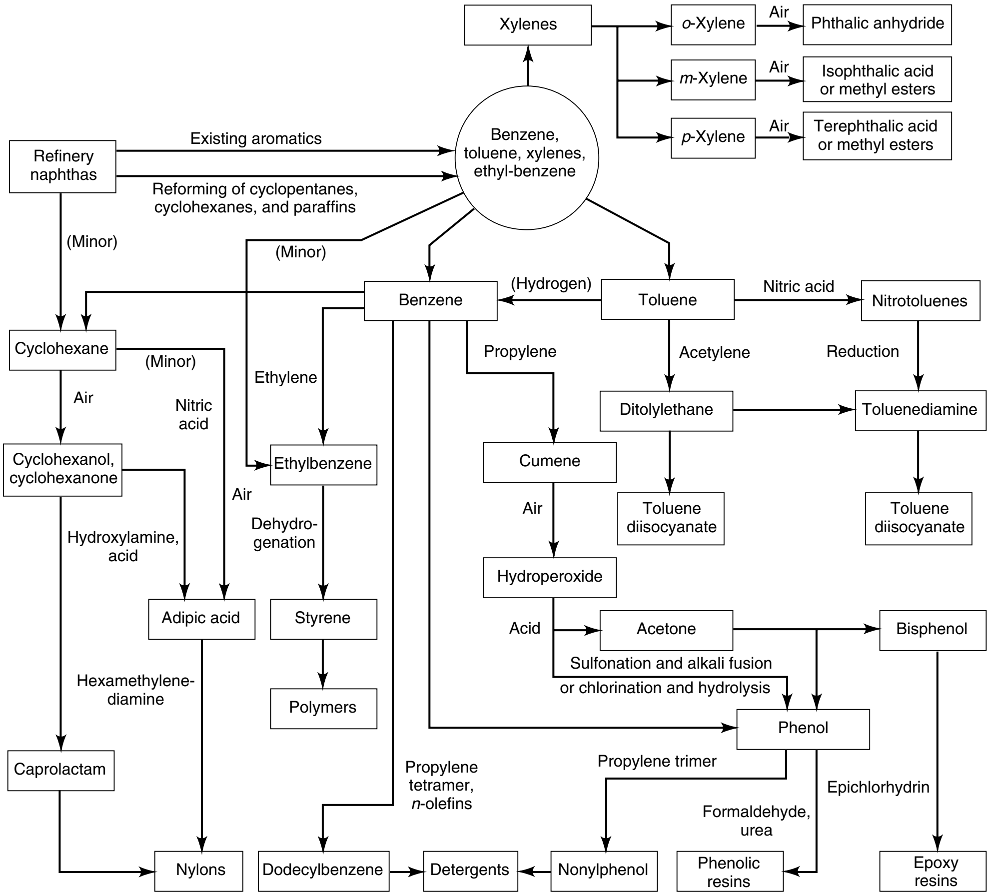


**Fig. 14.** Aromatic and cycloaliphatic compounds as sources of petrochemicals.